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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 ºC 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 ºC 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.

Keywords: Glycerol carbonate production; Deactivation mechanism; Catalytic activity; Catalyst deactivation; Biomass waste derived catalyst; Fatty acid methyl ester.

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 under vacuum (ca. 0.02 MPa-0.1 MPa) operating condition can obtain moderate to high of GC yield[14, 15] but energy intensive due to the vacuum processing.[16] The transesterification of glycerol with dimethyl carbonate (DMC) is another potential pathway as it requires mild operating conditions. Not only this route obtains high glycerol conversion and GC yield, but also offers easy separation of product due to the difference of boiling points between reactants and products.[17, 18] CaO is a promising catalyst as it is inexpensive and widely available, and demonstrates high activity[19, 20]. Generally, CaO can be derived from natural calcium sources, such as dolomite, crab shell, and eggshell, having calcium carbonate ($CaCO_3$) as a major component that can be transformed to CaO by calcination. Among those, eggshells are the most superior resource as it mainly contains calcium carbonate (96% by weight).[21] Hence, the waste eggshells have been effectively utilized as CaO source in several catalytic processes such as biodiesel production[22, 23], DMC synthesis [24], H_2/syngas synthesis [25-27] and in non-catalytic processes such as CO_2 capture[28] and wastewater treatment.[29] There are several researches presenting the preparation and performance of CaO based catalyst in GC production.[30] CaO could achieve the complete glycerol conversion and 95.3% of GC yield under the molar ratio of DMC to glycerol 3.5:1 at 95 ºC of reaction temperature and 90 min of reaction time, as reported by Ochoa-Gomez et al. (2009) [31]. It has been well known that the recycling of CaO shows dramatic decrease in catalytic activity; however, explanation of catalyst deactivation remained controversial due to contrasting hypothesis and observable evidence. From the literature, the surface of CaO catalyst may expose to air during catalytic runs which considerd as a cause of deactivation [31]. Algoufi (2016) [32] described that the calcined dolomite as CaO-MgO mixed oxide catalyst presented decreasing catalytic activity for a consecutive cycle due to CaO transformation to unstable phase which reacted with CO_2 in air to carbonate phase whereas MgO phase enhanced the stability of CaO phase which concluded that calcined 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),

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

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

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

3. Results and discussion

3.1 Characterization of CaO-based catalyst

It was observed that the surface area of eggshell-derived CaO was equal to 4.92 m^2/g (Table 1). CaO derived from eggshell was a mesoporous material (pore diameter range 2-50 nm) (Fig.S1). This mesoporous structure could promote diffusion and adsorption of reactants and products since the molecular diameters of glycerol and glycerol carbonate are 0.52 and 0.65 nm, respectively[42, 43], leading to an increase in glycerol conversion and GC yield when compared with previously demonstrated microporous material.[44] A SEM image shown in supporting information Fig.S2, confirms mesoporous geometry with generally irregular crystal structure as an aggregate of CaO eggshell, particle size between 5-10 µm, corresponding to other works.[45, 46] CaO eggshell exhibits high strength of basic site $15.0 < H\_ < 18.4$ and the total basicity of CaO eggshell is 0.481 mmol/g, leading to high basic-site density within the allocated pore volume and surface area of the dense egg-shell derived CaO.

3.2 Factors influencing transesterification reaction using CaO as a catalyst

3.2.1 Effect of reaction temperature

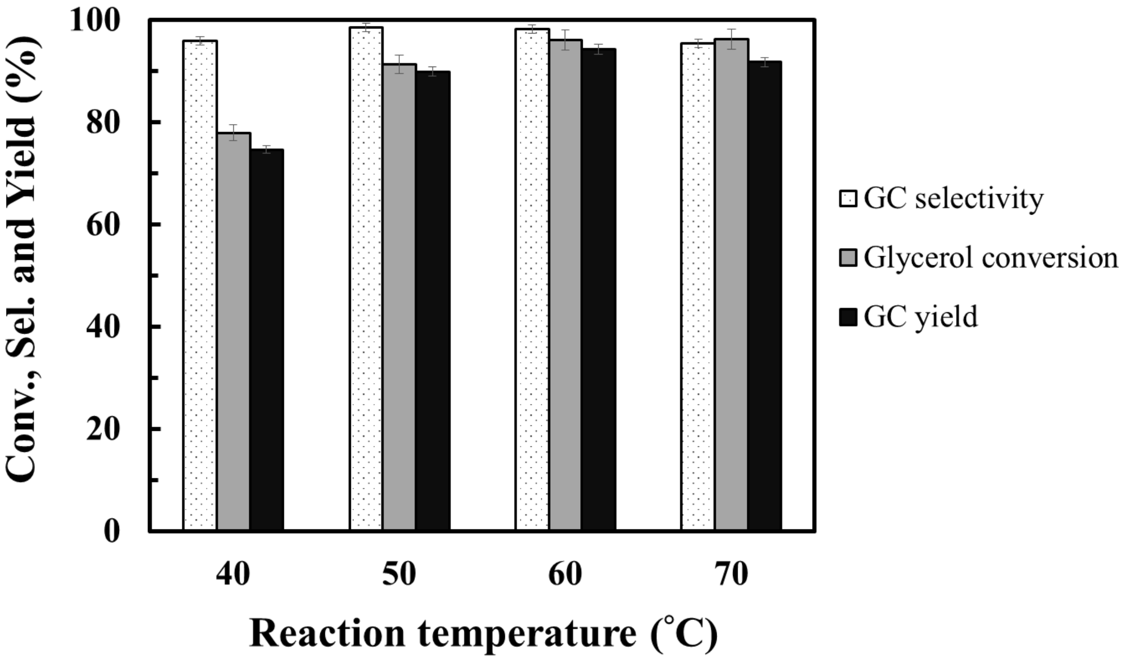


Fig.1. Effect of reaction temperature on catalytic activity (molar ratio of CaO : DMC : glycerol = 0.08 : 2.5 : 1, and reaction time = 180 min).

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

1). The lower reaction temperature lowering the cyclization rate of the methyl glyceryl carbonate intermediate to GC led to decreasing GC selectivity, similarly as observed by Wang et al. [47] On the other hand, the selectivity of GC decreases when increasing reaction temperature to 70 °C due to the formation of a side product as a glycidol which agrees with the previous report. [48, 49]

3.2.2 Effect of the molar ratio of DMC: glycerol

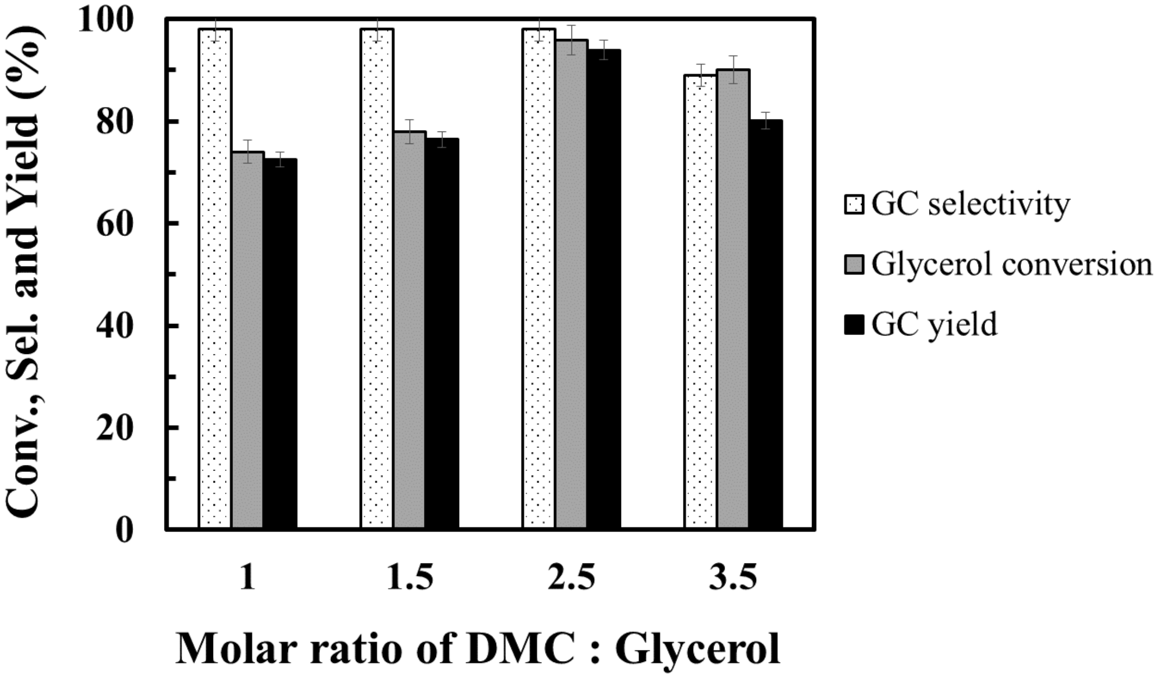
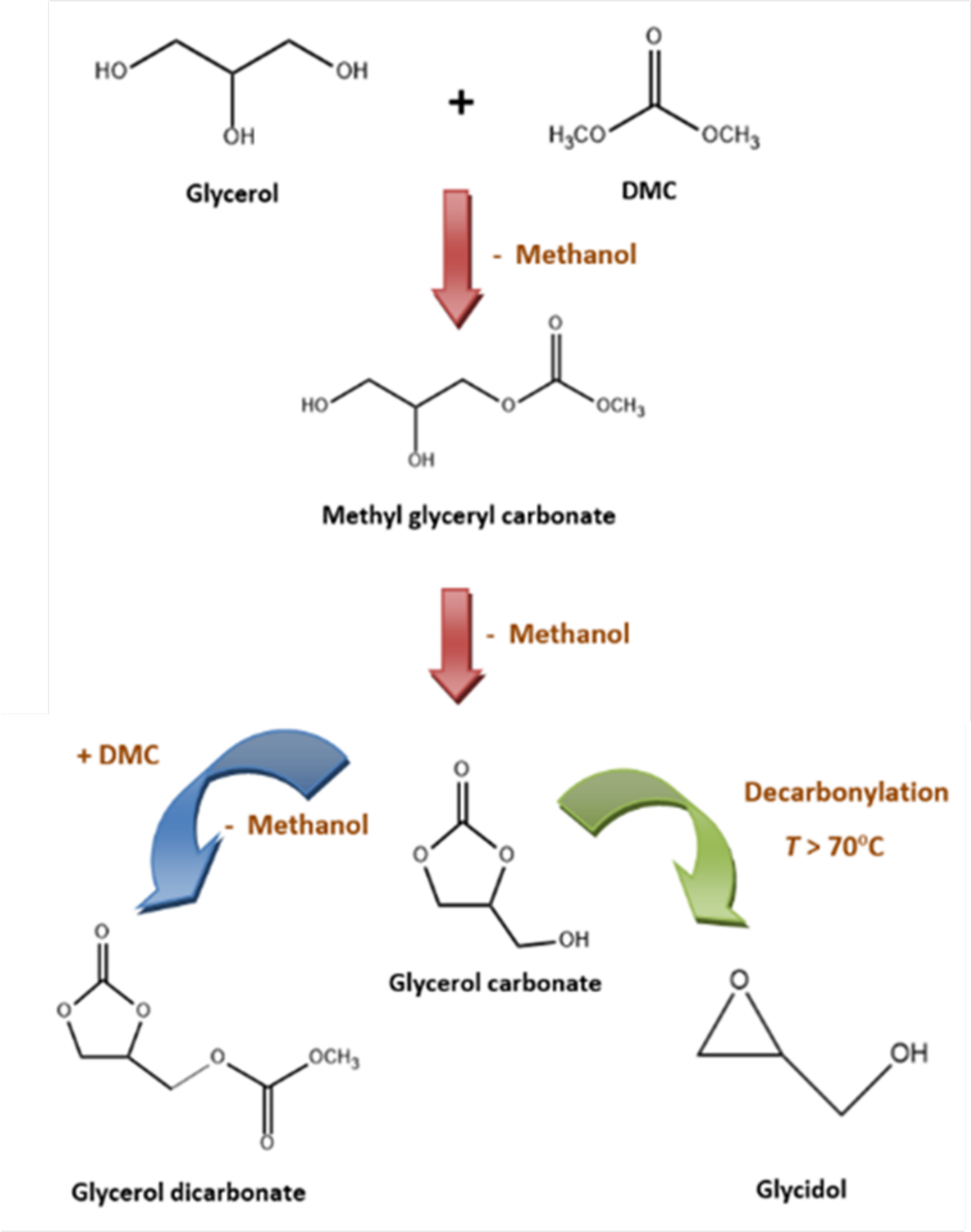


Fig.2. Effect of molar ratio of DMC: glycerol on catalytic activity (CaO : glycerol = 0.08 : 1, reaction temperature = 60 °C, reaction time = 180 min).

One of the most important factors which affect the glycerol carbonate yield is the molar ratio of DMC:glycerol. Other previous works on this reaction with heterogeneous catalysts were typically studied at the mole ratio of DMC to glycerol in the range of 2–5. [17, 50, 51] The excess mole of DMC was applied which also functioned as solvent in the transesterification reaction. Therefore, it was not necessary to add another solvent for mixing DMC and glycerol. In this work, when increasing the molar ratio of DMC: glycerol from 1 to 2.5 glycerol, the conversion and GC yield increased as driven by an excess amount of DMC towards GC formation and improved miscibility of glycerol with DMC. However, as observed in the reaction system, there was a possibility for phase separation between DMC and glycerol when their molar ratio was less than 2. Therefore, it was important to point out that adding a high amount of DMC to glycerol would lead to a decrease in GC yield according to the drop of GC selectivity at DMC:glycerol equal to 3.5 as illustrated in Fig.2. This was directly related to the formation of glycerol dicarbonate by-product from a side reaction [14] as shown in scheme 1. According to the results, the optimum mole ratio of DMC to glycerol of 2.5 was in agreement with previous research works and insignificantly depended on catalysts, i.e., dolomite, Na-based zeolite, K_2CO_3/MgO[32, 42, 52] and hydrotalcite.[53]



Scheme 1. Possible side reactions during GC production.

3.2.3 Effect of catalyst loading

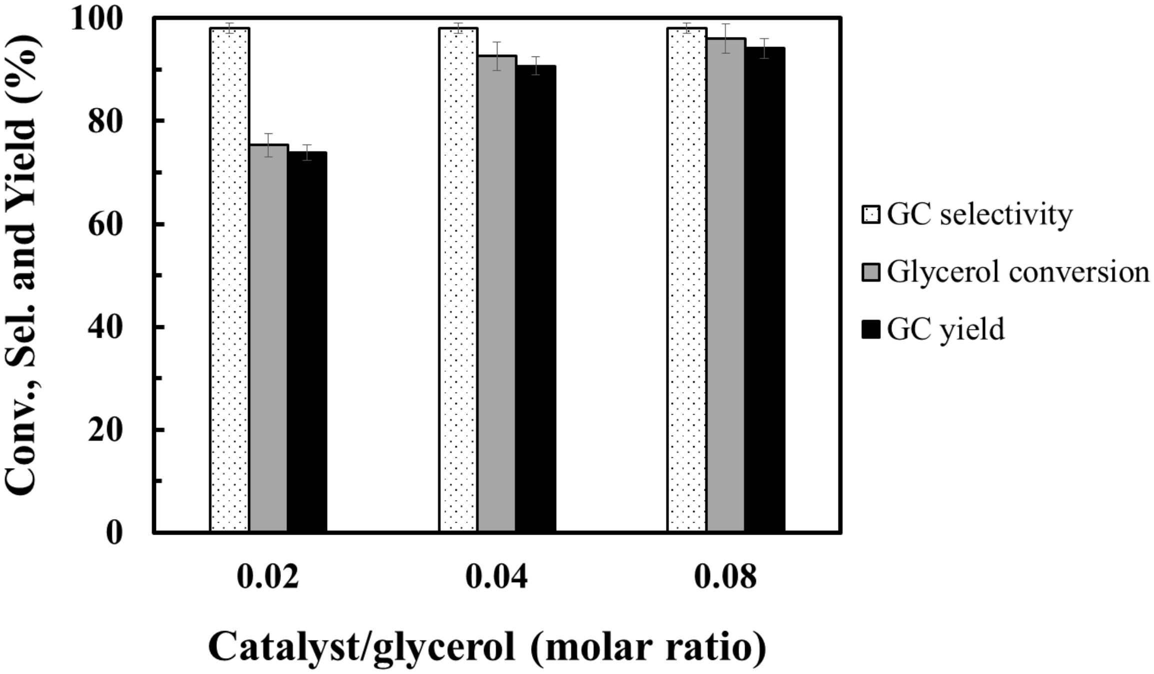


Fig.3. Effect of catalyst loading on catalytic activity (DMC: glycerol = 2.5:1, reaction temperature = 60 °C and reaction time = 180 min).

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

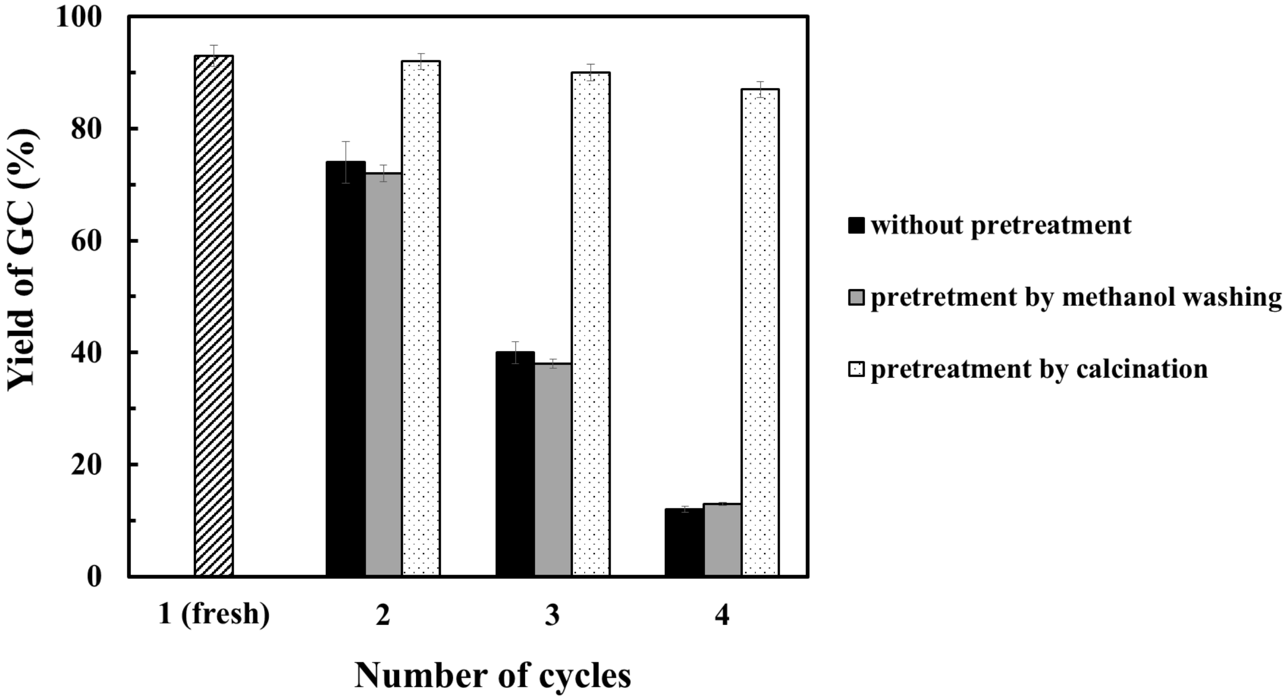


Fig.4. Reusability of eggshell-derived CaO.

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 °C overnight, and calcined at 900 °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 enhance the catalyst reusability. However, there was some gradual loss of catalytic activity which would be due to the structural change and sintering that occurred during the catalytic and regeneration process by calcination at high temperature as the surface area, mean pore diameter and total pore volume decreased to 1.43 m^2/g, 4.72 nm and 0.0053 cm^3/g, respectively as shown in Table 1.

The phase transformation can be ensured with XRD characterization of the used catalyst as shown in Fig.5 to investigate and compare the structure of the remaining number of active phases at each cycle with fresh CaO eggshell (Fig.5A). The first used catalyst possessed many peaks as calcium diglyceroxide, calcium methoxide and calcium carbonate which indicated that CaO phase was transformed to calcium diglyceroxide, methoxide and carbonate phase under reaction conditions as displayed in Fig.5B. The appearance of the active phases promoted conversion to methoxide, diglyceroxide and carbonate phases with a decrease of basic strength (see Table 1.) and reduced the performance of the catalyst. In addition, the 4th used catalyst contained essentially calcium carbonate phase (Fig.5C) and served negatively as an inactive phase in the transesterification reaction. Moreover, the TGA results (Fig.6) demonstrated the weight loss of the 1st used catalyst around 200 ºC and 700 ºC which was attributed to the decomposition of glyceroxide and carbonate, respectively. This indicated availability of glyceroxide and carbonate on surface of the catalyst. After the 4th used catalyst, comparing to the 1st used catalyst, drastical changes in TGA profile could be observed. The main weight loss around 650-750 ºC, owing to decomposition of $CaCO_3$ to CaO, confirmed that most of phase on catalyst surface was in carbonate form, an inactive phase in transesterification between glycerol and DMC. In addition, the characterization of the catalysts without calcination pretreatment indicated that the basic strength changed from strong basic ($15.0 < H\_ < 18.4$) of virgin catalyst to $9.8 < H\_ < 15.0$ after the 1st cycle and turn to weak basic strength ($7.2 < H\_ < 9.8$) after the 4th cycle. Meanwhile, the amount of basicity decreased from the virgin catalyst of 0.482 mmol/g to 0.360 and 0.023 mmol/g, respectively because CaO active phase transform to $CaCO_3$ as an inactive phase. The physical properties i.e. BET surface area, mean pore diameter and total pore volume determined by N_2 physisorption also exhibited the change during the cycles corresponding to the phase transformation as shown in Table 1. The SEM image (Fig. S2) showed the change from irregular crystal structure of CaO to spherical like $CaCO_3$ [54] of the 4th used catalyst which was in good agreement with the above characterization methods.

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

Catalysts	**BET surface area (m^2/g)**	**Mean pore diameter (nm)**	**Total pore volume (cm^3/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

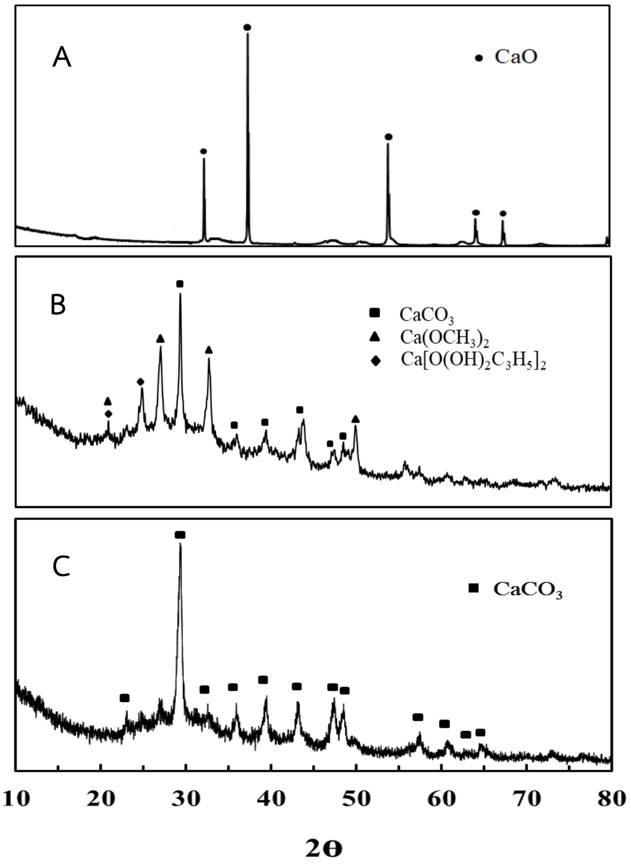


Fig.5. XRD patterns of (A) the fresh CaO eggshell, (B) the 1st used catalyst and (C) the 4th used catalyst.

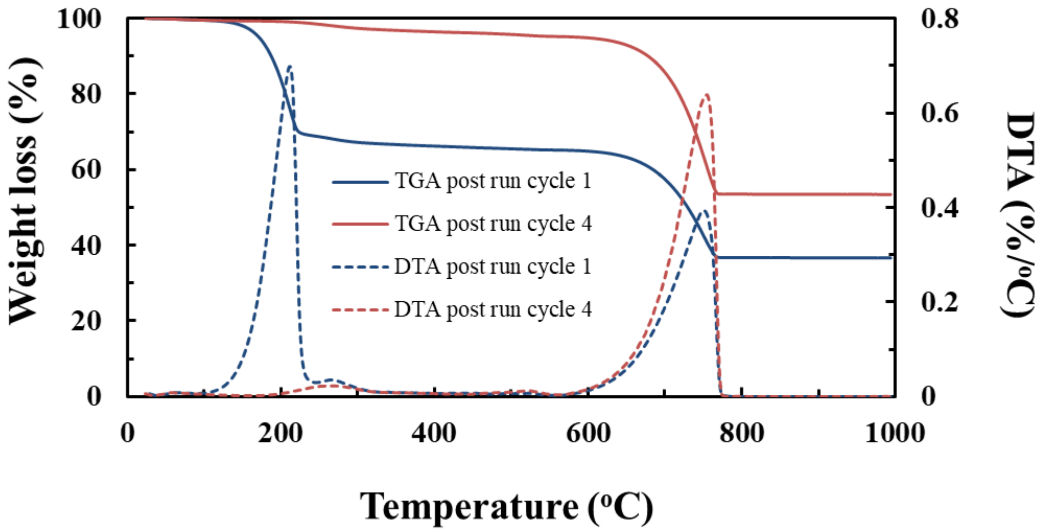


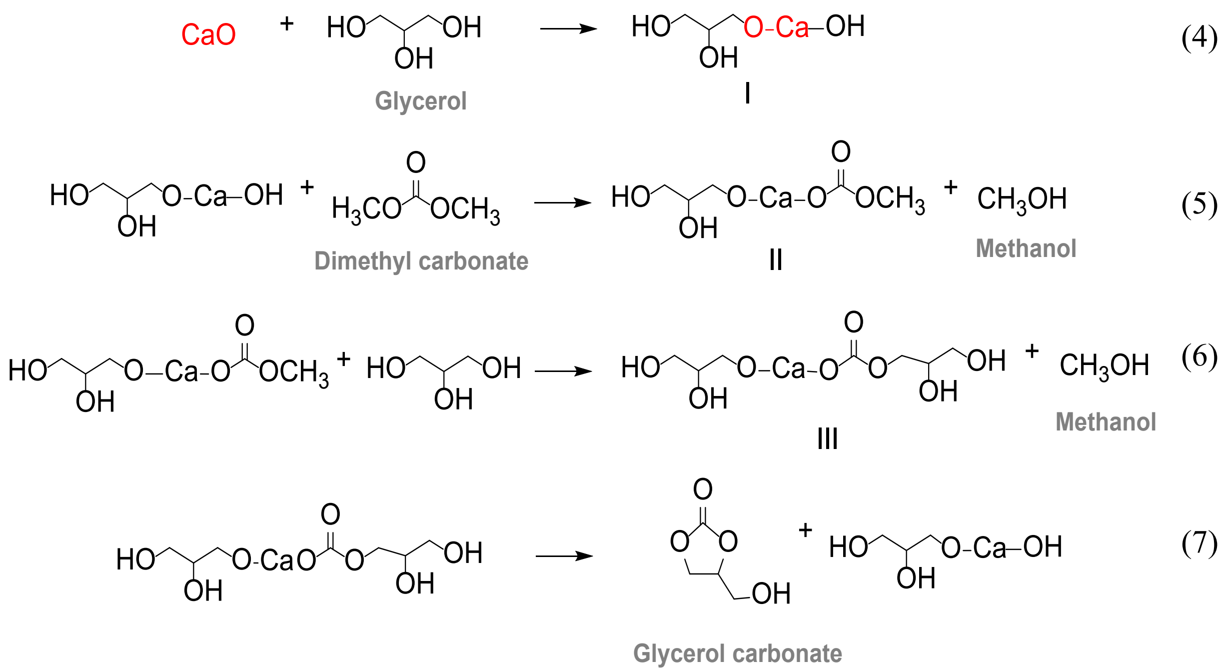
Fig.6. TGA (solid line) and DTA (dash line) of 1st used catalyst (blue) and 4th used catalyst (red).

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

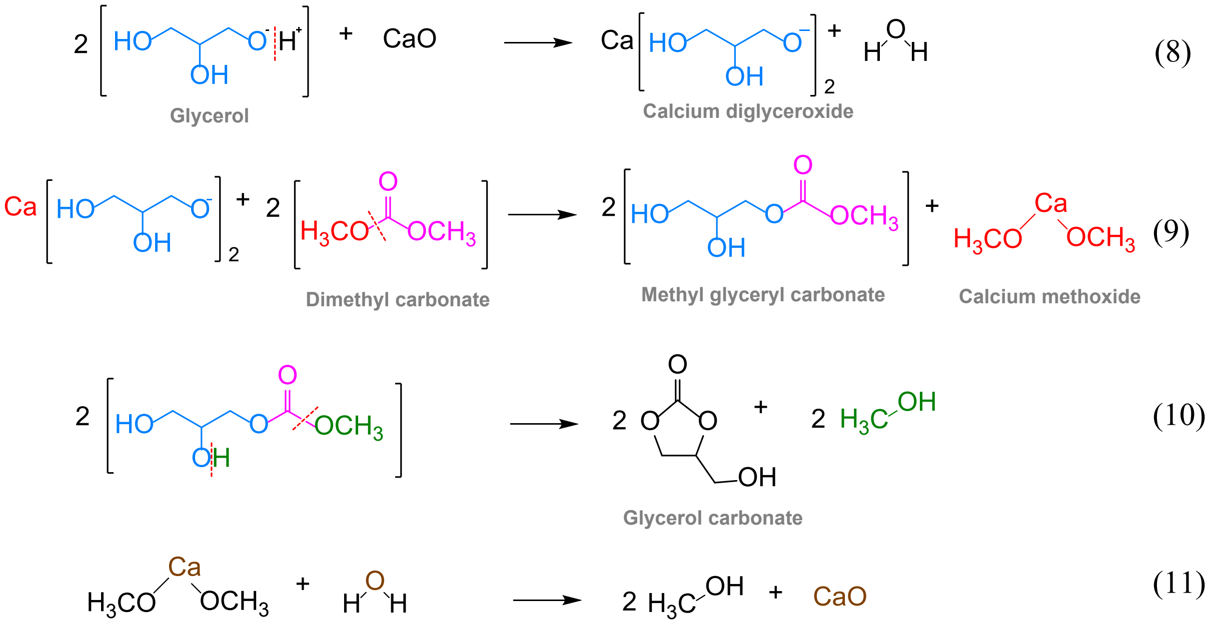
The general mechanism of heterogeneous base catalysts in transesterification of glycerol and DMC had been illustrated in many researches.[31, 42, 55] In the first step herein, glycerol interacted with base catalyst to glycerol anion which further reacted with DMC to hydroxyl alkyl carbonate and methanol 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 explicitely, 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

2. They also proved in another experiment that $Ca(C_3H_7O_3)(OCO_2CH_3)$ can be converted to $CaCO_3$ when exposing to the air for 1 h.

Consequently, this research investigates the difference of the mechanism of CaO catalysed transesterification between glycerol and DMC based on the condensation reaction between glycerol and CaO as illustrated in scheme 3, and previous work which described the mechanism based on the insertion reaction of glycerol and CaO. The calcium cation is a relatively weak acid attracting one of the primary hydroxyl groups of glycerol whereas the conjugated oxygen anion from CaO catalyst displays a strong basic site attracting H^+ from glycerol forming calcium diglyceroxide and water or somewhat water derivative species, respectively (Eq.8 in Scheme 3). Then, calcium diglyceroxide would attract carbonyl carbon of DMC as a co-reactant to generate calcium methoxide and methyl glyceryl carbonate as intermediates (Eq.9 in Scheme 3). Methyl glyceryl carbonate restructures would be transformed into glycerol carbonate and methanol (Eq.10 in Scheme 3). Finally, calcium methoxide would react with water to obtain methanol and regenerate CaO (Eq.11 in Scheme 3). According to scheme 3, the calcium diglyceroxide can be generated by the interaction of CaO and glycerol, as confirmed by Fuji et al. (1968) [56] Meanwhile, calcium methoxide appeared during the transesterification reaction.[57] Moreover, the occurrence of water (Eq.8 in Scheme 3) might cause the catalyst deactivation which relates to TOF-SIMS results, the presence of calcium species with water including $Ca(C_3H_7O_3)-H_2O$, $Ca(C_3H_7O_3)(OCO_2CH_3)-2H_2O-H$, $Ca(C_3H_7O_3)(OCO_2CH_3)$ H_2O-H, etc. by Simanjuntak et al. (2011) [34] We hypothesize, that the formation of water could cause the transformation of CaO to $CaCO_3$ and lead to catalyst deactivation. This point will be further described in the deactivation mechanism section.



Scheme 2. Proposed mechanisms of CaO-catalyzed transesterification of DMC and glycerol by Simanjuntak et al. (2011) [34] based on insertion reaction between glycerol and CaO.



Scheme 3. Possible mechanisms of CaO-catalyzed transesterification of DMC and glycerol by this research base on the condensation reaction between glycerol and CaO.

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 cause of catalyst deactivation. In addition, they proposed that the interaction of catalyst with reaction mixture would be responsible for conversion to the basic calcium carbonate $Ca_x(OH)_y(CO_3)_z$, leading to a decrease in catalytic activity. Furthermore, Simanjuntak et al. (2011) [34] observed calcium compound $Ca(C_3H_7O_3)(OCO_2CH_3)$ as an active phase that occurred *in situ* during the transesterification between glycerol and DMC and the later presented a similar activity to CaO. Once exposed to air, $Ca(C_3H_7O_3)(OCO_2CH_3)$ most likely reacted with CO_2 and then was converted to $CaCO_3$. From the above mentioned observations, although most researchers agreed that the deactivation of CaO catalyst is due to $CaCO_3$ formation [31, 32], in consistent with XRD result of the 4th used catalyst (Fig.5C), the detailed mechanism of the deactivation is still not fully revealed.

Another highlight in this study is the observation of difference between glycerol and DMC consumption and additional amount of methanol by-product even with high selectivity of GC (negligible glycerol dicarbonate and glycidol formation) when the reused catalyst was employed. Theoretically, the ratio of methanol to GC of ca. 2.0 is expected according to their stoichiometry. On the other hand, the mole of methanol to GC exhibited higher than the stoichiometric ratio as indicated in Fig.7 (A).

Without catalyst pretreatment by calcination at 900 °C, methanol to GC ratio increased with the number of cycles used as shown in Fig.7 (A) while it was only slightly larger than 2.0 and quite constant when the catalyst was calcined before reuse (Fig.7 (B)). In other words, the extent of methanol to GC ratio over stoichiometric ratio (Fig. 7(A)) increased along with the extent of $CaCO_3$ formation (Fig. 5).

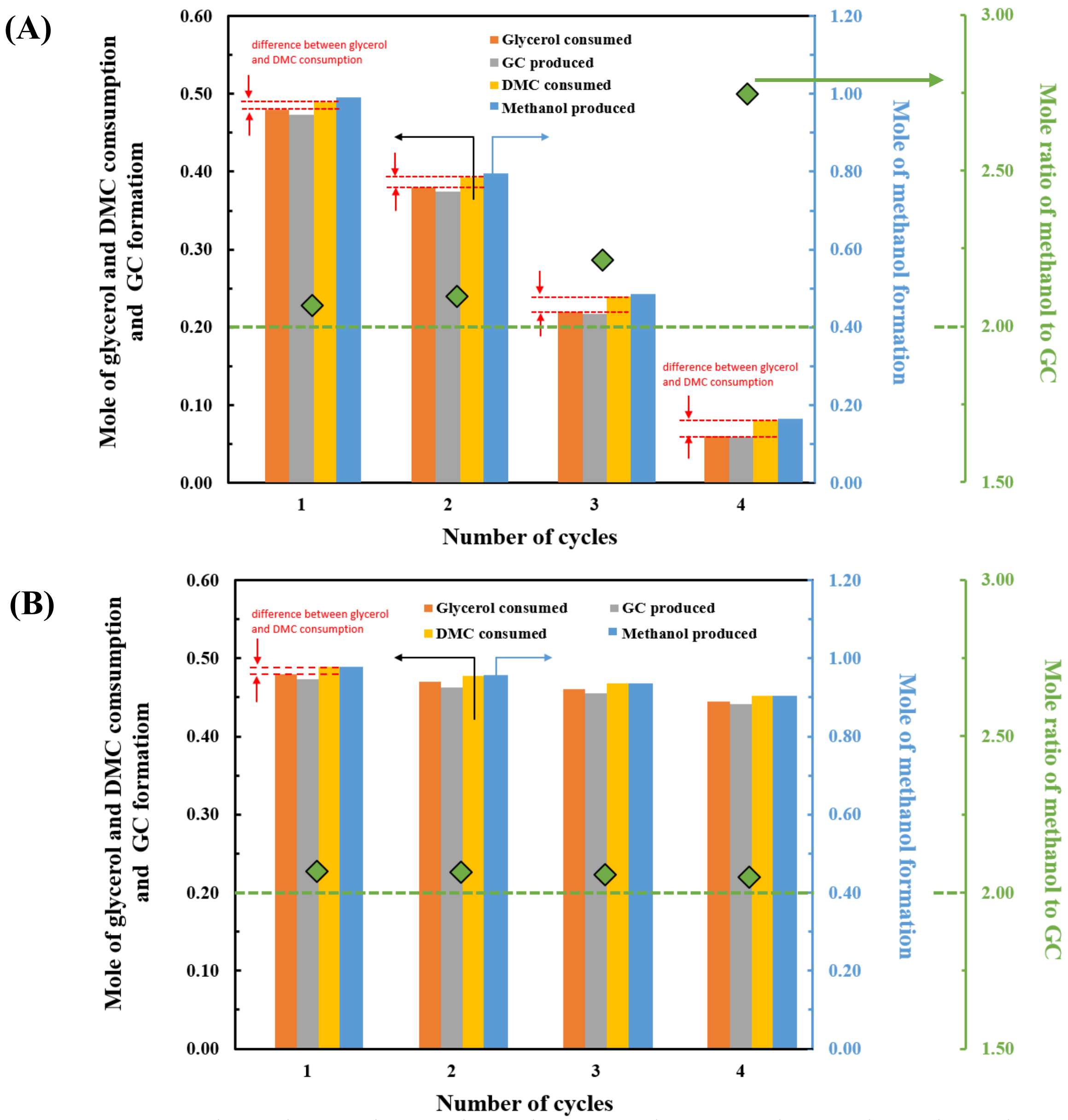


Fig.7. Mole of glycerol and DMC consumption and GC and methanol formation, and corresponding methanol to GC ratio at different catalyst cycles. (A) without catalyst pretreatment and (B) pretreatment by calcination. The dashed line denoted theoretical stoichiometric of methanol to GC of 2.0.

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 glycerol and DMC consumption which increased with the number of cycles. This result again occurred with high GC selectivity which implies that further DMC consumption through a side reaction.

The generation of water (as proposed Eq.8 in Scheme 3) with the observation of products/reactants that are not following their stoichiometric ratio allows to hypothesize CaO transformation in the reactions as follow.

Proposed *in situ* CaO deactivation reaction:

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

$$Ca(OH)_2 + C_3H_6O_3 \rightarrow 2CH_3OH + CaCO_3 \qquad (13)$$

This hypothesis was further supported by performing the reaction of CaO, DMC and water at an equivalent molar ratio of CaO, DMC and water at 60 ºC reaction temperature for 3 h. After the reaction, the collected catalyst was filtered and characterized by XRD to investigate the phase transformation of the catalyst. It was evidenced that CaO was converted to the $CaCO_3$ phase in CaO and DMC system after adding water, as shown in supporting information Fig.S4. Consequently, this XRD result corroborated with assumption that the generated water from Eq.8 would react with CaO and DMC to produce carbonate phase, and extra methanol mole, described in Eqs.12-13.

4. Conclusion

This research revealed a significant difference in the deactivation mechanism of CaO for glycerol carbonate production via the transesterification of glycerol with dimethyl carbonate. The appearance of the CaO as an active phase was converted to alkoxide phases such as methoxide, diglyceroxide and carbonate phases with a decreasing basic strength and reducing performance of the catalyst correlated with glycerol conversion from 96% to 12% after the 4th cycle. The ratio of methanol to GC occurrence, which was higher than 2.0 towards the desired reaction stoichiometric ratio, was a significant observation and correlated well with the extent of $CaCO_3$ formation. The proposed mechanism of CaO catalyzed transesterification of glycerol into GC based on the condensation reaction of glycerol with *in situ* formation of water or water-derivative species is consistent with that characterized previously.[34] These findings allowed us to hypothesize a deactivation mechanism which remains consistent with the outcome of independent experimental result that demonstrated that CaO can react with DMC and water into methanol and $CaCO_3$, corroborating with methanol to GC non-stoichiometric ratio of 2.0 and thus enabling alternative monitoring of catalyst deactivation.

However, it is of commendable to note that the calcination of post-run catalyst at 900 °C exhibited nearly constant catalytic activity and the mole ratio of methanol to GC remained constant at the desired reaction stoichiometry of ca. 2.0. Catalyst was therefore efficiently recovered and reused for at least four times.

Authors contribution statement

Wanichaya Praikaew: Conceptualization; Methodology; Formal analysis; Data Curation; Validation; Investigation; Visualization; Writing – original draft; Writing - Review & Editing.

Worapon Kiatkittipong: Conceptualization; Data Curation; Validation; Supervision; Writing Review & Editing; Funding acquisition**.**

Farid Aiouache: Writing - Review & Editing.

Vesna Najdanovic-Visak: Writing - Review & Editing.

Mutsee Termtanun: Writing - Review & Editing.

Jun Wei Lim: Writing - Review & Editing.

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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.

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