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Research Article

Green Mg-Ca-Al Mixed Oxide Catalyst for Synthesis of Glycerol Carbonate

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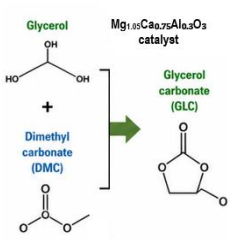
GRAPHICAL ABSTRACT



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ABSTRACT

Glycerol carbonate (GLC) is a value-added chemical with wide applications in polymers, solvents, surfactants, and lithium-ion batteries. The conversion of glycerol, a by-product of biodiesel production, into GLC has attracted considerable attention due to its economic and environmental benefits. This study aims to investigate the transesterification of glycerol with dimethyl carbonate (DMC) to produce glycerol carbonate (GLC) using a heterogeneous Mg–Ca–Al mixed-oxide catalyst. Catalysts with different molar ratios of Mg, Ca, and Al ($Mg_{3.5x}Ca_{0.5y}Al_xO_3$) were synthesized and calcined at 500 °C for 5 hours to determine the optimal composition for achieving a high GLC yield. Among the synthesized catalysts, $Mg_{1.05}Ca_{0.75}Al_{0.3}O_3$ was identified as the most effective. The results revealed that the $Mg_{1.05}Ca_{0.75}Al_{0.3}O_3$ catalyst exhibited higher catalytic activity when calcined at an elevated temperature of 800 °C. Characterization results confirmed the formation of well-dispersed Mg–Ca–Al mixed oxide phases with enhanced surface properties and catalytic activity.All transesterification reactions were conducted in a batch process under varying conditions: catalyst loading (2–5 wt%), reaction temperature (65–80 °C), DMC-to-glycerol molar ratio (1:1–4:1), and reaction time (0.5–2.0 hours). The optimum reaction conditions were identified as a catalyst loading of 3 wt%, reaction temperature of 70 °C, DMC-to-glycerol molar ratio of 3:1, and reaction time of 1.5 hours. Under these conditions, a GLC yield of 75% was achieved, with a glycerol conversion of 76%. The stability of the $Mg_{1.05}Ca_{0.75}Al_{0.3}O_3$ catalyst was evaluated over three consecutive cycles. The results indicated that aluminium plays a crucial role in enhancing catalyst stability by providing a high surface area and acting as a support. Furthermore, the presence of aluminium reduces the basicity of the catalyst, thereby minimizing the formation of glycidol.

Keywords: Transesterification, Glycerol, Glycerol carbonate, Dimethyl carbonate, Mg-Ca-Al mixed-oxide

1. INTRODUCTION

The escalating global demand for biofuels has led to a significant increase in crude glycerol production, a major byproduct of the transesterification process [1]The rapid growth of biodiesel production has led to a significant surplus of glycerol, creating economic and environmental challenges [2]. Improper disposal of crude glycerol and chemical wastes generated during conventional catalytic processes may contribute to water pollution and negatively affect aquatic ecosystems. Therefore, the effective utilization of excess glycerol has become an important research focus for improving the sustainability and feasibility of the biodiesel industry. Among the various glycerol derivatives, glycerol carbonate (GLC) and glycidol are considered high-value products. GLC possesses desirable physicochemical properties such as biodegradability, low toxicity, low flammability, high boiling point, and high chemical reactivity [3,4]. It can be used as a substitute for ethylene and propylene carbonate in various applications, including electrolyte solvents in lithium-ion batteries, fuel additives, surfactants in cosmetic formulations, intermediates in chemical synthesis, and precursors for polymeric materials such as polycarbonates, hyperbranched polyols, and non-isocyanate polyurethanes [5,6].

Various pathways have been explored for the synthesis of glycerol carbonate (GLC) from glycerol, including reactions with carbon monoxide, phosgene, carbon dioxide, urea, alkylene carbonates, and dialkyl carbonates [5,7–11]. However, several limitations have been reported for these approaches. Processes involving carbon monoxide and phosgene are hazardous due to their high toxicity and corrosiveness [8,10]. Reactions utilizing carbon dioxide often suffer from low conversion due to its high thermodynamic stability [5]. The use of alkylene carbonates produces by-products such as ethylene glycol, which complicates downstream separation due to its high boiling point [9]. Similarly, urea-based processes generate large

amounts of ammonia, requiring additional separation steps [7]. In contrast, the transesterification of glycerol with dialkyl carbonates, particularly dimethyl carbonate (DMC), has emerged as a promising and environmentally friendly route for GLC production [12]. DMC is considered a green reagent due to its low toxicity and environmental The development of environmentally friendly catalytic systems for glycerol valorization is essential to reduce hazardous waste generation and minimize impacts on water resources. In particular, efficient catalysts are required to improve the reaction rate, glycerol conversion, and selectivity toward glycerol carbonate during transesterification. Various catalytic systems, including homogeneous, heterogeneous, and enzymatic catalysts, have been investigated for GLC production. Basic catalysts generally exhibit higher catalytic activity compared to acidic catalysts, resulting in improved glycerol conversion and GLC yield [9]. Heterogeneous catalysts are particularly attractive due to their ease of separation, reusability, and environmental compatibility. Mixed oxide catalysts have gained attention because of their tunable surface properties, high thermal stability, and strong catalytic performance [13–15]. Therefore, the present study aims to synthesize glycerol carbonate via transesterification of glycerol with DMC using a heterogeneous Mg–Ca–Al mixed oxide catalyst, achieving 75% GLC yield and 76% glycerol conversion under optimum conditions. The effects of reaction parameters, including catalyst loading, reaction temperature, DMC-to-glycerol molar ratio, and reaction time, were systematically investigated. In addition, catalyst reusability and regeneration were evaluated to assess the stability and practical applicability of the developed catalyst system.

2. EXPERIMENTS

2.1 Catalyst Preparation

The Mg–Ca–Al mixed oxide catalyst was prepared using the co-precipitation method. Magnesium, calcium, and aluminium precursors were selected due to their synergistic roles in enhancing catalyst basicity, surface area, and structural stability. CaO is known to provide strong basic sites for transesterification, while MgO contributes to improved catalyst porosity and catalytic activity. Meanwhile, Al_2O_3 acts as a support material that enhances surface area, thermal stability, and resistance toward catalyst leaching. The catalyst preparation was based on a total of 20 g of salt mixture, consisting of 10 g of magnesium nitrate hexahydrate, $Mg(NO_3)_2{\cdot}6H_2O$ (99.5%), 7.14 g of calcium nitrate tetrahydrate, $Ca(NO_3)_2{\cdot}4H_2O$ (99%), and 2.86 g of aluminum nitrate nonahydrate, $Al(NO_3)_3{\cdot}9H_2O$ (98%). A 50 mL mixed salt solution was prepared by dissolving the salts in distilled water in a 250 mL beaker under vigorous magnetic stirring at 300 rpm for 30 minutes. The solution was then precipitated using 10 mL of 5.2 M NH_4OH. NH_4OH was used as the precipitating agent to maintain alkaline conditions and facilitate the formation of mixed hydroxide precursors. The resulting mixture was aged at 80 °C for 5 hours until a homogeneous mixture was obtained, while maintaining the pH in the range of 10–11. The solution was filtered and dried in an oven at 110 °C for 12 hours. Finally, calcination was carried out at two different temperatures (500 °C and 800 °C) for 5 hours, with a heating rate of 5 °C/min, to obtain the solid catalyst.

2.2 Catalyst Characterization

The total surface area, pore volume, and pore size distribution of the synthesized catalyst were measured by nitrogen adsorption–desorption isotherms at 77 K using the Brunauer–Emmett–Teller (BET) method on a Micromeritics ASAP 2020 instrument. The surface functional groups of the catalyst were identified using Fourier Transform Infrared (FTIR) spectroscopy. The spectra of the synthesized catalyst were recorded in the range of 4000–400 cm^{-1} using a PerkinElmer System 2000 spectrometer. X-ray diffraction (XRD) patterns were carried out using a Philips PW1710 model, with Cu Kα radiation (λ = 1.54178 Å) at 45 kV and 60 mA. The surface morphology of the catalysts was determined by Scanning Electron Microscopy (SEM) (VPFESEM, Zeiss SUPRA 35 VP model). The elemental composition of Ca, Mg, and Al present in the catalyst before and after the reaction was analyzed using an energy-dispersive X-ray (EDX) detector mounted on the microscope. High-resolution transmission electron micrographs of the catalysts were obtained using a 200 kV TECNAI G2 20 S-TWIN FEI field emission microscope equipped with an EDAX system, to provide detailed insights into the morphology and particle size of the solid catalysts.

2.3 Transesterification of glycerol to GLC

The synthesis of GLC via the transesterification reaction of glycerol with dimethyl carbonate (DMC) was carried out in a 50 mL round-bottom glass reactor equipped with a magnetic stirrer. The transesterification reaction was studied using 9.1 mL of glycerol reacted with 20.9 mL of DMC in the presence of a catalyst (2–5 wt.% based on the amount of glycerol used). The reaction mixture was maintained at a temperature of 60–85 °C ± 2 °C and stirred at a speed of 300 rpm for 0.5–2.0 hours. After the reaction was completed, the reaction mixture was allowed to cool down to room temperature. The reaction mixture was then separated from the catalyst by centrifugation. The reaction products were analyzed using gas chromatography (GLC-2010 Plus, Shimadzu, Japan) equipped with a flame ionization detector (FID), a split/splitless injection unit, and a ZB5-HT capillary column (30 m × 0.25 mm × 0.25 μm). Helium at 1.3 mL/min was used as the carrier gas. The injection was carried out at

a split ratio of 100:1. 20 µL of the product were dissolved in 1 mL of pyridine. Then, 1 µL of the prepared solution was withdrawn and injected into the gas chromatograph. The column temperature was initially set at 100 °C, followed by a ramping rate of 15 °C/min until it reached 150 °C, and then increased to 200 °C at a ramping rate of 8 °C/min. The flame ionization detector (FID) and injector temperatures were set at 280 °C and 325 °C, respectively. Glycerol conversion was determined based on GC analysis using the following equations:

$$C\ (\%) = \frac{C_{GO} - C_G}{C_{GO}}\ x\ 100 \quad (1)$$

$$Y\ (\%) = \frac{C_{gc}}{C_{GO}}\ x\ 100 \quad (2)$$

where C is glycerol conversion (%), C_{GO} is the initial concentration of glycerol; C_G is the glycerol concentration after reaction, C_{gc} is the glycerol carbonate concentration after reaction and Y is the glycerol carbonate yield.

3. RESULTS AND DISCUSSION

The powder X-ray diffraction (XRD) patterns of $Mg_{1.05}Ca_{0.75}Al_{0.3}O_3$ and $Mg_{1.05}Ca_{0.75}O_2$ catalysts after calcination at 800 °C are presented in Fig. 1. It can be observed that the XRD patterns of both catalysts show the presence of the CaO phase, with characteristic peaks at 2θ = 32.2°, 37.3°, 53.8°, 64.1°, 67.3°, and 78.9°, while the MgO phase is observed at 2θ = 42.8° and 62.3° [16]. Meanwhile, it can be observed that the $Mg_{1.05}Ca_{0.75}Al_{0.3}O_3$ catalyst exhibits lower peak intensities at 32.2°, 37.3°, and 42.8° compared to $Mg_{1.05}Ca_{0.75}O_2$, which may be attributed to the presence of an amorphous Al_2O_3 phase [17]. The XRD patterns of CaO and MgO appear less distinct due to the good dispersion of these oxides on the alumina surface. A low-intensity peak at 2θ = 29.4° indicates the presence of $CaCO_3$ [18].This suggests that $CaCO_3$ may have formed due to the adsorption of CO_2 by CaO.

$Mg_{1.05}Ca_{0.75}Al_{0.3}O_3$ catalyst has a high surface area of 53.67 m^2/g and a large pore volume of 0.130 cm^3/g as compared to CaO (2.7 m^2/g; 0.002 cm^3/g) and MgO (24.7 m^2/g; 0.081 cm^3/g) and mixed oxide catalyst, $Mg_{1.2}Ca_{0.8}O_2$ (31.7 m2/g; 0.091 cm3/g). This could be attributed due to the addition of aluminium content. The average pore size of $Mg_{1.05}Ca_{0.75}Al_{0.3}O_3$ catalyst is 98 Å. Fig. 2 shows the obtained nitrogen adsorption- desorption isoterms of $Mg_{1.05}Ca_{0.75}Al_{0.3}O_3$ mixed oxide catalyst. It is clearly proven that the obtained isotherm follows type IV isotherm with type H2 hysteresis loops which illustrate the mesoporous characteristics [19]. The hysteresis loops indicate the pore size, pore structure and shape of materials which have disordered distributions. As shown in the Figure 2, at a relative pressure range from 0.5 to 1.0, the isotherm presented the typical hysteresis loop of highly mesoporous material [20]. It can be observed that high volume or quantity of N_2 adsorption was occurred which corresponded by the values of Y-axis due to the larger pore volume of the catalyst.

FTIR spectroscopy was used to characterize the functional groups present on the surface of the catalyst, as shown in Fig. 3. The spectra were recorded for both fresh and reused $Mg_{1.05}Ca_{0.75}Al_{0.3}O_3$ catalysts over a wavenumber range of 4000–400 cm^{-1}. A broad band observed at 3200–3600 cm^{-1} is attributed to physisorbed water due to surface hydration. Two distinct peaks at 3462.4 and 3638.8 cm^{-1} correspond to surface hydroxyl groups (Mg–OH and Ca–OH), respectively [20]. The disappearance of the peak at 3638.8 cm^{-1} in the reused catalyst indicates the loss of surface hydroxyl groups after repeated calcination. Bands in the ranges of 800–880 cm^{-1} and 1400–1600 cm^{-1} present the antisymmetric stretching vibration of carbonate [21,22]. A strong peak at 1437 cm^{-1} confirms the presence of mono- and bidentate carbonates formed by the interaction of CO_2 with basic sites (CaO and MgO) on the catalyst surface [23]. The increased intensity of carbonate bands in the reused catalyst suggests progressive carbonation due to CO_2 adsorption during exposure to air. Additionally, bands observed at 400–600 cm^{-1} are attributed to metal–oxygen bonds. Overall, the FTIR results confirm the presence of hydroxyl and carbonate species, which is consistent with the XRD analysis.

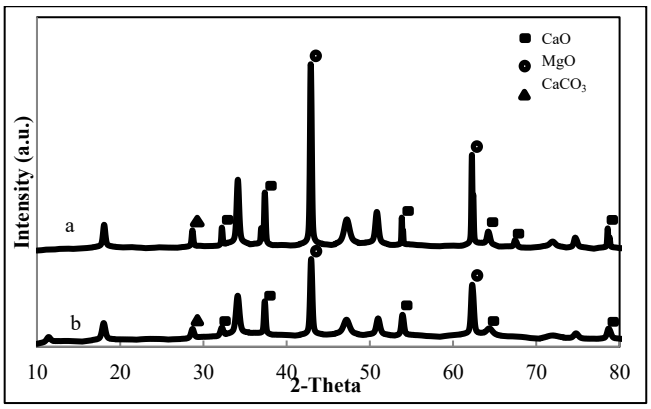

Fig. 1 XRD patterns of samples of catalyst;
a) $Mg_{1.05}Ca_{0.75}O_2$; b) $Mg_{1.05}Ca_{0.75}Al_{0.3}O_3$

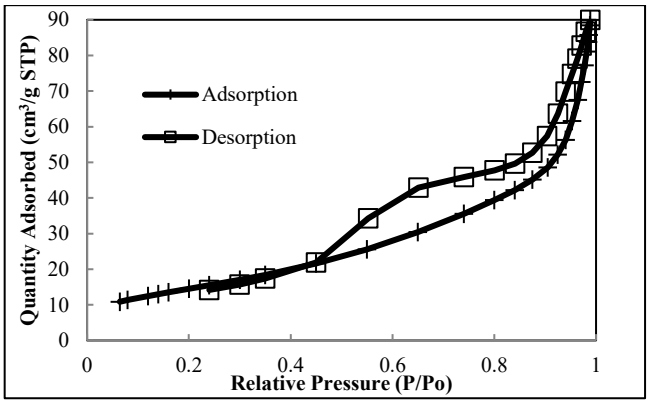

Fig. 2 Nitrogen adsorption-desorption isotherms for $Mg_{1.05}Ca_{0.75}Al_{0.3}O_3$ mixed oxide catalyst

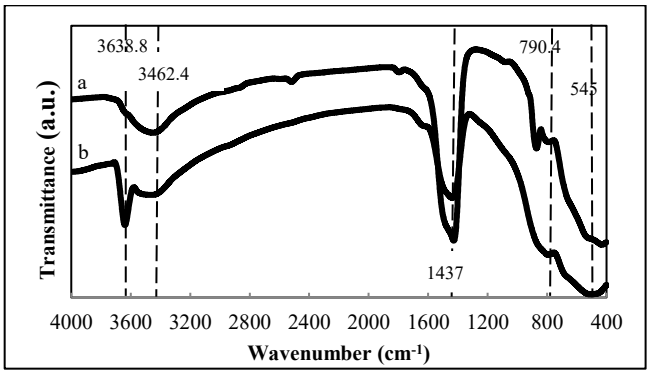

Fig. 3 FTIR spectra of a) reused $Mg_{1.05}Ca_{0.75}Al_{0.3}O_3$ catalyst; b) fresh $Mg_{1.05}Ca_{0.75}Al_{0.3}O_3$ catalyst.

Fig. 4 presents the SEM image of $Mg_{1.05}Ca_{0.75}Al_{0.3}O_3$ mixed oxide calcined at 800 °C. The morphology of the catalyst shows a closely packed arrangement of crystallites and a rough surface with irregular shapes. The HRTEM image, as shown in Fig. 5, provides useful information for identifying the presence of crystalline mixed oxide regions, such as CaO and MgO [24]. The analysis indicates the presence of darker regions, which are attributed to calcium and magnesium oxides. The composition of these particles was confirmed by EDX analysis (Table 1). The $Mg_{1.05}Ca_{0.75}Al_{0.3}O_3$ catalyst consists of atomic percentages (at.%) of 18.61% Mg, 10.07% Ca, 5.99% Al, and 65.33% O. However, the theoretical atomic percentages are 20.59% Mg, 14.71% Ca, 5.88% Al, and 58.82% O, as calculated based on the atomic ratio. The differences between the EDX results and theoretical values may be attributed to the presence of non-homogeneous mixed crystalline phases in the Mg–Ca–Al oxide system, as confirmed by XRD analysis. In addition, these discrepancies may also be due to the precipitation conditions during catalyst synthesis, as ammonia solution was used as the precipitating agent to maintain the pH at 10.

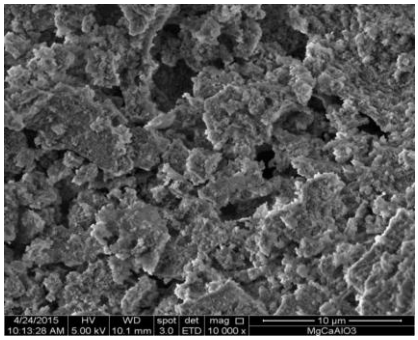

Fig. 4 Scanning electron micrograph image of $Mg_{1.05}Ca_{0.75}Al_{0.3}O_3$ calcined at 800 °C (magnification = 10 000 x).

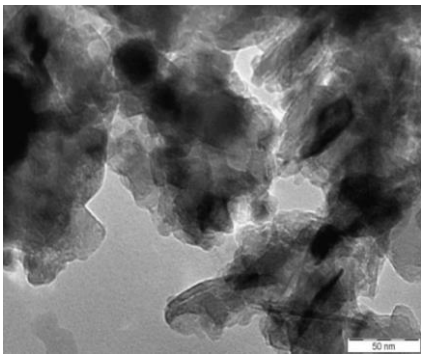

Fig. 5 High resolution transmission electron micrograph image of $Mg_{1.05}Ca_{0.75}Al_{0.3}O_3$ calcined at 800 °C.

Mixed oxide catalysts with different Mg–Ca–Al ratios were synthesized based on various chemical composition. MgO exhibited a higher glycerol conversion of 94% but a lower GLC yield of 23%, while CaO showed 79% glycerol conversion with a higher GLC yield (68%). This is attributed to by-product formation, such as methanol, which is continuously removed during glycerol transesterification

Table 1 EDX elemental analysis results for of $Mg_{1.05}Ca_{0.75}Al_{0.3}O_3$ catalyst.

Catalyst	Elemental content (%) $Mg_{1.05}Ca_{0.75}Al_{0.3}O_3$			
	Mg	Ca	Al	O
Theoretical (Calculated using formula)	20.59	14.71	5.88	58.82
EDX	18.61	10.07	5.99	65.33

with DMC, thereby enhancing GLC yield [21]. Therefore, two catalyst formulations were analyzed in this study: (1) increasing Mg content, and (2) increasing Ca content, while maintaining a constant Mg:Al ratio of 3.5:1. As the Mg content increased, the GLC yield also increased, reaching a maximum at an Mg:Ca ratio of 1.4 at a calcination temperature of 500 °C, as shown in Fig. 6. The increase in GLC yield can be attributed to the enhanced porosity of the

catalyst resulting from Mg incorporation. However, the GLC yield began to decrease at higher Mg content (Mg:Ca > 1.4), as observed for $Mg_{1.4}Ca_{0.5}Al_{0.4}O_3$ and $Mg_{1.75}Ca_{0.25}Al_{0.5}O_3$. This may be due to the encapsulation of Ca species by excess Mg, which reduces the availability of active sites and consequently lowers GLC yield. Among all the compositions tested, the $Mg_{1.05}Ca_{0.75}Al_{0.3}O_3$ catalyst exhibited the highest GLC yield (32.6%) compared to other catalyst formulations, with a glycerol conversion of 91%. Therefore, this catalyst formulation was selected for further investigation of its catalytic performance.

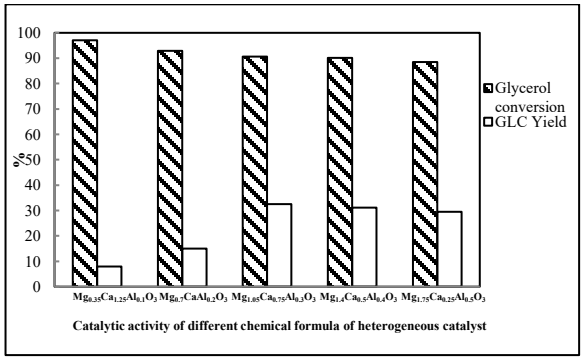

Fig. 6 Catalytic activity of Mg–Ca–Al catalysts at 500 °C (3 wt%, 70 °C, DMC:glycerol = 2:1, 1 h).

Two different calcination temperatures (500 °C and 800 °C) were applied to the $Mg_{1.05}Ca_{0.75}Al_{0.3}O_3$ catalyst, with a calcination time of 5 hours. The glycerol conversion obtained at 500 °C and 800 °C was 90.6% and 63%, respectively, while the corresponding GLC yields were 32.6% and 62.7%, respectively. As the calcination temperature increased from 500 °C to 800 °C, the GLC yield significantly increased from 32.6% to 62.7%. This suggests that the catalytic activity of the catalyst is strongly influenced by the nature and strength of basic sites. At lower calcination temperature (500 °C), the activity is mainly attributed to weak OH^- sites formed from the decomposition of surface bicarbonate species. Within the calcination temperature range of 500–800 °C, the catalytic activity is associated with both weak basic OH^- sites and medium-strength Mg–O and Ca–O pair sites, which undergo partial decomposition. At higher calcination temperature (800 °C), after complete decomposition, the activity can be attributed to the presence of three types of basic sites: weak OH^- sites, medium-strength Mg–O and Ca–O pairs, and strong O^{2-} sites [25]. A study by [26] on Mg/Al/La catalysts demonstrated that increasing the calcination temperature from 450 °C to 650 °C significantly enhanced the total density of basic sites, including weak, medium, and strong basic sites, which consequently improved the catalytic activity [26].

However, the glycerol conversion decreased from 90.6% to 63% with increasing calcination temperature. This may be due to the Lewis acidic nature of Al^{3+} cations, which can suppress the overall basicity of the catalyst as the surface concentration of Al^{3+} increases at higher calcination temperatures [25]. Overall, calcination temperature plays a significant role in determining the catalytic performance of the $Mg_{1.05}Ca_{0.75}Al_{0.3}O_3$ catalyst, with improved GLC yield observed at 800 °C.

The effect of catalyst loading on the transesterification of glycerol with DMC was investigated in this study. The catalyst loading was varied between 2–5 wt% (based on the amount of glycerol), while other reaction conditions were kept constant, i.e., a molar ratio of DMC:glycerol 2:1, reaction temperature of 70 °C, and reaction time of 60 min. Fig. 7 shows the glycerol conversion and GLC yield at different catalyst loadings (2–5 wt%). The results indicate that the GLC yield increased from 26.2% to 62.7% as the catalyst loading increased from 2 wt% to 3 wt%, due to the greater availability of active sites on the catalyst surface [6]. However, further increasing the catalyst loading to 4–5 wt% resulted in a decrease in GLC yield to 23%. This may be attributed to mass transfer limitations in the solid–liquid–liquid triphase system (catalyst–glycerol–DMC) [27]. In addition, glycerol conversion decreased significantly from 91% to 23% as the catalyst loading increased from 2 wt% to 5 wt%. This reduction may be due to the increased influence of Lewis acidic Al^{3+} sites at higher catalyst loading, which can suppress the overall basicity and hinder glycerol conversion. Furthermore, the formation of glycidol from GLC is closely related to the basicity of the catalyst, where higher basicity promotes glycidol formation [28].

The effect of reaction temperature on the transesterification of glycerol with DMC was studied by carrying out the reaction at different temperatures (65–80 °C). Figure 8 shows the effect of reaction temperature, while other reaction conditions, such as catalyst loading, DMC-to-glycerol molar ratio, and reaction time, were fixed at 3 wt%, 2:1, and 1 hour, respectively. As shown in Fig. 8, the $Mg_{1.05}Ca_{0.75}Al_{0.3}O_3$ catalyst exhibited the highest GLC yield at 70 °C.

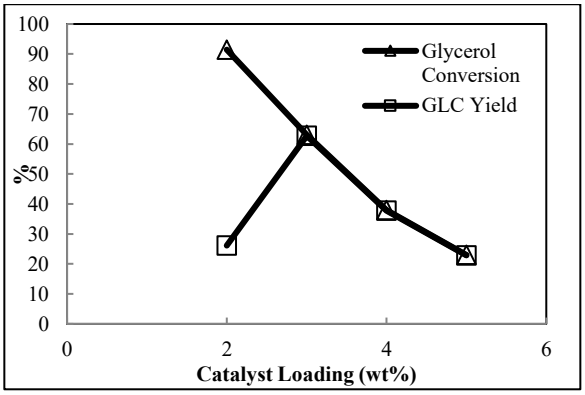

Fig 7 Effect of catalyst loading (70 °C, DMC:glycerol = 2:1, 1 h)

The GLC yield increased with increasing temperature up to 70 °C, which can be attributed to enhanced molecular interactions and reduced reactant viscosity at higher

temperatures [29]. However, a significant decrease in GLC yield was observed at higher temperatures (75–80 °C), which may be due to side reactions such as dehydrogenation and condensation involving methanol, occurring on the basic sites [25]. Meanwhile, glycerol conversion increased to above 85% at higher temperatures, likely due to enhanced reaction rates and the formation of methanol as a by-product. The increase in glycerol conversion can also be explained by the temperature dependence of reaction kinetics, where higher temperatures accelerate the reaction rate [30].

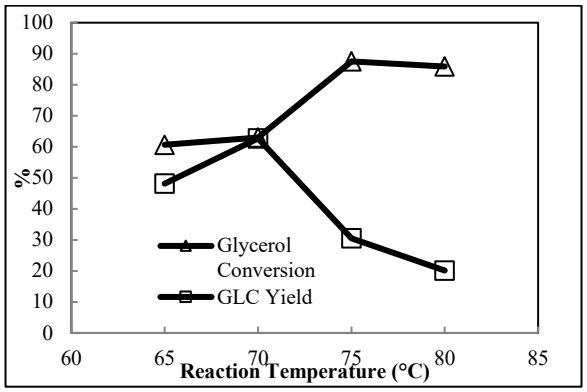

Fig.8 Effect of reaction temperature (3 wt%, DMC:glycerol = 2:1, 1 h).

reaction [21]. As shown in Fig. 9, glycerol conversion was relatively low (63–65%) at molar ratios of 1:1 and 2:1 (DMC:glycerol), and it increased to 84% when the molar ratio was increased to 3:1. Similarly, the GLC yield increased to 68% at a molar ratio of 3:1. Further increasing the DMC molar ratio to 4:1 enhanced glycerol conversion to 95%; however, the GLC yield decreased significantly. This may be attributed to the excessive DMC concentration, which reduces effective interaction between glycerol and the $Mg_{1.05}Ca_{0.75}Al_{0.3}O_3$ catalyst, thereby lowering the reaction efficiency [31]. Therefore, a DMC-to-glycerol molar ratio of 3:1 was identified as the optimum condition for achieving a high GLC yield.

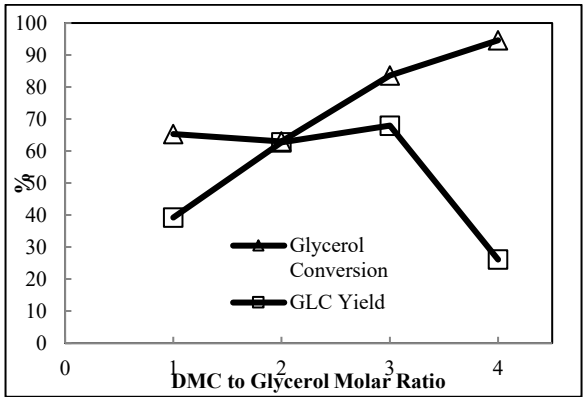

Fig. 9 Effect of DMC:glycerol ratio (3 wt%, 70 °C, 1 h).

The optimum catalyst loading, reaction temperature, and DMC-to-glycerol molar ratio were determined to be 3 wt%, 70 °C, and 3:1, respectively. Under these conditions, the effect of reaction time was investigated over a range of 0.5–2.0 hours. As shown in Fig. 10, at a reaction time of 0.5 hours, both glycerol conversion and GLC yield were relatively low, as the reaction time was insufficient for effective conversion of glycerol to GLC and its by-products. However, the GLC yield increased to 75% when the reaction time was extended to 1.5 hours. This increase can be attributed to enhanced molecular interactions and a greater extent of bond breaking and formation as the reaction proceeds. Further increasing the reaction time to 2 hours resulted in a decrease in GLC yield, which may be attributed to the solubility effect of methanol (by-product) in the reaction system. The presence of excess methanol can shift the equilibrium and increase reactant solubility, thereby reducing the selectivity toward GLC [29,32]. As a result, while glycerol conversion continued to increase, the GLC yield decreased at prolonged reaction time.

The effect of the DMC-to-glycerol molar ratio on the transesterification of glycerol with DMC was investigated by carrying out the reaction at different molar ratios (1:1–4:1). Fig. 9 shows the effect of the DMC-to-glycerol molar ratio, while other reaction conditions, such as catalyst loading, reaction temperature, and reaction time, were fixed at 3 wt%, 70 °C, and 1 hour, respectively. According to the stoichiometry of the transesterification reaction, 1 mole of glycerol reacts with 1 mole of DMC to produce 1 mole of GLC. However, a higher DMC molar ratio is required to enhance the GLC yield due to the reversible nature of the

Catalyst reusability is an important factor in minimizing process cost. The reusability of $Mg_{1.05}Ca_{0.75}Al_{0.3}O_3$ was evaluated over three consecutive batch cycles. After each run, the catalyst was recovered, washed with methanol, dried at 100 °C for 8 h, and subsequently calcined at 800 °C for 5 h to regenerate its activity. The results showed that the GLC yield decreased from 75% in the first cycle to 60% and 46% in the second and third cycles, respectively. This decline in catalytic activity may be attributed to Ca^{2+} leaching, loss of catalyst during recovery, and partial blockage of active sites by residual glycerol or GLC [31,33]. Calcination between cycles was essential to remove adsorbed species and restore

active sites, as well as to reconvert $CaCO_3$ to CaO. Despite regeneration, a gradual decrease in activity was still observed, indicating partial deactivation of the catalyst. The synergistic interaction between Mg and Ca plays a crucial role in catalytic performance, where MgO enhances activity, while Al improves catalyst stability by providing higher surface area and acting as a support [16]. Additionally, the presence of Al reduces catalyst basicity, thereby minimizing the formation of glycidol.

4.0 CONCLUSION

In conclusion, Mg–Ca–Al mixed oxide catalysts ($Mg_{3.5-x}Ca_{0.5-\gamma}Al_xO_3$) demonstrated good catalytic activity and stability for glycerol transesterification with DMC. The incorporation of aluminium plays a crucial role in enhancing catalyst stability by providing a higher surface area and acting as a structural support. In addition, the presence of aluminium reduces catalyst basicity, thereby minimizing the formation of the by-product glycidol. The catalysts were successfully synthesized via the co-precipitation method with varying Mg, Ca, and Al molar ratios and initially evaluated at a calcination temperature of 500 °C. Among the formulations, $Mg_{1.05}Ca_{0.75}Al_{0.3}O_3$ was identified as the optimal catalyst and exhibited improved catalytic performance when calcined at 800 °C. The optimum reaction conditions were determined to be 3 wt% catalyst loading, 70 °C reaction temperature, a DMC-to-glycerol molar ratio of 3:1, and a reaction time of 1.5 hours, resulting in a GLC yield of 75% with 76% glycerol conversion. Furthermore, a preliminary evaluation of the catalyst's stability was conducted over three consecutive cycles. While the catalyst could be recovered and regenerated, the GLC yield progressively decreased from 75% in the first cycle to 60% and 46% in the second and third cycles, respectively. This partial deactivation is likely attributed to Ca^{2+} leaching, mechanical loss of the catalyst during recovery, and the partial blockage of active sites by residual organic species. Further structural and elemental studies are necessary in the future to fully elucidate and mitigate this deactivation mechanism. While quantifying the exact metal leaching and performing characterization on the spent catalyst falls outside the scope of this current study, these preliminary stability results suggest that future work should focus on improving the anchoring of active sites to prevent deactivation. Overall, the $Mg_{1.05}Ca_{0.75}Al_{0.3}O_3$ catalyst shows strong potential as an efficient initial catalyst for sustainable GLC production.

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