

Lanthanum Oxide-catalyzed Transesterification of Dimethyl Carbonate with Glycerol: Effect of Surfactant

Seung Rok Lim,[†] Sang Deuk Lee, Hoon Sik Kim,[†] Fidelis Stefanus Hubertson Simanjuntak,^{*} and Hyunjoon Lee^{*}

Clean Energy Research Center, Korea Institute of Science and Technology, Seoul 136-791, Korea

^{*}E-mail: hjlee@kist.re.kr (H. Lee); fidelis.stefanus@gmail.com (F.S.H. Simanjuntak)

[†]Department of Chemistry and Basic Research Institute of Science, Kyung Hee University, Seoul 130-701, Korea

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Three kinds of lanthanum oxides (La₂O₃) were synthesized from different methods and used as a catalyst in the transesterification of dimethyl carbonate (DMC) with glycerol for the synthesis of glycerol carbonate (GLC). Lanthanum oxide synthesized using a surfactant (S-La) showed a much higher GLC yield of 89.9% compared to other lanthanum oxides synthesized by calcination (C-La) and precipitation (P-La) at the reaction conditions of 90 °C, DMC/glycerol = 2, and catalyst/glycerol = 5 wt %. The best catalyst was obtained when the surfactant/La weight ratio was 12. XRD study revealed that S-La has large amount of monoclinic and hexagonal La₂O₂CO₃ phases, which are assumed as active sites of the catalyst for the reaction.

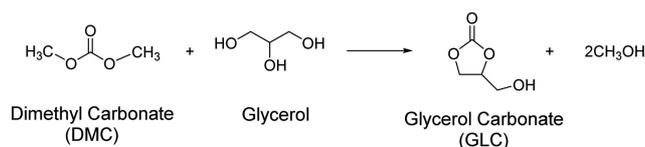
Key Words : Glycerol, Dimethyl carbonate, Glycerol carbonate, Lanthanum oxide, Surfactant

Introduction

Lanthanum oxide (La₂O₃) has been utilized in various fields, including as catalysts, strengthening agents in structural materials, optical filter, electrode material, and gas sensor.¹⁻⁵ As a catalyst, lanthanum oxide has been used in various reactions, including oxidative coupling of methane, 1-butene isomerization, 1,3-butadiene hydrogenation, and synthesis of phytoester from transesterification of fatty methyl ester.⁶⁻⁹

Lanthanum oxide is known to have very low surface area less than 15 m²/g. Therefore, to increase its surface area and thereby increase its catalytic activity, various syntheses methods for La₂O₃ have been developed, including conventional thermal decomposition of lanthanum nitrate or hydroxide, precipitation, and hydrothermal or solvothermal.¹⁰⁻¹⁴ La₂O₃ has also been supported on high surface area materials, such as carbon nanofibers, MgO and CaO, resulting in an increase of active sites.¹⁵⁻¹⁸ Surfactant-assisted precipitation and microwave irradiation using cetyl trimethylammonium bromide (CTAB) and tetra ethyl ammonium bromide (TEAB) are other methods that can increase the surface area of La₂O₃ as well as its catalytic activity. These methods produce lanthanum oxides with nanorods and flower-like shapes. Nevertheless, application of these materials has not been reported yet.¹⁹

Glycerol carbonate (GLC) is a valuable glycerol derivative due to its potential application as a membrane component for gas separation, as a component of coatings and detergents, and as a monomer of polycarbonate and polyurethane.²⁰⁻²⁴ Among the various glycerol carbonate synthetic routes such as direct reaction of glycerol and CO₂,²⁵ glycerolysis of urea,²⁶⁻²⁸ and oxidative carbonylation of glycerol,²⁹ transesterification of dimethyl carbonate (DMC)



Scheme 1. Synthesis of glycerol carbonate (GLC) from glycerol and dimethyl carbonate (DMC).

with glycerol (Scheme 1) is preferable in terms of mild reaction conditions and high glycerol carbonate yield.³⁰⁻³²

In the synthesis of GLC from glycerol and DMC, a heterogeneous catalyst is preferred due to the high boiling temperature of glycerol (bp 182 °C/20 mmHg) and glycerol carbonate (bp 160 °C at 0.1 kPa). Accordingly, some heterogeneous base catalysts have been studied in this reaction such as Mg-Al hydrotalcite, Mg-La mixed oxide, and Mg/Al/Zr. High yield of GLC was attained with those catalysts, but only with considerably large catalyst loadings of 5-50 wt % with respect to the substrate.^{16,33,34}

In this study, we synthesized lanthanum oxide catalysts using a surfactant, pluronic F127 (Figure 1), a triblock copolymer of ethylene oxide/propylene oxide/ethylene oxide, and employed the prepared catalysts in the transesterification of DMC with glycerol. The morphology, surface area, and catalytic activity were compared with those of other La₂O₃ catalysts synthesized by a surfactant-free method. The basic site concentration of the catalyst was determined by the titration method.

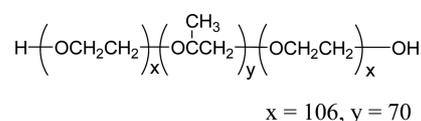


Figure 1. Structure of surfactant, Pluronic F127.

Experimental

Catalyst Preparation. All reagents were purchased from Sigma Aldrich and used as received without further purifications.

In this study, three kinds of lanthanum catalyst were synthesized: direct calcinations of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (C-La), precipitation of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ using K_2CO_3 and KOH (P-La) and calcination of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ –surfactant mixture (S-La).

In direct calcinations method, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was calcined at 680°C in air atmosphere for 4 h.

In precipitation method, a mixed solution of KOH (0.1 mol) and K_2CO_3 (0.026 mol) in 50 g of distilled water was drop-wised into the solution of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (16.7 g in 50 g of water) until the pH reached 10 and stirred for 24 h at room temperature. Formed white solid was filtered and washed with water, dried at 100°C for 12 h, and subsequently calcined at 680°C for 4 h.

In surfactant method, 26.40 g of triblock polymer, poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethyl ene oxide), Pluronic F127 ($\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$) in 50 g of ethanol was stirred with $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (2.2 g) and HNO_3 (1 g, 70 wt %). The mixture was stirred for 1 day at room temperature, then dried at 130°C for 1 day. The solid was collected and calcined at 680°C for 4h in air. Lanthanum oxides catalyst were marked as S-La(30), S-La(12), S-La(6), S-La(3), and S-La(1.5) for samples prepared with surfactant/La precursor weight ratio of 30/1, 12/1, 6/1, 3/1, and 1.5/1, respectively.

Transesterification of DMC with Glycerol. In typical reaction condition, glycerol (21.7 mmol, 2 g), DMC (43.4 mmol, 3.9 g) and lanthanum oxide (0.1 g) were added to the 100 mL round-bottomed flask having reflux condenser. The mixture was heated with stirring at a desired temperature using bath oil. After the reaction, the catalyst was separated from the reaction mixture using syringe filter. The synthesized GLC and unreacted glycerol were analyzed using HPLC (Waters) equipped with an Aminex HPX-87H column (Biorad) and a RI detector (Waters 410). The mobile phase used was a 5 mM H_2SO_4 aqueous solution and the flow rate was set at 0.6 mL/min.

Instrument. Structural characterizations of all samples were conducted using by X-Ray Diffraction (Shimadzu XRD-6000, Japan). The Brunauer-Emmett-Teller (BET) surface area was determined using a Belsorp-mini II apparatus (BEL Inc., Osaka, Japan). Basic site concentration on the surface of catalyst was measured by benzoic acid titration method using Hammet indicators. Basic site concentration measurement was conducted three times and the average value was used in this report. The particle shape image was measured using SEM (FEI Inc., Nova-Nano 200, Hillsboro).

Results and Discussion

Effects of Preparation Method. Three kinds of lanthanum catalysts were prepared by three different methods. C-

La was obtained from the direct calcination of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, while P-La was synthesized by calcining the precipitated lanthanum precursor from $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in a K_2CO_3 and KOH solution. The third sample, S-La(12), was obtained by calcining a lanthanum precursor that was obtained from a mixture of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and the surfactant Pluronic F127 ($\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$) with a weight ratio of surfactant/La precursor of 12. The XRD patterns of the catalysts, shown in Figure 2, revealed that all samples had a different crystal structure. C-La had only a clear La_2O_3 crystalline phase. In contrast, P-La and S-La(12) contained $\text{La}_2\text{O}_2\text{CO}_3$ monoclinic, $\text{La}_2\text{O}_2\text{CO}_3$ hexagonal, and La_2O_3 phases. The presence of $\text{La}_2\text{O}_2\text{CO}_3$ in P-La and S-La is ascribed to the reaction between the La precursor with CO_2 generated from the decomposition of carbonate species and surfactant F127 during calcination, respectively.

Transesterification of DMC with glycerol for the preparation of glycerol carbonate was conducted using the prepared lanthanum oxide as a catalyst. The reaction was performed at 90°C with a DMC/glycerol molar ratio of 2 and a catalyst/glycerol weight ratio of 0.05. Table 1 shows 89.9% yield of GLC was obtained from the S-La(12) catalyzed reaction within 30 min, while C-La and P-La showed very low yields of 19.9 and 24.2%, respectively for longer reaction time of 60 min. It is also interesting to notice that the surface area of the most active catalyst, S-La(12) is only $3.1\text{ m}^2/\text{g}$, which is one-third that of P-La, indicating that the surface area is not an important factor for catalytic activity.

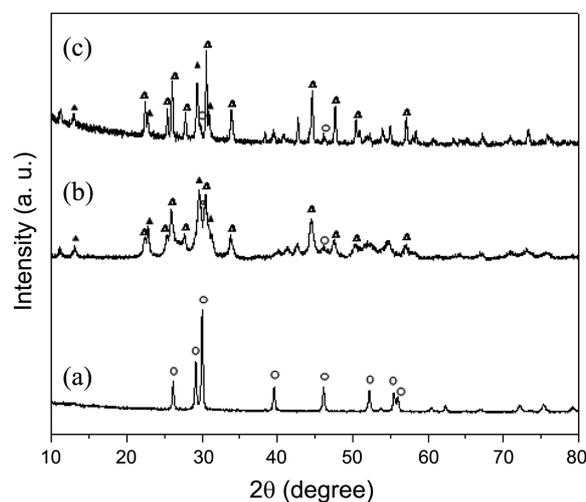


Figure 2. XRD patterns of (a) C-La, (b) P-La, and (c) S-La(12). ▲: $\text{La}_2\text{O}_2\text{CO}_3$ (monoclinic), △: $\text{La}_2\text{O}_2\text{CO}_3$ (hexagonal), ○: La_2O_3 .

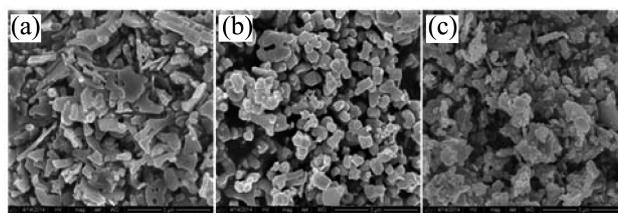


Figure 3. SEM images of (a) C-La, (b) P-La and (c) S-La(12).

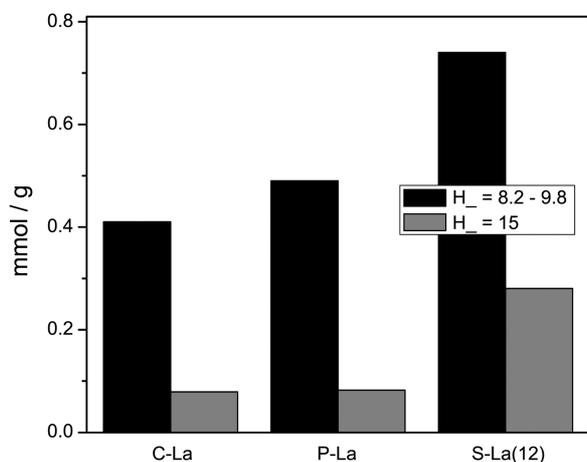
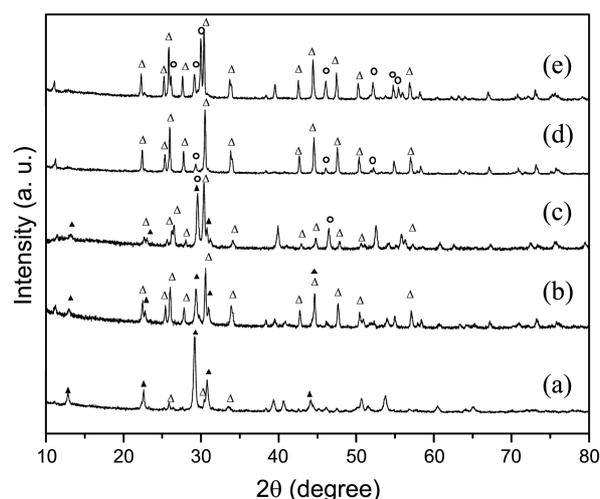
Table 1. Surface area and catalytic activity of various lanthanum oxides

Catalyst	Catalytic activity			Surface area (m ² /g)
	Conversion of glycerol (%)	Yield of GLC (%)	Selectivity to GLC (%)	
C-La ^a	22.1	19.9	90.0	2.0
P-La ^a	26.8	24.2	90.3	13.3
S-La(12) ^b	94.4	89.9	95.2	3.1

Reaction condition: DMC/glycerol = 2, catalyst/glycerol = 5 wt %, T = 90 °C, t = 60^a, 30^b min.

SEM images of the prepared catalysts in Figure 3 show that these catalysts have different morphologies. La-C is flake-like shapes, while P-La is much smaller rectangular particles. S-La(12) meanwhile showed an irregular shape.

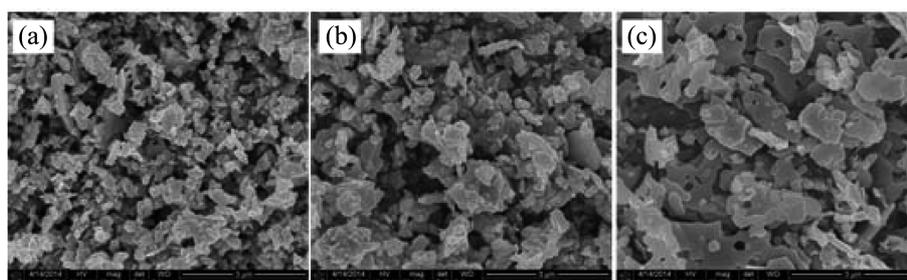
The higher catalytic activity of S-La(12) could be ascribed to its higher basic site concentration which was measured by titration of the catalyst with a benzoic acid solution in the presence of a Hammett indicator, phenolphthalein (base strength $H_- = 8.2-9.8$) and 2,4-dinitroaniline ($H_- = 15.0$). All catalysts changed the color of both Hammett indicators, indicating all catalysts have same base strength, but the amount of basic sites varies substantially, as shown in Figure 4. S-La(12) has 0.74 mmol/g of basic sites ($H_- \geq 9.8$). Furthermore, highly basic sites ($H_- \geq 15$) were found in a

**Figure 4.** Concentration of basic site on various lanthanum oxides.**Figure 5.** XRD pattern of (a) S-La(30), (b) S-La(12), (c) S-La(6), (d) S-La(3) and (e) S-La(1.5). \blacktriangle : La₂O₂CO₃ (monoclinic), \triangle : La₂O₂CO₃ (hexagonal), \circ : La₂O₃.

concentration of 0.28 mmol/g. In contrast, the basic site concentrations ($H_- \geq 9.8$) of C-La and P-La were 0.41 and 0.49 mmol/g, respectively.

Effect of Surfactant/La Precursor Ratio. To investigate the effect of the amount of surfactant, five different kinds of lanthanum oxides were prepared using different surfactant/La precursor weight ratios of 30/1 (S-La(30)), 12/1 (S-La(12)), 6/1 (S-La(6)), 3/1 (S-La(3)), and 1.5/1 (S-La(1.5)). XRD patterns of all samples are shown in Figure 5. The catalyst prepared using a large amount of surfactant, S-La(30), exhibited La₂O₂CO₃ monoclinic phase as a major phase with a weak peak ascribed to La₂O₂CO₃ hexagonal phase. Decreasing the surfactant ratio to 12, La₂O₂CO₃ hexagonal phase became more dominant than the La₂O₂CO₃ monoclinic phase. Further decrease of the surfactant amount to 3/1 caused complete disappearance of the La₂O₂CO₃ monoclinic phase, while the La₂O₂CO₃ hexagonal and La₂O₃ phases became predominant.

The amount of surfactant also affected the shapes of the catalysts. Figure 6 reveals that S-La(30) has a small irregular particle shape. Decreasing the amount of surfactant to S-La(1.5) resulted in larger size lanthanum oxide with a flake-like shape. Interestingly, the surface area was also affected by the amount of surfactant. Increasing the amount of surfactant increased the surface area as shown in Table 2, but

**Figure 6.** SEM images of (a) S-La(30), (b) S-La(12) and (c) S-La(1.5).

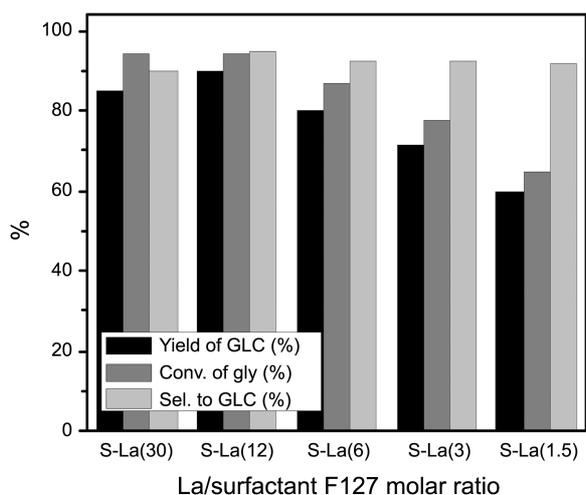


Figure 7. Catalytic activities of lanthanum oxides prepared with various surfactant/La precursor weight ratio. Reaction condition: DMC/glycerol = 2, catalyst/glycerol = 5 wt %, T = 90 °C, t = 30 min.

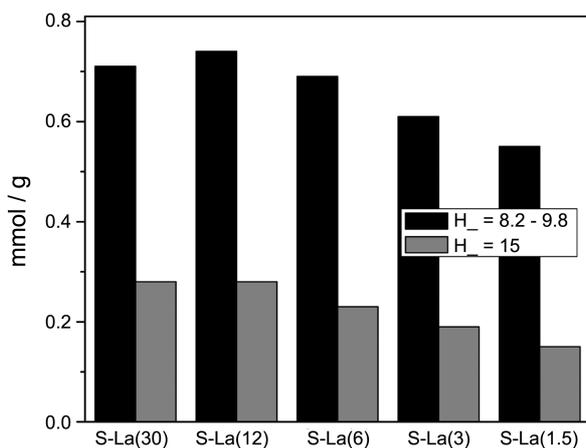


Figure 8. Concentration of basic site on lanthanum oxides with various surfactant/La precursor weight ratio measured by benzoic acid titration using Hammett indicators.

the difference was not significant. Table 2 also shows small amount of carbon (around 1.8–2.9 wt %) remained in all catalysts due to the presence of the $\text{La}_2\text{O}_2\text{CO}_3$ phase.

The effect of surfactant amount on the catalytic activity was investigated. Figure 7 shows the catalyst synthesized using large amounts of surfactant exhibited higher catalytic activity than the catalyst synthesized using a smaller amount of surfactant.

Basic sites concentration of the surfactant-assisted La catalyst shown in Figure 8 reveals that with an increase of the amount of surfactant used, the basic site concentration increased proportionally, which is consistent with the catalytic activity of the S-La series.

When S-La(30) and S-La(12) were used, the catalysts showed similar GLC yields of 85.2 and 89.9%, respectively. As discussed earlier, both $\text{La}_2\text{O}_2\text{CO}_3$ monoclinic and $\text{La}_2\text{O}_2\text{CO}_3$ hexagonal phases existed in the S-La(30) and S-La(12), while $\text{La}_2\text{O}_2\text{CO}_3$ monoclinic phase was not observed in the

Table 2. Surface area and elemental analysis of lanthanum oxide prepared with various surfactant/La precursor weight ratio

Sample	Surfactant/La ^a	Surface area (m ² /g)	%		
			C	H	N
S-La(30)	30	3.8	1.8	< 0.3	< 0.3
S-La(12)	12	3.1	1.9	< 0.3	< 0.3
S-La(6)	6	2.8	1.9	< 0.3	< 0.3
S-La(3)	3	2.7	2.8	< 0.3	< 0.3
S-La(1.5)	1.5	2.0	2.9	< 0.3	< 0.3

^aweight ratio

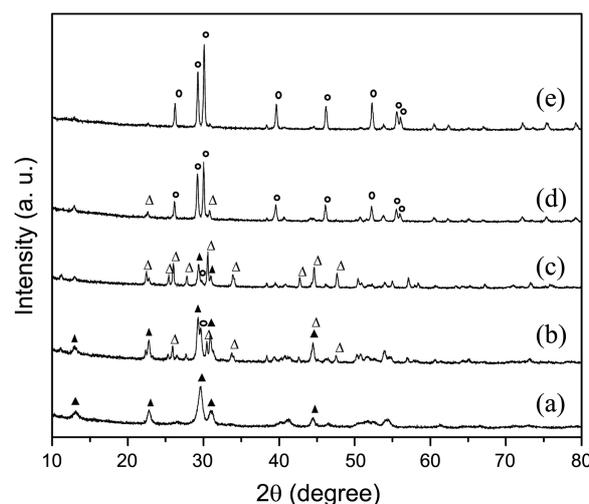


Figure 9. XRD pattern of S-La(12) calcined at (a) 450 °C, (b) 600 °C, (c) 680 °C, (d) 720 °C, and (e) 800 °C. ▲: $\text{La}_2\text{O}_2\text{CO}_3$ (monoclinic), △: $\text{La}_2\text{O}_2\text{CO}_3$ (hexagonal), ○: La_2O_3 .

other lanthanum catalysts synthesized using a smaller amount of surfactant, S-La(3) and S-La(1.5). Based on these results, it is assumed $\text{La}_2\text{O}_2\text{CO}_3$ is catalytically more active than La_2O_3 , presumably due to the presence of basic $-\text{OCO}_2^-$ species on the surface, which was also reported by R.P Taylor *et al.* in the $\text{La}_2\text{O}_2\text{CO}_3$ -catalyzed CH_4 oxidative coupling reaction.³⁵

Effect of Calcinations Temperature. In order to investigate the effect of calcination temperature on catalytic activity, S-La(12) catalysts calcined at 450, 600, 680, 720 and 800 °C were prepared.

Figure 9 shows the XRD patterns of all prepared catalysts. S-La(12) calcined at 450 °C had a $\text{La}_2\text{O}_2\text{CO}_3$ monoclinic phase. When the calcination temperature was increased to 600 °C, $\text{La}_2\text{O}_2\text{CO}_3$ hexagonal peaks started to appear and this became the dominant phase when the calcination temperature was 680 °C. A further increase to 720 °C resulted in the disappearance of $\text{La}_2\text{O}_2\text{CO}_3$ monoclinic completely with the appearance of La_2O_3 . At the calcination at 800 °C, only the La_2O_3 phase was observed in S-La(12).

The calcination temperature also affected the particle size of the catalysts. As shown in the SEM image (Figure S1 Supporting Information) and in Table S1 (Supporting Information), higher temperatures produce bigger particle size having lower surface area.

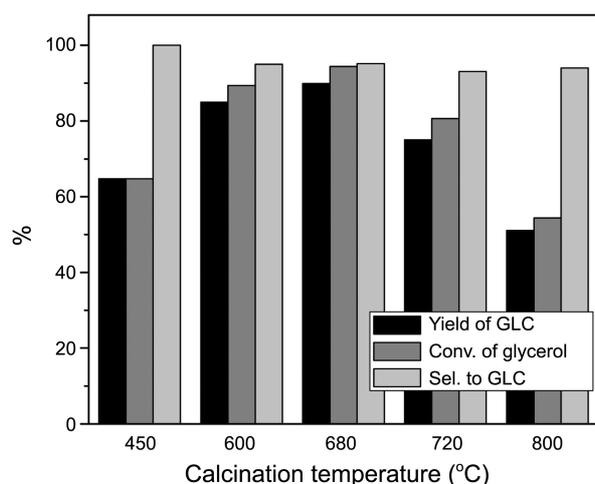


Figure 10. Catalytic activities of of S-La(12) calcined at (a) 450 °C, (b) 600 °C, (d) 680 °C, (e) 720 °C, and (e) 800 °C.

Figure 10 shows S-La(12) calcined at 450 °C, which had only $\text{La}_2\text{O}_2\text{CO}_3$ monoclinic phase, exhibited 64.7% yield of glycerol. On the other hand, S-La(12) calcined at 600 °C and 680 °C, which had both $\text{La}_2\text{O}_2\text{CO}_3$ monoclinic and $\text{La}_2\text{O}_2\text{CO}_3$ hexagonal phases, exhibited higher yields of 84.9% and 89.9%, respectively. The increase of calcination temperature to 720 and 800 °C decreased the yield of glycerol to 75.0% and 51.1%.

These results showed again that the presence of $\text{La}_2\text{O}_2\text{CO}_3$ hexagonal and/or monoclinic phases is important in the catalytic activity of lanthanum oxide. Furthermore, comparison of the catalytic activity of S-La(12) calcined at 800 °C (GLC yield: 51.1%) and P-La (GLC yield 24.2%), both of which have only the La_2O_3 phase, reveals that the effect of surfactant still exists irrespective of the presence of crystalline $\text{La}_2\text{O}_2\text{CO}_3$. It can be assumed that, besides its role in the synthesis of $\text{La}_2\text{O}_2\text{CO}_3$, the surfactant also play a role in increasing the basicity of lanthanum oxide during the preparation step. More specifically, electron-rich ether oxy-

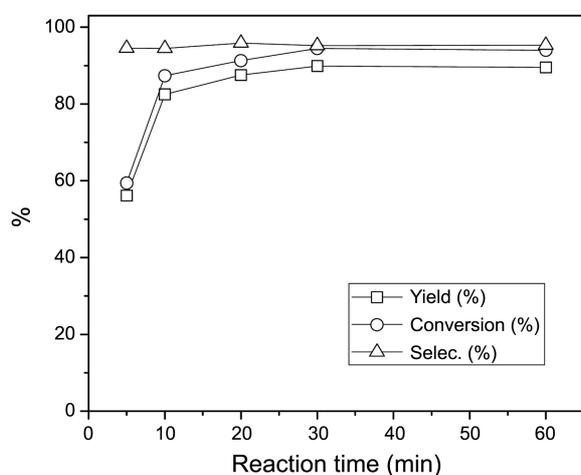


Figure 11. Effect of reaction time on the transesterification of DMC with glycerol. Reaction condition: DMC/glycerol = 2, catalyst/glycerol = 5 wt %, T = 90 °C.

gen in the surfactant binds on the lanthanum atoms during the preparation process and when the surfactant decomposes during the calcinations step, numerous defect sites could be formed on the surface of La_2O_3 , which is also known as a highly basic site.³⁶

Effect of Reaction Conditions. The effect of reaction time on the transesterification of DMC with glycerol was investigated using S-La(12) in a range of 5–60 min at 90 °C with a DMC/glycerol molar ratio of 2 and a catalyst to glycerol ratio of 5 wt %. As can be seen in Figure 11, within 5 min, 56.1% yield of GLC was obtained. The yield of GLC significantly increased to 89.9% as the reaction time was increased to 30 minutes. Further increase of the reaction time over 30 min led to a similar yield of GLC, indicating that the reaction reached the equilibrium concentration at the reaction condition.

The effect of the DMC/glycerol ratio was also investigated with reaction for 10 min and the results are shown in Figure 12. An increase of the DMC/glycerol molar ratio from 1 to 6 increased the yield of GLC from 31.1% to 87.3%. Further

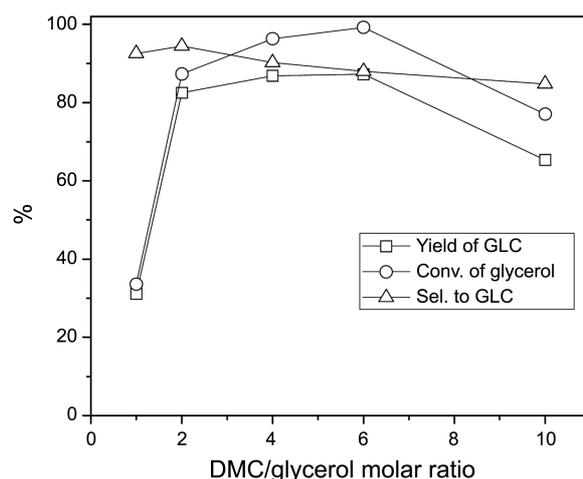


Figure 12. Effect of DMC/glycerol molar ratio on the transesterification of DMC with glycerol. Reaction condition: Catalyst/glycerol = 5 wt %, T = 90 °C, t = 10 min.

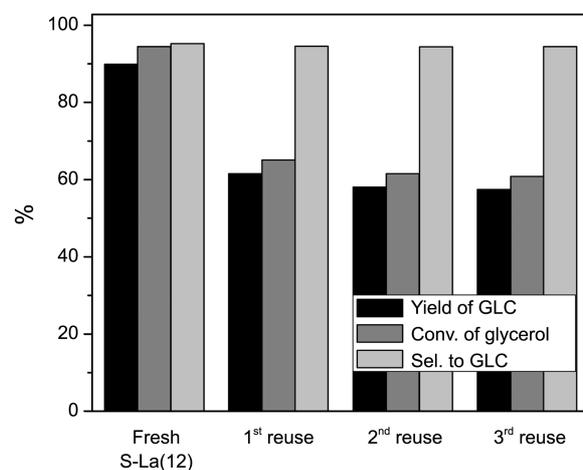


Figure 13. Reuse of S-La(12). Reaction condition: DMC/glycerol = 2, catalyst/glycerol = 5 wt %, T = 90 °C, t = 30 min.

increase of the DMC led to a decrease of the yield and selectivity of GLC. It appears that the increase of DMC concentration in the reaction solution generates side products such as diglycerol tricarboxylate from the secondary reactions of GLC with DMC or glycerol.²³

Reusability. The reusability of the catalyst was investigated using S-La(12). Before reuse, the catalyst was heated to 400 °C in a nitrogen atmosphere to remove organic residue remaining on the surface of the catalyst, and subsequently calcined at 500 °C in air for 2 h. The yield of GLC decreased from 89.9 to 61.5% for the first recycle as shown in Figure 13.

The yield of GLC slightly decreased to 58.1 and 57.4% for the 2nd and 3rd recycles, respectively, but the selectivity was maintained at 94%. The decrease of catalytic activity seems caused by the change of crystal structure of the catalyst, as shown in Figure S2.

After the catalyst was filtered and calcined at 500 °C, the intensity of La₂O₂CO₃ hexagonal phase was decreased. In contrast, La₂O₂CO₃ monoclinic phase became predominant and weak intensity of La₂O₃ phase was observed.

Conclusion

The use of a surfactant (pluronic F127) during the preparation of lanthanum oxides resulted in enhanced catalytic activity in the transesterification of DMC with glycerol. XRD study revealed that the lanthanum oxides synthesized using the surfactant (S-La) had highly crystalline monoclinic and hexagonal La₂O₂CO₃ phases compared to lanthanum oxides synthesized by calcinations (C-La) and precipitation (P-La). It was found that S-La had higher basic site concentration ($H_{-} > 8.2$) than C-La and P-La. The amount of surfactant and calcination temperature also affected the catalyst constitution as well as catalytic activity. With an increase the weight ratio of surfactant/La precursor to 30/1, La₂O₂CO₃ phase became dominant than La₂O₃ phase along with an increase of the catalytic activity. Furthermore, 600–680 °C was identified as the optimal calcination temperature in terms of producing lanthanum oxide having higher catalytic activity and possessing a large quantity of crystalline La₂O₂CO₃ phase. Although first reuse of catalyst after the calcination of the used catalyst at 400 °C resulted in a decrease of activity to 75% compared to that of the fresh catalyst, its catalytic activity was maintained after that.

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