

Selective Conversion of Glycerol to Lactic Acid by $\text{CaO}/\gamma\text{-Al}_2\text{O}_3$ Supported Catalyst

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Abstract: *Selective conversion of glycerol to lactic acid by CaO/MgO and $\text{CaO}/\gamma\text{-Al}_2\text{O}_3$ supported catalysts synthesised with different calcium oxide (CaO) loadings (20 to 50 wt. %) was studied. The catalysts were prepared using impregnation method and calcined at 700°C to be followed by surface analysis to elucidate their surface properties. The activity study was based on selective glycerol conversion to lactic acid at different temperatures (270°C to 330°C) for up to 4 h. The highest yield of lactic acid was recorded by 30 wt. % $\text{CaO}/\gamma\text{-Al}_2\text{O}_3$ catalyst with 95% of glycerol conversion and 49% of lactic acid yield. Effects of reaction conditions such as catalyst loadings (5 to 20 wt. %), reaction temperature (270°C to 330°C), reaction time (0.5 to 4 h) were also demonstrated and correlated with the characteristics of the catalysts. This catalyst could also be reused up to three times with only a slight decrease in its activity.*

Keywords: glycerol, lactic acid, $\text{CaO}/\gamma\text{-Al}_2\text{O}_3$ catalyst, conversion, product yield

1. INTRODUCTION

Biodiesel is an alternative fuel to diesel that is produced through transesterification process of triglycerides (such as animal fats or vegetables oils) with an alcohol (commonly methanol) to generate fatty acid methyl ester with glycerol (glycerin) as a co-product. Glycerol is a simple polyol compound that involves of three hydroxyl functional groups that has poor demand in industry.¹ The conversion of glycerol to high value-added substances is crucial due to the high demand for the glycerol derivatives in pharmaceutical, personal care, food industry and healthcare industries.² For instance, lactic acid is widely used as the monomer to produce eco-packaging materials that have good biodegradability.³

Several options described in the literature for the production of lactic acid include (1) fermentation and (2) chemical synthesis route. Fermentation of carbohydrate is relatively effective route and can give good lactic acid yield, but the process is rather slow and it has high production cost. The downstream distillation process for the product separation is also very difficult due to the low volatility of lactic acid.⁴ Meanwhile, the drawback for the chemical route is due to the limitation of its raw material.⁵ Usually, it is synthesised from acetaldehyde that often comes from crude oil or coal. A new method with glycerol as the feedstock has been successfully demonstrated by using high concentration NaOH or KOH as the homogeneous catalyst. The yield of lactic acid 90% was achieved when the reaction was conducted at around 300°C for 90 min with 1.25 M NaOH or KOH catalyst.⁶ Although the reaction was fairly efficient, the high concentration of the catalyst and high reaction temperature caused severe corrosion to the stainless-steel reactor.^{7,8}

Unlike homogeneous catalysts, heterogeneous catalysts serve as environmentally friendly alternatives. They can save energy by lowering the reaction temperature and simplifying catalyst/products/separation, providing possibility of continuous operation of the reactor and reducing the chemical waste production. Calcium oxide (CaO) has been reported as one of the strong solid base catalysts for this reaction.⁸ Unfortunately, it has low porosity to result in low catalytic activity. Therefore, CaO supported on highly porous supports such as gamma alumina (γ -Al₂O₃) and magnesium oxide (MgO) can be considered an active catalyst for the glycerol reaction. The supported catalysts can eliminate certain degree of diffusional resistance within the internal pores to result in accelerated reaction.^{9,10}

The aim of this work was to directly convert crude glycerol to lactic acid. CaO/ γ -Al₂O₃ catalysts with varying CaO loading were used to selectively produce lactic acid. The physical, chemical and structural properties of the catalysts were elucidated for correlations with their catalytic activity. The catalytic behaviors in the glycerol etherification under various process conditions were demonstrated to identify the most suitable reaction conditions to give high yield of lactic acid.

2. EXPERIMENTAL DETAILS

2.1 Catalyst Preparation

Glycerol (C₃H₈O₃), calcium acetate (C₄H₆CaO₄), sulfuric acid (H₂SO₄) were purchased from R&M Marketing, Essex, UK. CaO was purchased from ChemPur, Germany. γ -Al₂O₃ and MgO supports were obtained from Merck, Germany.

Wet impregnation method was used for catalyst preparation as described by Zabeti et al.¹⁰ Pre-calculated calcium acetate salt was initially dissolved in 50 mL of distilled water. Then, the previously dried γ -Al₂O₃ support at 120°C for 24 h was mixed with the acetate solution and the suspension was stirred for 4 h at room temperature and then heated at 120°C in an oven overnight to dry it. Finally, the dry catalyst was calcined in air at 700°C for 5 h. The catalyst was kept in a desiccator in the presence of silica gel and potassium hydroxide (KOH) pellets in order to avoid any contact with water and carbon dioxide (CO₂) during storage.

2.2 Catalyst Characterisation

Surface characteristics such as specific surface area (SSA), total pore volume (V_p), average pore size (d_p), mesopore diameter (d_{meso}) and micropore area (A_{micro}) were determined by means of a Micromeritics ASAP 2020 system. Meanwhile, transmission electron microscope (TEM) images were taken using a Philips CM 12 TEM operated at an accelerating voltage of 120 kV while small angle X-ray Diffraction analysis was performed by means of a Siemen 2,000× system using CuK α radiation in the range of small angle 1° to 5° (2θ) with a step size of 0.01°. Thermogravimetric analysis (TGA) was also carried out to observe significant change in the weight loss of the catalyst using a Perkin Elmer TAC 7/DX system.

2.3 Catalyst Activity and Reusability Tests

The catalytic reaction of liquid glycerol to lactic acid was carried out in a 150 mL of high-pressure stainless steel batch reactor equipped with a nitrogen tube, pressure gauge and thermocouple. In a typical procedure, 30 mL of glycerol was first added into the stainless-steel reactor and then a given amount of catalyst was added and mixed well in the reactor for 30 min at a stirring speed of 200 rpm. The reactor was then flushed with nitrogen gas (N₂) at a flow rate 2 L min⁻¹ to displace air for about 15 min before the reaction. In order to study the effect of reaction conditions, 25 mL of glycerol with different weight percentages the supported catalyst (20 to 50 wt. %) were added into the reactor and heated to different temperatures (270°C to 330°C). Then, different amounts of catalyst (5 to 20 wt. %) were added into the reactor and the mixture was subsequently stirred for different reaction times (1 to 4 h). For the reusability test, the catalyst was first separated from the reaction mixture by centrifugation and then washed with 10 mL of hydrochloric acid (HCl). The washed catalyst was then dried at 120°C for 2 h to reactivate it before being used for the subsequent cycle.

2.4 Product Analysis

The liquid product after reaction was collected and washed out with deionised water and then centrifuged at 4,000 rpm for 20 min. The clear liquid obtained at the upper layer was collected and acidified with H₂SO₄ to pH value between 3 to 4 (tested by pH meter) in order to convert the unconverted calcium lactate to lactic acid for high-performance liquid chromatography (HPLC) analysis. The HPLC unit was equipped with a Shodex SH1011 (8 mm × 300 mm) column and a refractive index (RI) detector. 5 mm of H₂SO₄ in deionised water was used as the mobile phase at a flow rate 0.6 mL min⁻¹. The detection was done at a wavelength of 250 nm and the column temperature was set at 60°C. Samples (25 µl) were then injected automatically into the HPLC. Glycerol conversion, lactic acid yield, lactic acid selectivity and lactic acid productivity are calculated using the following equations;

$$X_{\text{gly}} = \frac{\text{initial glycerol} - \text{glycerol in product}}{\text{initial glycerol (mole)}} \times 100 \quad (1)$$

$$Y_{\text{lac/gly}} = \frac{\text{lactic acid produced (mole)}}{\text{initial glycerol (mole)}} \times 100 \quad (2)$$

$$S_{\text{lac/gly}} = \frac{\text{lactic acid produced (mole)}}{\text{initial glycerol} - \text{glycerol in product (mole)}} \times 100 \quad (3)$$

where;

X_{gly} = conversion of glycerol (mol %)

$Y_{\text{lac/gly}}$ = yield of lactic acid (mol %)

$S_{\text{lac/gly}}$ = selectivity of lactic acid (mol %)

3. RESULTS AND DISCUSSION

3.1 Role of Different Supports

The surface characteristics of the MgO and γ -Al₂O₃ supported catalysts with 5 wt. % CaO loading that had been calcined at 700°C are presented in Table 1. It can be observed that CaO had a surface area of 18.19 m² g⁻¹ with an d_p of 6.23Å indicating that the commercial CaO had rather low porosity to be sufficiently active as a heterogeneous catalyst. The CaO catalyst with γ -Al₂O₃ support (5 wt. % CaO/ γ -Al₂O₃) showed a dramatic increase in the

total surface area ($108.56 \text{ m}^2 \text{ g}^{-1}$). This indicated the positive role of the porous support. The pore volume for 5 wt. % CaO/ γ -Al₂O₃ ($0.153 \text{ cm}^3 \text{ g}^{-1}$) was found to be significantly higher than that of 5 wt. % CaO/MgO due to the fact that γ -Al₂O₃ was more porous than MgO.

Table 1: Surface characteristics of commercial CaO and CaO supported catalysts.

Materials	Characteristics*				
	SSA ($\text{m}^2 \text{ g}^{-1}$)	A_{micro} ($\text{m}^2 \text{ g}^{-1}$)	A_{ext} ($\text{m}^2 \text{ g}^{-1}$)	V_{micro} ($\text{cm}^3 \text{ g}^{-1}$)	d_{pore} (\AA)
CaO	18.19	10.28	19.38	0.003	6.23
MgO	60.6	23.6	38.10	0.13	42.30
γ -Al ₂ O ₃	122.4	63.6	112.09	0.63	50.10
5 wt. % CaO/MgO	75.89	39.81	76.75	0.089	20.56
5 wt. % CaO/ γ -Al ₂ O ₃	108.56	56.29	111.34	0.153	37.38

Notes: *SSA: Specific surface area, A_{micro} : Micropore surface area, A_{ext} : External surface area, V_{micro} : Volume of micropores, d_{pore} : Average pore diameter.

The adsorption-desorption isotherms and pore size distribution of 5 wt. % CaO/MgO and 5 wt. % CaO/ γ -Al₂O₃ catalysts are illustrated in Figures 1(a) and 1(b), respectively. As shown in the Figure 1(a), CaO active component had low adsorption capacity. With the incorporation into MgO and γ -Al₂O₃ supports to form respective supported catalyst, the amount of N₂ adsorption exceeded $300 \text{ cm}^3 \text{ STP}^{-1}$ at saturation. STP stands for Standard Temperature and Pressure. The type IV adsorption isotherm with hysteresis loops at high partial pressures as shown by both catalysts suggested that they were mesoporous materials, to be consistent with data in Table 1.^{3,9} Mesoporous catalysts were desirable in this catalytic application as glycerol and lactic acid were constantly in liquid phase during the course of the reaction. Liquid phase substances generally require larger pored catalytic materials to avoid significant internal diffusion limitation.¹⁰

Meanwhile, it can be observed in Figure 1(b) that the incorporation of CaO into MgO and γ -Al₂O₃ resulted in mono-modal pore distributions in the range of 30 to 40 \AA which is in meso size range.⁷ Higher peak height of 5 wt. % CaO/ γ -Al₂O₃ catalyst correctly suggests its higher pore volume that that of 5 wt. % MgO/ γ -Al₂O₃ catalyst. Meanwhile, the profile of CaO indicates its low porosity and its incorporation into the two support materials managed to reduce the pore size distribution to be more suitable for the intended reaction. Lower pore size could be beneficial to suppress the occurrence of side reactions leading to the formation of larger products.

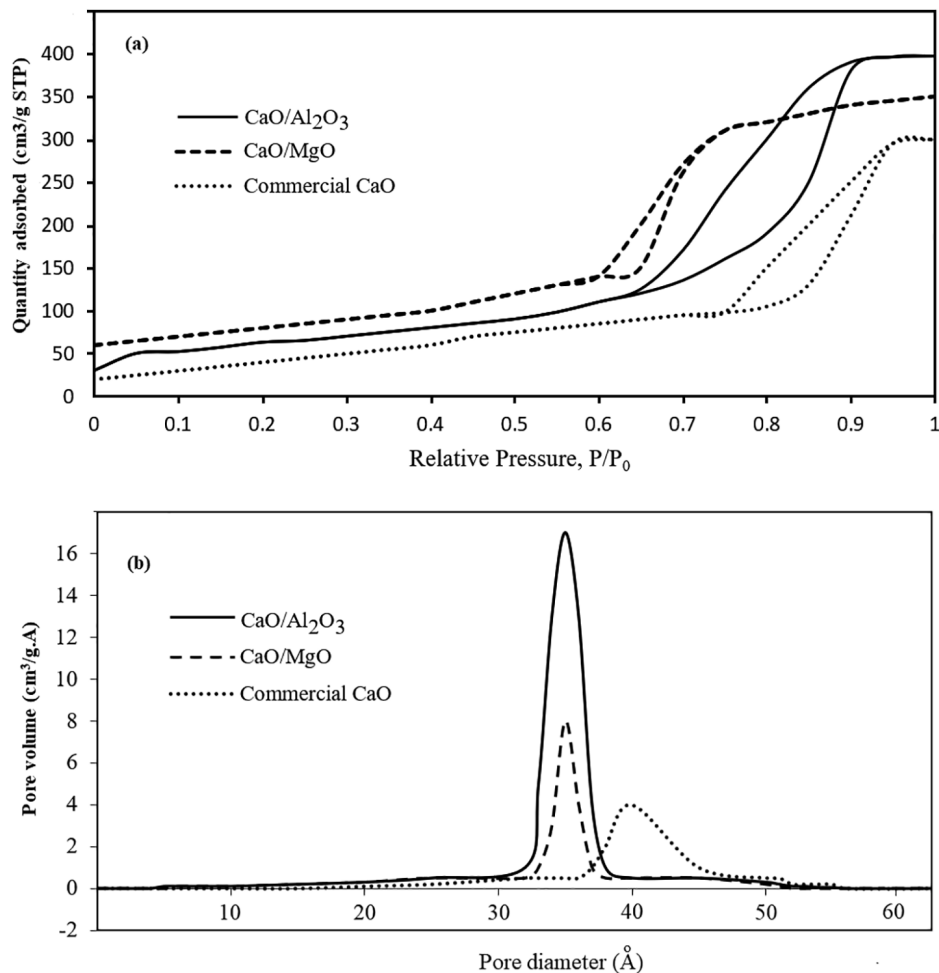


Figure 1: (a) N₂ adsorption-desorption isotherms and (b) pore size distribution of CaO, 5 wt. % CaO/MgO and 5 wt. % CaO/γ-Al₂O₃ catalysts.

3.2 Activity Screening of CaO Supported Catalysts

The supported catalysts were then used in the etherification reaction of glycerol to selectively form lactic acid for catalytic activity demonstration. The reaction was conducted at 290°C for 2 h and the results are presented in Figure 2. A blank experiment was also performed under the same reaction conditions and a glycerol conversion of 23% without the formation of lactic acid was observed. This glycerol conversion was attributed due to the autocatalytic effect at such a high reaction temperature leading to the formations of products other than lactic acid.³

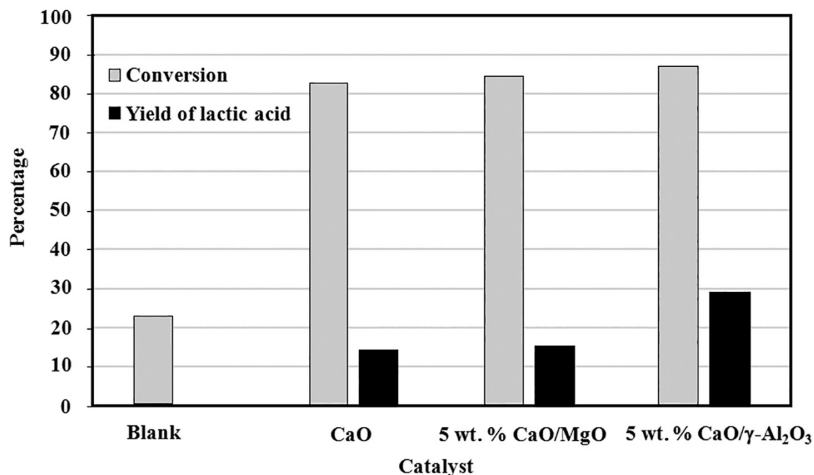


Figure 2: Comparison of glycerol conversion and lactic acid yield using different catalysts (Reaction conditions: Reaction temperature: 290°C, Reaction time: 2 h).

With the presence of CaO in the reactor, significant increases in the glycerol conversions could be observed with the significant formation of lactic acid as the desired product. This clearly suggested the positive role of CaO in this conversion. After the incorporation of CaO into MgO, the activity of the catalyst slightly increased to give 85% glycerol conversion and 15% yield of lactic acid. When CaO/ γ -Al₂O₃ catalyst was used, the system registered 87% conversion and 29% yield of lactic acid. These results clearly pointed to the positive role of γ -Al₂O₃ support. Smaller pore size of γ -Al₂O₃ support was deemed to have restricted the formation of undesired products, to the benefit of lactic acid yield. As such, this support was then used for the subsequent studies.

3.3 Characteristics of CaO/ γ -Al₂O₃ Catalysts with Different CaO Loadings

The physical properties of CaO/ γ -Al₂O₃ catalyst prepared at different CaO loadings (20, 30, 40 and 50 wt. %) for surface analysis are presented in Table 3. After the incorporation of γ -Al₂O₃ with increasing CaO loading, the Brunauer–Emmett–Teller (BET) surface area and pore volume of CaO/ γ -Al₂O₃ catalysts experienced significant decreases compared to that of the parent γ -Al₂O₃ support. It was observed that CaO deposits could have partially blocked the internal pores of γ -Al₂O₃ indicating the influence of the active components on the surface characteristics of the support.¹¹ Otherwise, probably the incorporation of CaO led to some pore wall collapse and led to a decrease in the pore size diameter.

Table 2: Surface characteristics of CaO, γ -Al₂O₃ and CaO/ γ -Al₂O₃ catalysts with different CaO loadings.

Material	SSA (m ² g ⁻¹)	A _{micro} (m ² g ⁻¹)	A _{Ext} (m ² g ⁻¹)	V _{micro} (cm ³ g ⁻¹)	d _{pore} (Å)
CaO	18.19	10.28	19.3787	0.01	6.23
γ -Al ₂ O ₃	122.4	63.6	112.09	0.63	50.10
20 CaO/ γ -Al ₂ O ₃	108.56	56.29	111.34	0.58	37.38
30 CaO/ γ -Al ₂ O ₃	105.87	52.98	111.87	0.43	35.90
40 CaO/ γ -Al ₂ O ₃	102.89	50.63	100.87	0.32	35.64
50 CaO/ γ -Al ₂ O ₃	100.67	44.87	98.09	0.28	33.89

Figure 3 shows the nitrogen adsorption-desorption isotherms for catalysts with different active metal loadings (20%, 30%, 40% and 50%). Nevertheless, all the isotherms still possess a type IV isotherm with H1 type hysteresis loop which are typical for mesoporous materials indicating that the structure of alumina was not significantly altered after being incorporated CaO loadings of up to 50 wt. %.^{12,13} Higher nitrogen adsorption amounts of exceeding 400 and 380 cm³ g⁻¹ STP at saturation were observed for the catalysts prepared with 20 and 30 wt. % of CaO. However, the amount significantly dropped to about 350 cm³ g⁻¹ STP for 40 wt. %, implying the significant reduction of pore volume as a result of partial pore plugging. At 50 wt. % of CaO loading, the quantity of adsorbed nitrogen was around 250 cm³ g⁻¹ to indicate even more serious internal pore blockages. This was likely to cause internal diffusion limitation effect during the glycerol conversion reaction to the detriment to the reaction rate. However, smaller pore size could also hinder the undesired formation of relatively larger molecules as by-products.^{14,15}

3.4 Effect of Reaction Parameters

3.4.1 Effect of active component loading

Effects of CaO loading in the CaO/ γ -Al₂O₃ catalysts on glycerol conversion as well as the selectivity and yield of lactic acid as the desired product are shown in Figure 4. It was observed that an increase in the CaO loading from 20 to 30 wt. % resulted in a slight improvement in the conversion of glycerol. Increasing CaO loading brought about the corresponding increase in the number of active sites to effectively contribute to the increase in the extent of the reactant's conversion and lactic acid formation. However, increasing the CaO loading beyond 30 wt. % did not result in any significant improvement in the extent of reaction as measure by glycerol conversion.

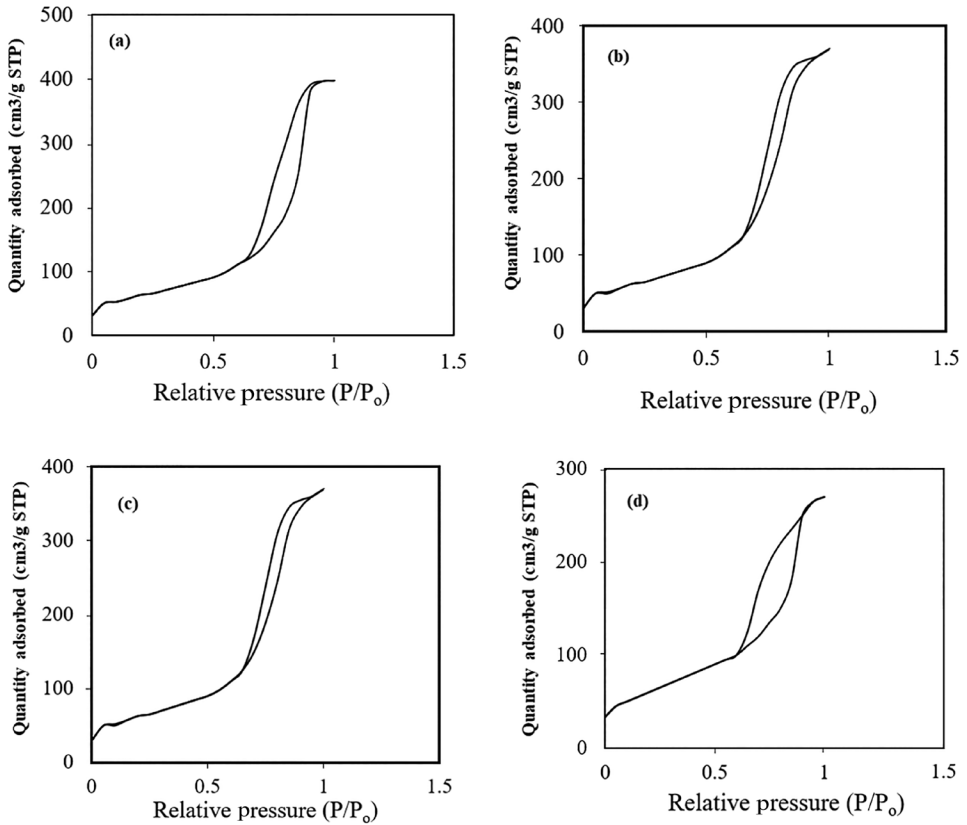


Figure 3: N_2 -adsorption-desorption isotherms of (a) 20 CaO/ γ - Al_2O_3 , (b) 30 CaO/ γ - Al_2O_3 , (c) 40 CaO/ γ - Al_2O_3 and (d) 50 CaO/ γ - Al_2O_3 catalysts.

Despite its high surface area, 20 CaO/ γ - Al_2O_3 showed the lowest conversion (87%) and lactic acid yield (32%) compared to the other catalysts. The poor results were attributed to the lower content of active component. With the addition of CaO loading to 30 wt. %, the activity was significantly improved, yielding 95% conversion and 45% lactic acid yield. The beneficial role of the γ - Al_2O_3 support in promoting the formation of lactic acid could be seen in this catalyst. Among all the catalysts prepared at different CaO loadings, 30 CaO/ γ - Al_2O_3 catalyst demonstrated the highest activity and gradual loss of activity could be seen in the performance of 40 CaO/ γ - Al_2O_3 and 50 CaO/ γ - Al_2O_3 catalysts. The relatively poorer activity of these two catalysts could be attributed to the loss of active surface area as a result of significant internal pore plugging.

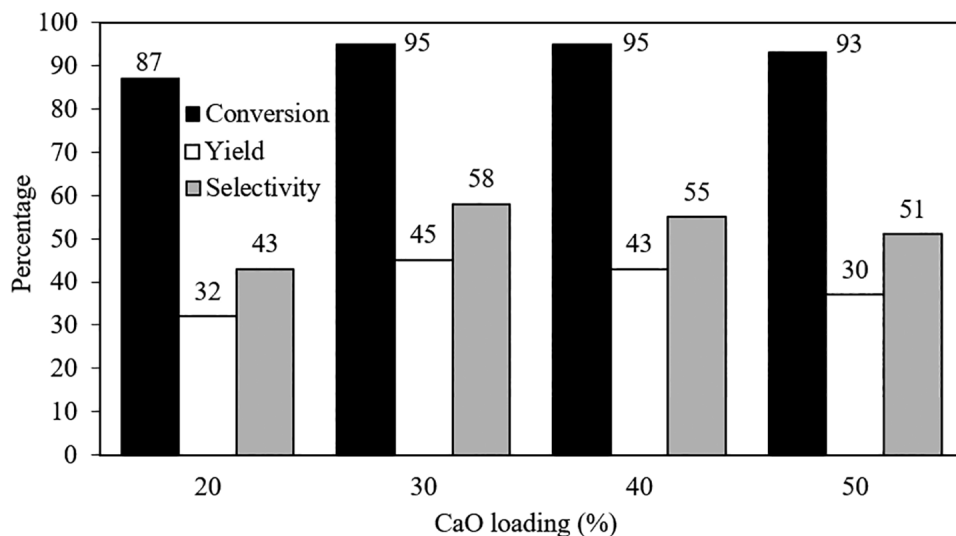


Figure 4: Effects of CaO loading in CaO/ γ -Al₂O₃ catalyst on glycerol conversion as well as yield and selectivity of lactic acid (Reaction temperature: 290°C, Reaction time: 2 h, Catalyst loading: 10 wt. % of CaO/ γ -Al₂O₃).

3.4.2 Effect of 30 CaO/ γ -Al₂O₃ catalyst loading

Effects of catalyst loading on glycerol conversion and lactic acid yield are shown in Figure 5. As noted, increasing catalyst loading from 5 to 20 wt. % did not bring about significant change in the glycerol conversions that were maintained between 94% and 95%. However, significant improvement could be observed in the lactic acid yield and selectivity when the catalyst loading was increased to 10 wt. %. The highest lactic acid of 48% was achieved at this catalyst loading. This was significantly higher than that achieved using an unsupported CaO catalyst to suggest the positive role of the support material.⁷ However, further increase in the loading did not bring about the desired effect as the selectivity and yield were observed to gradually drop. As such, it could be concluded that more catalyst amount might not be beneficial at high conversions as the reaction could be governed by the equilibrium.¹⁶

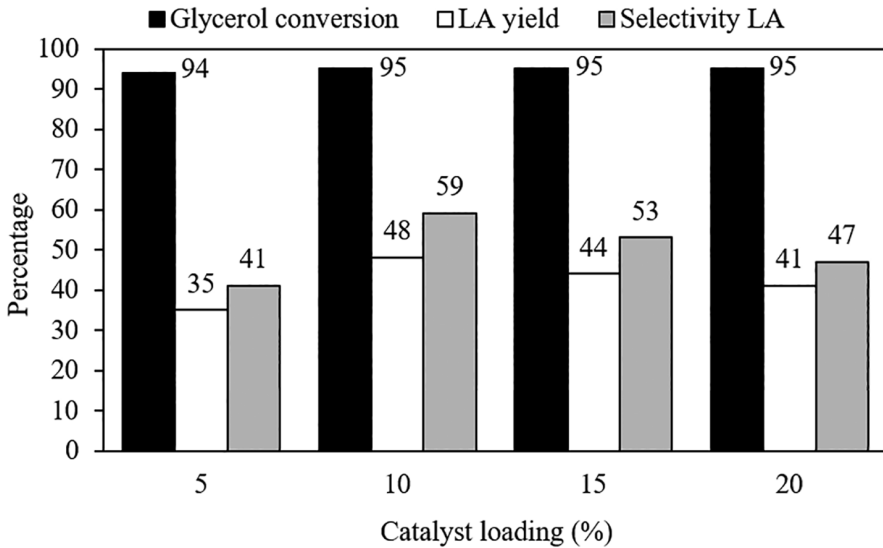


Figure 5: Effects of 30 CaO/ γ -Al₂O₃ catalyst loading on glycerol conversion as well as lactic acid selectivity and yield (Reaction temperature: 290°C, Reaction time: 2 h).

Note: LA = Lactid acid

3.4.3 Effect of reaction time

Profiles of glycerol conversion, yield and selectivity of lactic acid versus reaction time are as seen in Figure 6. It can be concluded that glycerol conversion and lactic acid yield rapidly increased with the increasing reaction time until about 2 h after which they seemed to level off at certain values. At a reaction time of 0.5 h, the conversion of glycerol increased rapidly to 70% due to the fact that higher reactant concentration could result in higher reaction rate. Longer reaction time allowed more interaction between reactants molecules and the active sites of the catalyst to produce more lactic acid and other by-products but in rather more gradual manner. As the reaction time was increased to 2 h, the conversion of glycerol gradually increased to about 95%. This result indicated the high activity of the catalyst. However, as the reaction time was further increased from 2 h to 4 h, the glycerol conversion was only slightly improved from 95% to 97%, suggesting that the reaction started to achieve the equilibrium. Further increase in the reaction time was not able to bring about significant desirable results with regards to the glycerol conversion.

The yield of lactic acid significantly increased to 59% when the reaction was carried out for 2.5 h. However, the desired product yield only slightly increase to 61% at a reaction time was extended to 3 h. It should be noted that despite the highest yield of lactic acid achieved in 3 h, the colour of the reaction mixture also became darker with unpleasant odour especially after 2 h to indicate the significant formation of undesired by-products.¹⁷ This occurrence could complicate the product separation after the reaction. Therefore, the reaction time of 2 h was deemed sufficient so that the significant formation of undesired by-products could be avoided.

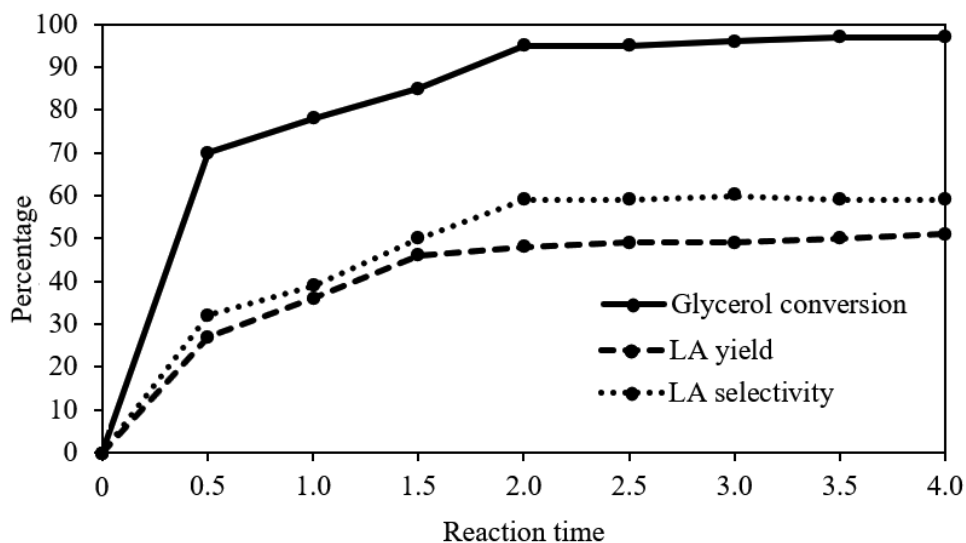


Figure 6: Effects of reaction time on glycerol conversion and product yield (Reaction temperature: 290°C, Catalyst loading: 10 wt. % of 30 CaO/ γ -Al₂O₃).

3.4.4 Effect of reaction temperature

Figure 7(a) shows the effects of reaction temperature on glycerol conversion. As shown in the figure, the glycerol conversion increased with increasing temperature. The catalytic activity for all these reaction temperatures was very fast at the beginning of the reaction as demonstrated by the rapid increase in the conversion of glycerol within short reaction times. As the reaction reached 3 h, the conversions of glycerol at 270°C, 290°C, 310°C and 330°C were found to be 88%, 96%, 97% and 98%, respectively. In short, reaction temperatures in this range were sufficiently high to initiate the glycerol reaction leading to the formation of lactic acid and other by-products.

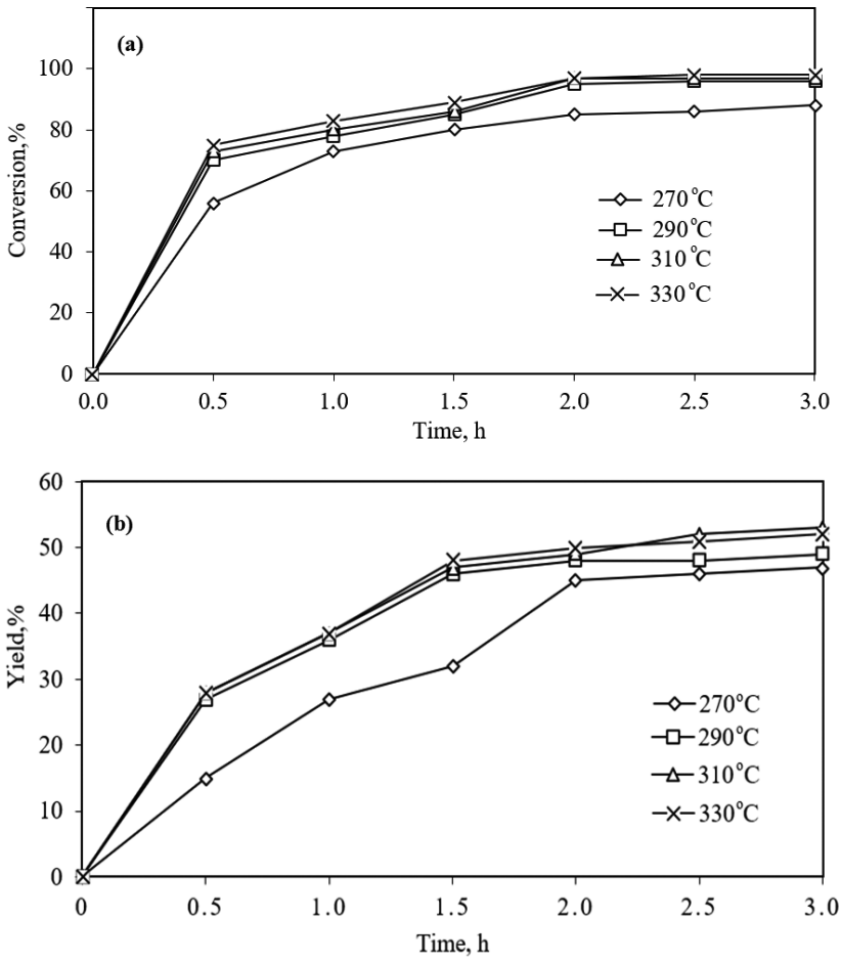


Figure 7: Effects of reaction temperature on (a) glycerol conversion and (b) lactic acid yield (Catalyst loading: 10 wt. % of 30 CaO/ γ -Al₂O₃).

The profiles of lactic acid yield as a function of reaction time for various reaction temperatures are shown in Figure 7(b). In general, they showed similar trends as shown by glycerol conversions to indicate the stability of lactic acid in the system. It was also found that by increasing the reaction temperature to 310°C or 330°C, no significant increase in the lactic acid yield could be achieved as compared to those achieved at 290°C. The lactic acid yield was quite low at 270°C due to low glycerol conversion. At 290°C, the lactic acid yield reached its plateau at around 2 h. Based on these results, 290°C was identified as most suitable reaction temperature for this selective conversion.

3.5 Reusability of the Catalyst

Catalyst stability and reusability are important aspects in all reactions in order to minimise the cost of the production.¹⁸ The reusability of the catalyst was investigated using 30 CaO/ γ -Al₂O₃. Figure 8 shows the conversion glycerol and lactic acid yield versus the run numbers. After each catalytic run, the catalyst was recovered, washed with water, then dried in the oven overnight at 120°C, after that, the spent catalyst was calcined at 500°C for 2 h in order to activate the catalyst and remove the organic molecules trapped inside the catalyst pores. The conversion of glycerol using the fresh catalyst was 95% in the first run and decreased to 86% in the second run. The glycerol conversion significantly decreased to 73% in the third run. The result indicated the slight activity decay of the catalyst. Similar trend was observed for the lactic acid yield which decreased from 47% to 27%. The slight drop in the activity could be dedicated to the catalyst leaching that might take place after each reaction run.¹⁹

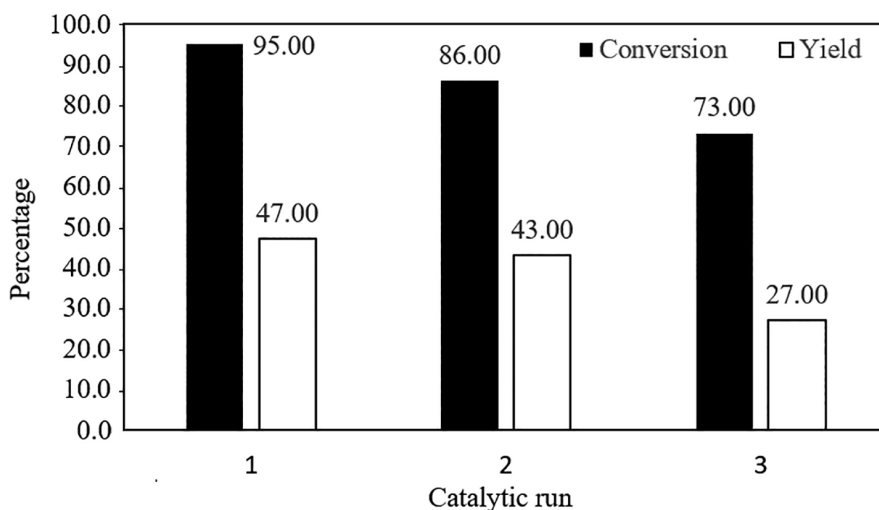


Figure 8: Glycerol conversion and lactic acid yield over 30 CaO/ γ -Al₂O₃ for three consecutive runs (Reaction temperature: 290°C, Reaction time: 3 h, Volume of glycerol: 25 mL, Catalyst loading: 10 wt. %).

4. CONCLUSION

CaO/ γ -Al₂O₃ catalyst was more selective for the formation of lactic acid compared to CaO/MgO catalyst. Increasing the CaO loading decreased the surface area, pore volume and pore size but slight increased the lactic acid yield. An increase

in CaO loading from 20 to 40 wt. % increased the activity of the catalyst but activity was found to decrease with further increase in the CaO loading. 30 CaO/ γ -Al₂O₃ (30 wt. % of CaO loading) demonstrated the highest activity in the production of lactic acid. Moreover, an increase in the reaction time, reaction temperature and catalyst loading increased the conversion of glycerol and yield of lactic acid but yield of lactic acid achieved was limited to less than 50% due to the pore characteristics that limited the diffusion of bulky molecules within the pores. The best reaction conditions were identified at 290°C, 2 h of reaction, and 10 wt. % of 30 CaO/ γ -Al₂O₃ with a glycerol conversion and a lactic acid yield of 95% and 48%, respectively. This catalyst could also be reused up to three times with only a slight decrease in its activity.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

1. Ooi, Z. X., Chan, K. L., Teoh, Y. P. & Muniyadi, M. (2019). A comparative study of glycerol and urea-modified polyvinyl alcohol/oil palm ash biocomposite films. *J. Eng. Sci.*, 15(2), 1–16, <https://doi.org/10.21315/jes2019.15.2.1>.
2. Tan, H. W., Aziz, A. R. A. & Aroua, M. K. (2013). Glycerol production and its applications as a raw material: A review. *Renew. Sust. Energ. Rev.*, 27, 118–127, <https://doi.org/10.1016/j.rser.2013.06.035>.
3. Takagaki, A., Goto, H., Kikuchi, R. & Oyama S. T. (2019). Silica-supported chromia-titania catalysts for selective formation of lactic acid from a triose in water. *Appl. Catal. A Gen.*, 570, 200–208, <https://doi.org/10.1016/j.apcata.2018.11.018>.
4. Khunnonkwao, P., Boontawan, P., Haltrich, D., Maischberger, T. & Boontawan, A. (2012). Purification of l-(+)-lactic acid from pre-treated fermentation broth using vapor permeation-assisted esterification. *Proc. Biochem.*, 47(12), 1948–1956, <https://doi.org/10.1016/j.procbio.2012.07.011>.
5. Datta, R. & Henry, M. (2006). Lactic acid: Recent advances in products, processes and technologies: A review. *J. Chem. Technol. Biotechnol.*, 81(7), 1119–1129, <https://doi.org/10.1002/jctb.1486>.

6. Kishida, H., Jin, F., Zhou, Z., Moriya, T. & Enomoto, H. (2005). Conversion of glycerin into lactic acid by alkaline hydrothermal reaction. *Chem. Lett.*, 34(11), 1560–1561, <https://doi.org/10.1246/cl.2005.1560>.
7. Chen, L., Ren, S. & Ye, X. P. (2014). Lactic acid production from glycerol using CaO as solid base catalyst. *Fuel Proc. Technol.*, 120, 40–47, <https://doi.org/10.1016/j.fuproc.2013.11.019>.
8. Li, S., Deng, W., Li, Y., Zhang, Q. & Wang, Y. (2019). Catalytic conversion of cellulose-based biomass and glycerol to lactic acid. *J. Energ. Chem.*, 32, 138–151, <https://doi.org/10.1016/j.jechem.2018.07.012>.
9. Evangelista, J. P. D. C., Gondim, A. D. & Araujo, A. S. (2016). Alumina-supported potassium compounds as heterogeneous catalysts for biodiesel production: A review. *Renew. Sust. Energ. Rev.*, 59, 887–894, <https://doi.org/10.1016/j.rser.2016.01.061>.
10. Zabeti, M., Daud, W. M. A. W. & Aroua, M. K. (2009). Optimization of the activity of CaO/Al₂O₃ catalyst for biodiesel production using response surface methodology. *Appl. Catal. A Gen.*, 366(1), 154–159, <https://doi.org/10.1016/j.apcata.2009.06.047>.
11. Yu, J., Ge, Q., Fang, W. & Xu, H. (2011). Influences of calcination temperature on the efficiency of CaO promotion over CaO modified Pt/γ-Al₂O₃ catalyst. *Appl. Catal. A Gen.*, 395, 114–119, <https://doi.org/10.1016/j.apcata.2011.01.031>.
12. Marinkovi, D. M., Avramovi, J. M., Stankovi, M. V., Stamenkovi, O. S., Jovanovi, D. M. & Veljkovi, V. B. (2017). Synthesis and characterization of spherically-shaped CaO/γ-Al₂O₃ catalyst and its application in biodiesel production. *Energ. Conver. Manag.*, 144, 399–413, <https://doi.org/10.1016/j.enconman.2017.04.079>.
13. Wang, Y., Xiao, Y. & Xiao, G. (2019). Sustainable value-added C3 chemicals from glycerol transformations: A mini review for heterogeneous catalytic processes. *Chinese J. Chem. Eng.*, 27(7), 1536–1542, <https://doi.org/10.1016/j.cjche.2019.03.001>.
14. Rodriguez-Blanco, J. D., Shaw, S. & Benning, L. G. (2011). The kinetics and mechanisms of amorphous calcium carbonate (ACC) crystallization to calcite and viavaterite. *Nanoscale*, 3(1), 265–271, <https://doi.org/10.1039/C0NR00589D>.
15. Hemalatha, J., Prabhakaran, T., & Pratibha-Nalini, R. (2011). A comparative study on particle–fluid interactions in micro and nanofluids of aluminium oxide. *Microfluid. Nanofluid.*, 10(2), 263–270, <https://doi.org/10.1007/s10404-010-0666-4>.

16. Echeverri, D. A., Rios, L. A. & Rivas, B. L. (2015). Synthesis and copolymerization of thermosetting resins obtained from vegetable oils and biodiesel-derived crude glycerol. *Eur. Polym. J.*, 67, 428–438, <https://doi.org/10.1016/j.eurpolymj.2014.11.046>.
17. Ren, S. & Ye, X. P. (2015). Catalytic conversion of glycerol to value-added chemicals in alcohol. *Fuel Proc. Technol.*, 140, 148–155, <https://doi.org/10.1016/j.fuproc.2015.09.008>
18. Feng, S., Takahashi, K., Miura, H. & Shishido, T. (2020). One-pot synthesis of lactic acid from glycerol over a Pt/L–Nb₂O₅ catalyst under base-free conditions. *Fuel Proc. Technol.*, 197, 106202, <https://doi.org/10.1016/j.fuproc.2019.106202>.
19. Varma, R. S. & Len, C. (2019). Glycerol valorization under continuous flow conditions-recent advances. *Curr. Opinion Green Sust. Chem.*, 15, 83–90, <https://doi.org/10.1016/j.cogsc.2018.11.003>.