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# Glycerol carbonate synthesis from glycerol and dimethyl carbonate using trisodium phosphate

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## ABSTRACT

Glycerol, a major biodiesel byproduct, was valorized using anhydrous trisodium phosphate (TSP) as a reusable heterogeneous catalyst in glycerol carbonate (GC) synthesis. The reaction progressed via catalytic carboxylation pathway of glycerol with dimethyl carbonate (DMC) under various reaction conditions. The TSP catalyst was characterized using TPD-CO<sub>2</sub>, TGA and XRD technique. Under reaction conditions of 70 °C, glycerol/DMC molar ratio of 2, 60 min, and 3 wt% catalyst loading, TSP achieved 99.5% glycerol conversion and GC yield, respectively. The appreciable high basicity and strong basic sites of TSP catalyst contributed to its remarkable performance. Also, the crystalline phase was preserved after the nine times reusability indicating high structural stability of TSP catalyst. The catalyst was heterogeneous without leaching and can easily be recovered and reused. Hence, the catalyst was repeatedly used in nine successive cycles of experiment without deactivation.

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## 1. Introduction

Biodiesel (BD) demand as a renewable and green energy alternative source has increased, and its projected global production will reach  $4.2 \times 10^{10}$  l by 2020 [1]. Glycerol, which is a major byproduct of BD production, will increase because 10 g of glycerol is produced in every 100 g of BD produced [2]. Processes, such as saponification of fats and brewery industries, generate glycerol in addition to the estimated volume of BD-derived crude glycerol. However, direct applications are limited because of impurities in its crude form. This result leads to an excess supply of glycerol, thereby rendering it a low-cost material that requires defunctionalization for urgent utilization. Research effort in the past five years has focused on synthesizing glycerol-free BD using lipids and acyl acceptors as methanol alternative. However, most conducted studies indicated that enzymes, which are expensive and often require longer reaction times, can be utilized as a catalyst to effectively drive the reaction [3].

Conducted studies indicate that physicochemical properties of glycerol make it suitable for fine chemical synthesis. However, a well-developed and cost-effective pathway to valorize over-supplied glycerol averts challenges in disposal and boosts the BD market. Moreover, these pathways are relatively low energy intensive, thereby further reducing the overall energy require-

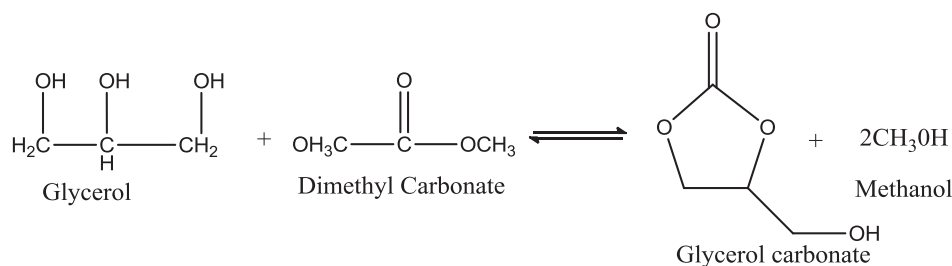
ment for BD production. Therefore, upgrading pathways, such as etherification, carboxylation, acetylation, oligomerization, 1,3-propanediol, and glycerol dehydration to acrolein, among others, have been developed to synthesize fine chemicals from glycerol [4–7]. Researchers have also adopted several of these pathways to transform crude BD-derived glycerol to fine chemicals that have extensive potential application in process industries [8–14].

Carboxylation via transesterification of glycerol is a popular route. The transesterification process utilizes glycerol with either phosgene, urea, dialkyl carbonates, or alkylene carbonates as carbonate sources to synthesize glycerol carbonate (GC). The use of dialkyl carbonates, particularly dimethyl carbonate (DMC), is favorable because it is an environment-friendly chemical and can be utilized in a one-step-one pot reaction system [15]. Moreover, the use of this chemical does not require rigorous separation procedures and high energy, and is time efficient compared with phosgene and alkylene carbonates sources. Scheme 1 presents the glycerol transesterification with DMC to produce GC and methanol. The reversible equilibrium reaction is positively shifted. This reaction also utilizes DMC in excess of glycerol to produce appreciably high GC. GC carbonate has immense industrial and agro-based applications, which are highlighted in our earlier review article [2].

Tailoring the transesterification reaction faster to appreciably high product yield requires homogeneous or heterogeneous catalysts or enzymes. However, serious limitations, such as difficulties in catalyst separation, considerably long reaction times, and corrosion of pipelines and reactors, characterized homogeneous catalysts and enzymes. These limitations favor the use of

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**Scheme 1.** GC Synthesis via glycerol transesterification with DMC.

heterogeneous catalysts. Therefore, catalysts with basic active centers are required to activate glycerol molecule via deprotonation to synthesize GC. Catalysts, such as  $\text{CH}_3\text{OK}$  [16],  $\text{LiNO}_3/\text{MgAl}$  [17], K-zeolite [18],  $\text{Mg}/\text{Al}$  hydrotalcites [19],  $\text{Mg}-\text{Ca}$  mixed oxides [20], and Zn or Mg or Ca/La mixed oxides [21,22], have been employed to drive the transesterification reaction to appreciable product yield. A reusable solid carbon catalyst can also be developed using glycerol as carbon source and functionalized to tailor the active sites to either basic or acidic [23]. These heterogeneous catalysts have shown promising potentials toward the appreciable conversion of glycerol and GC yield. However, they suffer serious deactivation in not more than seven cycles of reuse. Moreover, steps to recover and regenerate the catalysts often require several washings with methanol, drying above  $100\text{ }^\circ\text{C}$  for 2 to 5 h, and occasionally high temperature re-calcination before reuse [2].

Basic catalysts that are capable of undergoing many cycles of reuse without serious deactivation and can easily be recovered and regenerated without high energy input are desirable. The deactivation of catalysts is caused by the loss of active sites, poisons in feed or products, or thermal degradation of the catalytic material. Trisodium phosphate (TSP) has been identified as an active catalyst for BD production. The solubility in methanol was determined to be negligible and displayed stable catalytic activity for several successive runs of experiments [24,25]. The current study utilized TSP as an efficient catalyst to valorize BD-derived glycerol with DMC to produce GC. The activity, reaction parameters, and recyclability were also probed.

## 2. Materials and methods

### 2.1. Materials

Anhydrous TSP (>95% purity) was purchased from R & M Chemicals. Anhydrous DMC ( $\geq 99.8\%$  high purity), HPLC grade methanol ( $\geq 99.0\%$  purity), NaOH pellets (99%), HCl (fuming 37%), and anhydrous glycerol ( $\geq 99\%$  purity) was purchased from Merck. Gas chromatography standard (93 to 95% purity) was acquired freely from Hunstman, USA. All reagents and chemicals were of analytical grades and utilized without further purification.

### 2.2. Transesterification reaction

GC was synthesized via glycerol transesterification with DMC in a 250 ml three-neck round bottom glass reactor mounted on automated heater that is equipped with a magnetic stirrer. Different ratios of glycerol (19.069 g)/DMC (19.5 to 97.7 g) and TSP (0.19 to 0.76 g) (1 to 4 wt% relative to glycerol weight) were charged in the reactor at reaction temperatures from 50 to  $80\text{ }^\circ\text{C}$  and 30 to 120 min reaction time. Unreacted excess DMC was separated through slow evaporation under reduced pressure. The conversion and yield of glycerol and GC were determined quantitatively from gas chromatography.

### 2.3. Catalyst stability and reusability

After each reaction, TSP catalyst was separated by centrifugation, washed several times with methanol (approximately 50 ml per wash), and dried for 5 h under ambient conditions. The recovered TSP was reused directly in successive multi-cycles of experiment adopting the same regeneration step for each reuse. Furthermore, TSP stability against the leaching of functional groups was probed using hot filtration method [26].

### 2.4. Analytical method

A gas chromatograph (Shimadzu 2010 plus, Japan) fitted with a flame ionization detector (FID) was used to analyze the drawn reaction samples. The gas chromatograph–FID column is a capillary column (ZB5-HT) of 30 m length, 0.25-mm I.D., and 0.25- $\mu\text{m}$  film thickness (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ ). Samples to be analyzed were prepared by pipetting 20  $\mu\text{l}$  of the sample using a micro-pipette into a vial containing  $1 \times 10^{-3}$  l of pyridine. The gas chromatography–FID detector settings adopted for this study has been reported [18].

### 2.5. Characterization of TSP catalyst

#### 2.5.1. Determination of TSP base amount

The base amount of TSP (both fresh and nine times reused TSP) was determined using acid–base titration method [27]. Typically, 0.10 g of TSP was circulated in a 10 ml aqueous HCl (0.5 mol/l) for 24 h. Thereafter, the residual acid in the liquid phase was titrated against 0.1 mol/l of NaOH aqueous solution. Phenolphthalein was used as the indicator during titration.

Hammett indicators which includes bromthymol blue ( $H_- = 7.2$ ), phenolphthalein ( $H_- = 9.3$ ), 2,4-dinitroaniline ( $H_- = 15.0$ ), 4-nitroaniline ( $H_- = 18.4$ ), and aniline ( $H_- = 27.0$ ) were used to investigate the basic strength distribution of TSP catalyst [18,28,29]. 50 mg of TSP powder was transferred into 10 ml cyclohexane and sonicated for 3 h. Then, 0.75 wt% indicator dissolved in benzene was added dropwise to the catalyst suspension in cyclohexane. Thereafter, it was left to equilibrate for 2 h, until no further color changes were observed. The color changes on the catalyst surface were monitored virtually; where, the relative base strength is described as being stronger than the weakest indicator that produces a color change but weaker than the strongest indicator that shows no color change.

Also, the temperature programmed desorption of  $\text{CO}_2$  using Micromeritics AutoChem 2920 II apparatus equipped with thermal conductivity detector (TCD) was used to confirm the base amount of TSP. Initially, the TSP catalyst was degassed by heating 0.05 g of TSP under inert helium flow (100 ml/min,  $20\text{ }^\circ\text{C}/\text{min}$ ) from ambient temperature to  $600\text{ }^\circ\text{C}$  for 1 h. Then, the sample was cooled to  $70\text{ }^\circ\text{C}$  and  $\text{CO}_2$  was introduced for 1 h. The temperature desorption of the adsorbed  $\text{CO}_2$  was carried out under inert helium gas flow ( $10\text{ }^\circ\text{C}/\text{min}$ , 30 ml/min) between 70 to  $600\text{ }^\circ\text{C}$  and

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