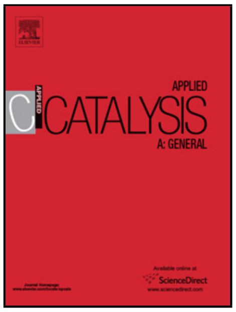

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# Reusable Gypsum Based Catalyst for Synthesis of Glycerol Carbonate from Glycerol and Urea

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## Highlights

- First report on utilizing gypsum as catalyst for synthesis of organic carbonate.
- Different pre-treatment produced different crystalline structure of catalyst.
- The yield of glycerol carbonate depends on the specific phase of gypsum.
- Accelerated formation of glycerol carbonate via glycerol carbamate intermediate.
- The catalyst is reusable.

## Graphical abstractReusable Gypsum Based Catalyst for Synthesis of Glycerol Carbonate from Glycerol and Urea

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## Abstract

In this study, the catalytic carbonylation of glycerol with urea in the presence of gypsum based heterogeneous catalyst is reported for the first time. Gypsum ($CaSO_4 \cdot 2H_2O$) is one of the two calcium sulphate minerals found in nature and also one of the waste materials produced from advanced material industrial processing plant. The effect of physical and chemical pre-treatment procedures on gypsum was investigated. To obtain the catalyst structure-activity relationship, the treated catalysts were characterized by means of several characterization techniques (*i.e.* XRD, TGA, BET surface area, SEM, FTIR, $CO_2$-TPD, $NH_3$-TPD and Hammett test). Tuneable physico-chemical properties of gypsum based catalysts were successfully prepared by varying the pre-treatment techniques, which later on contributed to the variation of catalytic activity toward glycerol carbonate formation from glycerol. The highest catalytic activity obtained was for catalyst consisting ß-$CaSO_4$ phase where it produced 92.8% conversion of glycerol, 90.1% selectivity and 83.6% yield of glycerol carbonate, respectively. The gypsum catalyst is easily recoverable and reusable for subsequent cycles of reaction. Similar physico-chemical properties of fresh and used catalyst were confirmed through XRD, FTIR and Hammett test analysis. Besides, the mechanistic pathway of glycerol carbonate was confirmed through the formation of glycerol carbamate as intermediate compound which was further established through time online analysis study using $^{13}C$ NMR and ATR-FTIR, respectively. The study also clearly supports conversion of waste into wealth while promising proper disposal of waste to produce value added product.

**Keywords**: Glycerol; Glycerol Carbonate; Gypsum; Heterogeneous catalyst; Pre-treatment

## 1. Introduction

The development of new routes of chemical products from renewable feedstock is one of the critical importance for a sustainable future. Nowadays, the expanding production of biodiesel has generated glycerol in quantities exceeding the current demand. This leads a drop of the glycerol price and the risk of seeing a surplus of glycerol. By the year 2016, the world biodiesel market is estimated to be at 308 billion kg, which means more than 33 billion kg of crude glycerol will be produced every year [1]. The production cost of biodiesel increases by U.S. $0.0022/L for every U.S. $0.022/kg reduction in glycerol selling price [2]. The potential sale of this product could make biodiesel cheaper. Thus, it is important to find alternative uses for glycerol. Recently, the new opportunities for conversion of glycerol waste into high value-added product have increased due to the special structure, properties and the renewable feature of glycerol [3]. The glycerol waste can make a comfortable place in the global market by using it as a source of feedstock for value-added product such as glycerol carbonate [4].

Glycerol carbonate is one of the important building blocks for chemical industry and characterized by a low toxicity, good biodegradability and high boiling point, which are useful for solvents and chemical intermediate [5]. Due to the combination of wide reactivity and bio based origin, carbonates become a versatile and renewable building block for organic chemistry as well as possibility to become a major chemical intermediate, for instance, in the manufacturing of polymer, adhesives, foams, coatings and lubricants [6-8].

Glycerol carbonate is produced from glycerol in many different routes. Previously, it was synthesized in conventional method via phosgenation of methanol [9]. However, due to high toxicity, chemical and corrosive nature of phosgene, the alternative routes were suggested such as from ethylene carbonate and propylene [10]. Glycerol carbonate also synthesized from glycerol with dimethyl carbonate. This route has its disadvantages because the reaction required expensive catalyst and higher ratio of dimethyl carbonate to glycerol as well as a shift in chemical equilibrium [11]. Alternatively, an equally attractive route to prepare glycerol carbonate is the reaction of glycerol with urea. This phosgene-free process utilised low cost raw material with low toxicity [12]. Besides, there is a possibility to convert ammonia formed during reaction back into urea using carbon dioxide captured technology [9].

Gypsum is the most common naturally occurring sulphate minerals with the chemical formula of $CaSO_4 \cdot 2H_2O$. Gypsum is also produced as a waste product from advanced material manufacturing industry, such as titanium dioxide ($TiO_2$) processing plant [13]. Titanium (IV) oxide is extracted from ilmenite ores by sulphuric acid digestion and the spent acid is neutralized by calcium carbonate thus produces the waste gypsum [14]. Hunstman Tioxide is one of the largest companies that produce $TiO_2$ in the world. The capacity of their plant in Malaysia alone is about 56 000 metric tons per year. This industry is estimated to produce ~ 400 000 tonnes of waste gypsum annually [15-16]. Therefore, for the first time this present research utilizes commercial gypsum material as a model catalyst for the synthesis of glycerol carbonate from glycerol and urea.

## 2. Experimental

### 2.1. Chemicals

Glycerol (99.5%) and urea (AR grade) were purchased from Friendemann Schmidt Chemical. Standard glycerol carbonate, hydrogen peroxide (30% w/w $H_2O_2$ in water) and tetraethylene glycol (TEG) were purchased from Sigma-Aldrich while commercial gypsum ($CaSO_4 \cdot H_2O$) and calcium oxide (CaO) were purchased from R&M chemical. All other chemicals except gypsum and calcium oxide were used directly without further purification and pre-treatment.

### 2.2. Catalyst preparation

The commercial gypsum (denoted as GypF) is calcined in static air using a vertical furnace for 3h at 150°C and 800°C respectively. The catalysts obtained were denoted as Gyp150 and Gyp800. The gypsum treated with $H_2O_2$ was prepared by treating the fresh commercial gypsum material with 30% $H_2O_2$ in $H_2O$. In specific, 11.5g of GypF was added into 20ml of $H_2O_2$. Then the solution was stirred for 3h with the heating at 40°C. The solution was then filtered and washed with hot water for 3 times. Next, the sample was dried in the oven at 110°C for 16h. Then, the catalyst obtained was denoted as GypH. For calcium oxide, the fresh commercial sample was calcined in the furnace at 800°C for 3h and the catalyst obtained was denoted as CaO800.

## 2.3. Catalyst characterization

Thermo-gravimetric Analyser Mettler Toledo TGA/DSC-HT/1600 was used to monitor the weight loss and phase transformation in the range of temperature between 25°C to 1000°C under static air environment.

X-ray diffraction (XRD) patterns of the catalysts were recorded on a Rigaku Miniflex II diffractometer and were set to be analysed at the range of 15 degree to 80 degree at 2 Theta (θ) for crystalline phase determination with Cu Kα radiation.

The BET (Brunauer-Emmett-Teller) method was used to measure the total specific areas of catalysts using Micromeritics TriStar II 3020.

Scanning Electron Microscopy (SEM) brand Zeiss Evo 50 was used to study the surface morphology of the catalyst.

The acido-basic property of catalyst was determined by three different methods (Hammett test, $CO_2$-TPD, and $NH_3$-TPD). Firstly, by utilizing Hammett test, the indicator 2,4-Dinitroaniline, Phenolphthalein, Methyl red and Methyl orange were used to determine the qualitative acidic as well as basic properties of the catalyst. In specific, 25mg of catalyst was weighed and prepared in four batches and 5ml of methanol was added to the catalyst. Then, 1ml of the indicator was added to 4ml of methanol. Final volume of 5ml indicators were added separately to the catalysts weighed in batches. The mixture was then left to equilibrate for 2h. The colour changes were observed and noted.

The quantitative basicity strength was analysed using Temperature Programmed Desorption of $CO_2$ ($CO_2$-TPD), (Thermo Finnigan TPD/R/O 1100). The TPD was equipped with a thermal conductivity detector (TCD). 50mg of the catalyst sample was treated at 200°C for 1h by passing helium at a flow rate of 20ml/min. Then, the sample was saturated with $CO_2$ at a flow rate of 30ml/min and at a temperature ramping from 10°C/min up to 200°C for 1h. After that, the system was flushed with helium (20ml/min) at 200°C for 1h to eliminate physisorbed $CO_2$. Desorption was carried out from ambient temperature of 900°C at a heating ramp of 5°C/min.

Temperature Programmed Desorption of $NH_3$ ($NH_3$-TPD) was used to determine the quantitative acidity strength. Approximately, 50mg of sample was placed in a quartz tube and treated for 1h at 200°C under a nitrogen flow of 20ml/min. Then, the sample was dosed with $NH_3$, again at 20ml/min. After dosing, the samples were cooled down to 50°C and then heated to 900°C at 10°C/min, under helium flow of 20 ml/min.

## 2.4. Catalytic Testing

The reaction was carried out using a three neck round bottom flask. Firstly, 13.8g of glycerol was added into the 100ml three necks round bottom flask as the solution was heated until 150°C and stirred at 340 rpm under the flow of nitrogen gas. The temperature and stirring rate were controlled by using a temperature controller (IKA@ ETS-D5). When the temperature of the glycerol is reaching 150°C, 13.5g of urea and 0.25g of catalyst were added into the reaction solution. The sample of liquid product produced was sampled at specific sampling time then subjected for analysis.

## 2.5. Catalyst Reusability Procedure

For catalyst reusability test, the tested catalyst was removed after completing the catalytic reaction by using centrifugal, washed with excess of water then drying it in oven for 16h at 110°C. The catalyst obtained denoted as GypR. It then undergoes another catalytic reaction directly without any further treatment.

In addition to that, the reaction solution after the reaction process was also subjected to ICP-MS and CHNOS analysis, which in order to analyse any possibility of metal components leach-out into the reaction medium. The amounts of metal leach-out can be calculated and compared to the actual amount of metal available in catalyst prior to the reaction. For ICP-MS analysis procedure, 0.5ml of sample diluted to 50ml of 2% $HNO_3$ (Fischer Chemical). Five different standards of 2% $HNO_3$ were prepared before the analysis, which are (0, 0.5. 1.0, 2.0, 5.0 and 50.0 ppm) respectively. Then, the analysis was completed using Agilent 7700x ICP-MS. CHNOS analysis was carried out by combustion method using Vario Macro Elemental Analyser CHNSO.

## 2.6. Analysis of product

Gas Chromatography GC-FID Agilent Technologies 7890A equipped with a Varian Capillary Column, CP-PoraBOND Q (25m, 0.53mm, 10µm) was used to analyse the product of reaction. 50µl of sample was taken at each time and diluted into 1450µl of deionised (DI) water. Helium gas was used as the carrier gas with a flow rate of 35ml/min. The temperature of the injector and the detector were 225$^{o}$C and 250$^{o}$C, respectively. The temperature of the column was programmed to be at 2min with initial hold at 80$^{o}$C, a 10$^{o}$C/min ramp from 80$^{o}$C to 250$^{o}$C and 15$^{o}$C/min ramp from 250$^{o}$C to 300$^{o}$C with 3min holding time. The split ratio was 1:10 and injection volume was 1µl. Tetraethylene glycol (TEG) was used as an external standard. Standard glycerol and glycerol carbonate with different range of concentration were used for calibration purpose.

Time online analysis of products was also analysed using Nuclear Magnetic Resonance (NMR) BRUKER Ultra Shield Plus 500MHz and Attenuated Total Reflectance-Fourier Transform Infrared spectroscopy (ATR-FTIR) Perkin Elmer, USA. For the case of analysis of liquid product using ATR-FTIR, 50µl of sample was immediately sampled and one drop was placed onto the sample holder. The sample was then immediately analysed. In case of NMR, the sample for 13C NMR analysis was prepared by sampling 150µl of liquid sample into the NMR tubes and then diluting with 500µl of deuterated methanol-$d_4$.

## 3. Results and discussion

### 3.1. Characterization of catalyst

### 3.1.1. Thermo-gravimetric analysis (TGA)

In order to determine the calcination temperature as well as the effect of temperature on GypF ($CaSO_4 \cdot 2H_2O$), the GypF was subjected to thermogravimetric analysis. Fig. 1 illustrates the TGA curve for GypF catalyst. Single stage decomposition was clearly observed from the TGA thermogram. The decomposition of the precursor started at 80°C and completed at 200°C. The total weight loss was about 0.74mg from 3.63mg of sample placed at the beginning of the test equal to 20.5% of weight loss. The magnitude of weight loss (about 20% of the original sample weight) complies with stoichiometrically expected for complete dehydration of the gypsum to the anhydrite ($CaSO_4$) form [17]. The weight losses are more easily determined by integrating the peaks at 130°C in the first derivative (DTG) curve, which also indicates apparently only one weight loss.

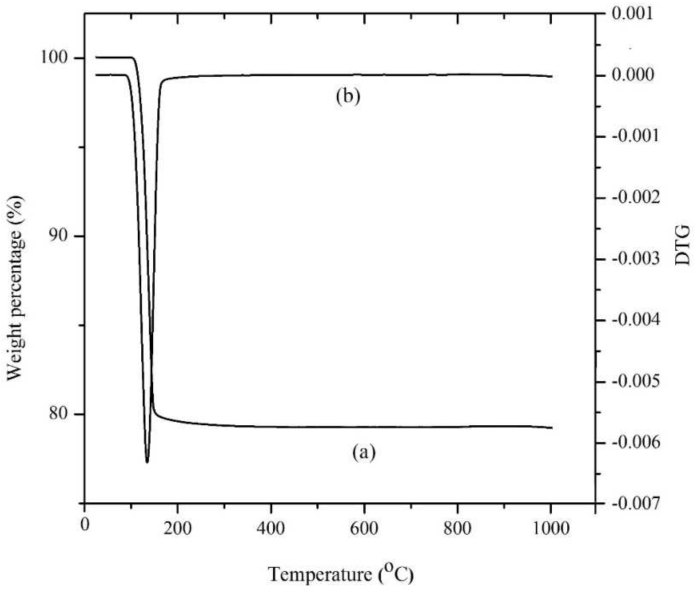


Fig. **1.** Thermo-gravimetric analysis (TGA) of GypF (a) weight percentage (%) loss and (b) derivative thermal gravimetric (DTG)

### 3.1.2. X-ray diffraction (XRD)

Fig. 2 illustrates the X-ray diffractogram of GypF, Gyp150, Gyp800 and GypH labelled as a, b, c and d, respectively. XRD pattern of GypF showed characteristics of $CaSO_4 \cdot 2H_2O$ presence at 2θ = 20.90º, 23.58º, 29.31º and 48.02º (JCPDS File: 33-0311). Gyp150 showed the characteristic of ß-$CaSO_4$ diffraction peaks presence at 2θ = 25.88°, 29.94° and 32.02°. Lopez-Delgado and co-workers in their study stated that $CaSO_4 \cdot 2H_2O$ will transform into a different phase of anhydrite ($CaSO_4$) after subjected to different temperature treatment [18]. ß-$CaSO_4$ will be produced in the temperature range between 163 to 360°C, while at higher temperature up to 370°C, the beta (ß) phase will be transformed into gamma (γ) phase. Their observation is in-line with the XRD pattern obtained for Gyp800 catalyst where the diffraction pattern showed characteristic of γ-$CaSO_4$. The gamma phase of anhydrite was reported to be insoluble compared to beta phase [19]. In addition to heat treatment, chemical treatment of fresh gypsum with hydrogen peroxide ($H_2O_2$ 30% in water) GypH showed the characteristic of $CaSO_4 \cdot 0.5H_2O$ [20].

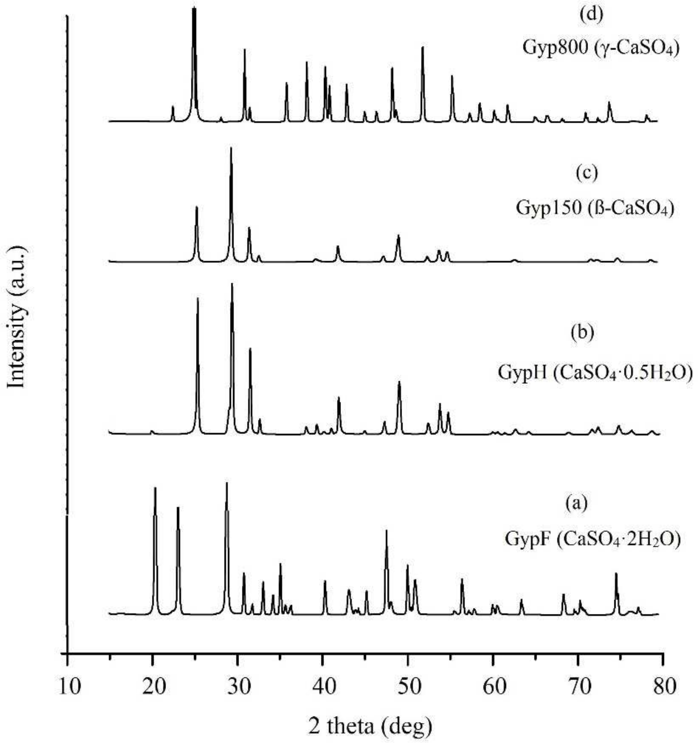


**Fig. 2.** X-ray Diffraction pattern of a) GypF b) GypH c) Gyp150 d) Gyp800

The crystallographic data were summarised in Table S1 using Debye-Scherrer Equation [21]

$$D = 0.90\lambda \,/\, \text{FWHM} \cos\theta \qquad (1)$$

*D* is the average crystallite size in mm, λ is the wavelength of the X-ray radiation (Cu Kα, 0.1548 nm), FWHM is the full width at half-maximum, and θ is the diffraction angle.

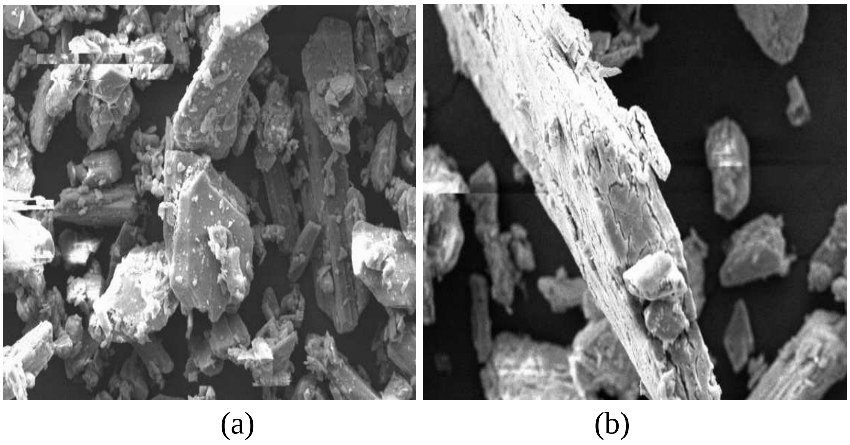
The crystallite sizes were such calculated using Debye–Scherrer Equation shows that GypF has smaller particles compared to the treated samples. The difference in crystallite size between treated and untreated commercial gypsum is expected since heat treatment will induce the agglomeration of particle, which subsequently increase the crystallite size. The variation of crystallite size is also in-line with the surface area data analysed using BET method whereby smaller crystallite size material showing bigger specific surface area.

### 3.1.3. BET Surface Area ($S_{BET}$)

The specific surface area for GypF (10.8m$^2$/g) is five times higher compared to the treated samples. As previously mentioned, the heat treatment was responsible in inducing the agglomeration of the sample. The effect is more pronounce at higher temperature and causing sample to bind closely to each other thus decreasing the surface area. Indran and co-workers also reported this phenomenon where higher temperature will decrease the surface area of catalyst [22]. It was clearly true since gypsum calcined under static air at 800$^o$C for similar calcination duration shows almost half BET surface area value (i.e. 1.4 m$^2$/g) than the one observed with gypsum calcined at 150$^o$C (i.e. 2.6 m$^2$/g).

### 3.1.4. Scanning Electron Microscope (SEM)

Surface morphology using SEM analysis in Fig. 3 showed that the different pre-treatment did not significantly alter the morphology of the gypsum based catalyst. Gyp150 and Gyp800 showed a slight difference in morphology from GypF due to the deformation of water during calcinations thus altered the composition from $CaSO_4 \cdot 2H_2O$ to $CaSO_4$. GypH showed the morphology of gypsum hemihydrate ($CaSO_4 \cdot 0.5H_2O$) that is similar to the SEM morphology of similar material reported in literature [23].


(a) (b)

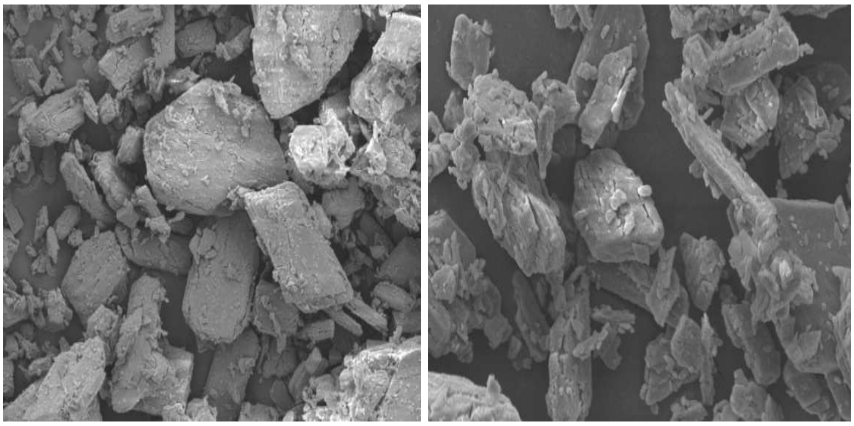

(c) (d)

**Fig. 3.** SEM of a) GypF b) GypH c) Gyp150 d) Gyp800

### 3.1.5 Acidity and Basicity Analysis

#### 3.1.5.1. Hammett Test

Hammett test has found a wide application in the examination of acid-base properties of heterogeneous catalysts. Visual or spectrophotometric observation of the colour change of an absorbed indicator makes it possible for the assessment of the basic or acid strength of the surface of catalyst [24]. GypF, GypH, Gyp150 and Gyp800 showed negative results for both basic (2,4-dinitroaniline, H_=15 and phenolphthalein, H_=8.2) and acidic (methyl red, H_=5.1 and methyl orange, H_=3.7) indicator. Thus, it is suggested that gypsum are neutral in nature due to the counter effect of both strong acid from $(SO_4)^{2-}$ and strong base from Ca. It is important to note that gypsum was known to be neutral material as reported by Azimi et al [25]

#### 3.1.5.2. Temperature Programmed Desorption ($CO_2$-TPD and $NH_3$-TPD)

It can be seen from $CO_2$-TPD profile of Gyp800 (Fig. S1) that the catalyst does not have the characteristic of basic material where there is no peak corresponds to $CO_2$ desorption as being observed for the range of tested temperature. However, with $NH_3$ as a chemical probe instead of $CO_2$, one desorption peak was observed at the maximum desorption peak at 211°C accounted to amount desorbed $NH_3$ of 119.7μmol/g (Fig. S2). Nevertheless, the value was relatively low which suggests a weak acidic site. The $NH_3$-TPD data obtained for anhydrite gypsum ($CaSO_4$) is in agreement with similar analysis reported by Hu et al [26]. In their study, $NH_3$-TPD of sample containing $CaSO_4$:CaO with the ratio of 9:1 produced significantly weak $NH_3$ desorption signal compare to the lower ratio of $CaSO_4$ (1:9) presence in the sample. Both TPD results clearly confirmed the Hammett test analysis, which indicated Gyp800 is relatively neutral in nature.

### 3.2. Catalytic activity

### 3.2.1. The effect of catalyst pre-treatment on gypsum towards glycerol conversion, glycerol carbonate selectivity and yield.

Table 1 shows the catalytic activity of gypsum based catalysts towards glycerol conversion, glycerol carbonate selectivity and yield respectively. The yield of glycerol carbonate obtained through catalysed reactions is significantly higher compared to uncatalysed reaction. The reaction without catalyst only produced 25.8% yield of glycerol carbonate. It is therefore apparent that the important role of the catalyst is to direct the selectivity towards the required product, glycerol carbonate. It was reported in previous literatures that the first step of the reaction involving conversion of glycerol into glycerol carbamate which proceeds at higher rate via uncatalysed homogeneous reaction, whereas the catalyst played a crucial role to selectively converted carbamate intermediate into glycerol carbonate [9,27]. The statement was further supported by proposed mechanistic pathways carried out in this study. The highest catalytic activity obtained from Gyp150 was 92.8% conversion of glycerol, 90.1% selectivity and 83.6% yield of glycerol carbonate respectively. The turnover frequency (TOF) for Gyp150 also showed the highest value compared to other gypsum samples. It is worth to note that the TOF value calculated for Gyp150 is also higher and comparable to the TOF value reported in recently published works [28-29]. It is important to note that different phase of $CaSO_4$ also plays a significant role in controlling the catalytic activity and selectivity since only 73.8% of glycerol carbonate yield observed with γ-$CaSO_4$ (Gyp800) as a catalyst. However, it is essential to point out here that γ-$CaSO_4$ is insoluble anhydrite material compared to ß-$CaSO_4$ identified in Gyp150. Thus, it is suggested that higher yield of glycerol carbonate observed with ß-$CaSO_4$ might have been contributed by some of the metal component leach-out during reaction and involved as homogeneous reaction instead of fully surface reaction. This assumption was supported by the analysis of solution reaction after reaction for both Gyp150 and Gyp800 using ICP-MS and CHNOS analyser, respectively. The ICP-MS results show that 0.54% of Ca is detected in the liquid solution for the reaction in the presence of Gyp150 compared to 0.21% quantified for Gyp800. Besides that, analysis of possible sulphur leach-out during the catalytic reaction was determined using CHNOS analyser. The data analysis showed 0.47% of sulphur leach-out for Gyp150, which is almost 3 times higher compared to the similar analysis for Gyp800.

**Table 1**

Reaction conditions: Temperature, 150°C; Gas, $N_2$; Glycerol: Urea, 1: 1.5 (Molar ratio); Catalyst mass 0.25g; Time: 4h; Standard stirring rate, 340 rpm, TOF: calculated based on the glycerol carbonate yield per gram catalyst per total reaction time (h). RSD: <5%. Note: Gly. is Glycerol; GC : Glycerol carbonate; (3) is 2,3-dihydroxypropyl carbamate; (5) is 4-(hydroxymethyl)oxazolin-2-one; (6) is (2-oxo-1,3-dioxolan-4-yl) methyl carbamate.

Compared to calcined samples, the uncalcined gypsum (GypF) shows inferior catalytic performance whereby the observed glycerol carbonate yield is only at 59.9%. The inferior catalytic activity of this particular catalyst may partially attribute to the presence of water molecule inside the catalyst lattice that consequently affects the catalytic process. This argument further proved by the data obtained from $H_2O_2$ treated catalyst (GypH) where it showed the lowest yield and selectivity of glycerol carbonate compared to others. The effect of water content in glycerol was also studied by Lu and co-workers [30]. The yield of glycerol carbonate will rapidly decrease in the presence of water more than 2.0wt%.

Since acido-basic properties were shown to have significant effect on overall catalytic activity for glycerol carbonate via carbonylation of glycerol with urea [9], detailed characterizations have been carried out. Though, the qualitative and quantitative analysis performed using TPD technique with $NH_3$ and $CO_2$ as chemical probe, respectively and Hammett test showed that gypsum based catalyst is neutral in nature. However, $\gamma$-$CaSO_4$ phase of Gyp800 consists of $Ca^{2+}$ and $(SO_4)^{2-}$ where these ions present at the catalyst surface could act as Lewis acid and conjugate base respectively. It is reported by Climent et al. that Lewis acid sites activates the carbonyl group of urea while the conjugated base site activates hydroxyl group on glycerol to form glycerol carbonate [9]. On top of that, it has been reported that neutral catalyst could catalyse glycerol carbonylation to yield glycerol carbonate [31]. Thus, it is believed that gypsum offers ions at its surface that could particularly act as the active site for the synthesis of glycerol carbonate using glycerol and urea.

In order to identify whether Ca plays a major role in superior activity of gypsum based catalyst, CaO has been subjected to similar reaction conditions. For the record, CaO as catalyst for glycerol carbonate formation via carbonylation of glycerol using urea was not reported in any previous literature. Though, CaO has been used by Simantujak and co-workers for converting glycerol into glycerol carbonate through transesterification of dimethyl carbonate with glycerol and the reaction produced 90.2% yield of glycerol carbonate [32]. However, glycerol carbonate synthesis via carbonylation approach involving urea and CaO as catalyst clearly produced lower yield of glycerol carbonate (51.0%) compared to 73.8% attained with $\gamma$-$CaSO_4$ catalyst. It is important to note here that the level of glycerol conversion between CaO and $\gamma$-$CaSO_4$ is almost similar which is 89.5% for CaO and 89.1% for $\gamma$-$CaSO_4$, respectively. Conversely, the selectivity of glycerol carbonate which is believed to originate from selective transformation of glycerol carbamate is observed to be higher with the presence of $\gamma$-$CaSO_4$ (82.8%) compared to CaO (57.0%). The observation is clearly in-line with the role of Lewis acid and conjugate based as mentioned previously. Thus, it is postulated that $(SO_4)^{2-}$ presence in anhydrite phase of gypsum may act as more efficient conjugate base compare to $O^{2-}$ available with CaO catalyst.

Theoretically, for the catalytic reaction involving heterogeneous catalyst, the specific surface area and particle size of catalyst plays a crucial role in assisting the catalytic activity and selectivity [33]. However, both factors are clearly not contributing for this study as GypF with higher specific surface area and smaller crystallite size produced lower yield of glycerol carbonate.

### 3.2.2. Time Online Analysis (TOL)

Since the γ-$CaSO_4$ is an insoluble phase of anhydrite, Gyp800 was then used as catalyst for time-online study. Fig. 4 illustrates the time online analysis (TOL) for 10h conducted in the presence of Gyp800 catalyst. The conversion increased up to 80% for the first 2h with maximization to 96% at 6h whereas the selectivity of glycerol carbonate gradually decreased from 6h to 10h. The decreases in glycerol carbonate selectivity at prolong reaction tie is attributed to the transformation of this target product into compound 6 and at the same time formation of compound 5, which is originated from carbamate intermediate had also increased. It also clear from the figure that glycerol carbamate (compound 3) was formed and quickly decomposes into glycerol carbonate.

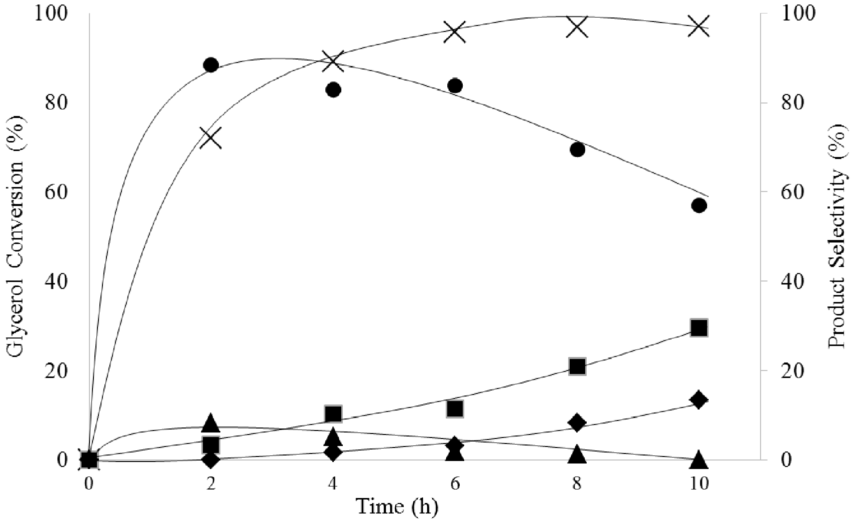


**Fig. 4.** Time online profile of glycerol carbonate synthesis in the presence of Gyp800. Reaction conditions: glycerol/urea molar ratio: 1 : 1.5, temperature: 150°C, catalyst mass: 0.25g. Key: x glycerol conversion (%), ■ selectivity (%) to glycerol carbonate, ● selectivity (%) to 2,3-dihydroxyproyl carbamate (3), ▲ selectivity (%) to 4-(hydroxymethyl) oxazolidin-2-one (5), ♦ selectivity (%) to (2-oxo-1,3-dioxolan-4-yl) methyl carbamate (6)

### 3.2.3. Mechanistic study

*Fig.* 5a showed the $^{13}C$ NMR analysis for the time online analysis (TOL) of Gyp800. The $^{13}C$ NMR patterns prove that glycerol carbonate (4) was selectively formed through the carbonylation of intermediate 2.3-dihydroxypropyl carbamate (3). At 6h of reaction time, 4-(hydroxymethyl) oxazolin-2-one (5) and (2-oxo-1,3-dioxolan-4-yl) methyl carbamate (6) were present. It is evident that selectivity towards glycerol carbonate formation decreased from 6h onwards due to the formation of compound (5) and (6). Further reaction of glycerol carbonate with excess of urea will form (6) and the intermediate 2,3-dihydroxyl carbamate (3) forms compound (5) [34]. Besides that, Fig. 5b indicates the chemical shift at 165 ppm which corresponds to urea (compound 2) is steadily reducing with prolonged reaction time. For the record, Hasbi and co-workers in 2012 have reported the same mechanistic pathway with this current study as well with Kim and co-workers in 2013 [34,35]. However, in this study the glycerol carbamate was selectively decomposed in an accelerated way to glycerol carbonate and this observation is similar to recently reported study by Indran and co-researchers [22].

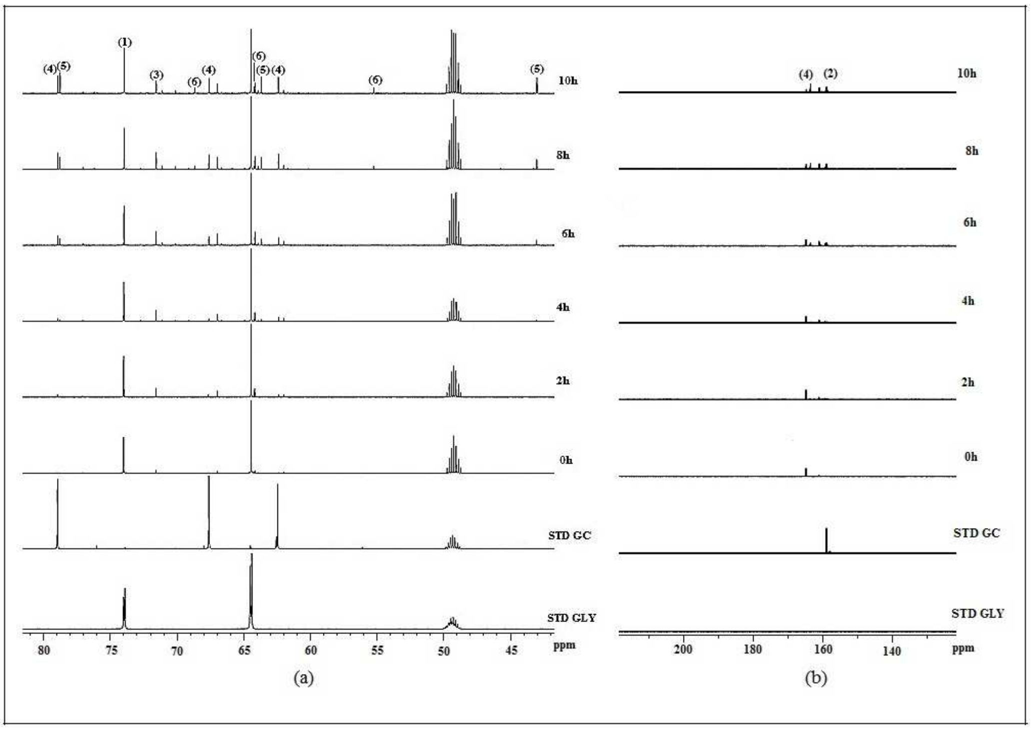


**Fig. 5.** a) $^{13}$C NMR overlay of standard glycerol (STD GLY), standard glycerol carbonate (STD GC) and TOL of Gyp800. Key: (1) glycerol; (2) urea; (3) 2,3-dihydroxypropyl carbamate; (4) glycerol carbonate; (5) 4-(hydroxymethyl)oxazolin-2- one. b) $^{13}$C NMR overlay of standard glycerol (STD GLY), standard glycerol carbonate (STD GC) and TOL of Gyp800. Key: (2) urea and (4) glycerol carbonate.

An analysis using ATR-FTIR was carried out to validate the mechanistic study using $^{13}$C NMR. Fig. 6 showed the ATR-FTIR spectra obtained from the reaction sampling at 0.5h to 10h. IR peak unique to glycerol was identified at 1450cm$^{-1}$ whereas the IR peaks for urea assigned at 1620cm$^{-1}$ and 1665cm$^{-1}$ were clearly observed at 0.5h. However, IR peak of glycerol carbamate (3) was not clearly observed during 0.5h due to the reaction occurred in an accelerated way to directly decompose glycerol carbamate into glycerol carbonate (4) and this phenomena agreed well with the analysis of $^{13}$C NMR. Glycerol carbamate (3) was observed at 2h and 4h with peak at (1715cm$^{-1}$). The peak of glycerol carbamate was gradually shifted to the 4-(hydroxymethyl) oxazolidin-2-one (5) at a longer reaction time. On the other hand, peak at 1790cm$^{-1}$ indicated C=O stretching from glycerol carbonate. This indicated formation of glycerol carbonate from 2h onwards. Isocyanic acid compound with N=C=O stretching that usually exist in range peak

$2250 cm^{-1}$ that was previously reported by Aresta and co-workers was not observed in this reaction [12]. Thus, it was confirmed that the formation of glycerol carbonate does not follow the isocyanic acid pathway but follows the pathway of selective transformation of glycerol carbamate.

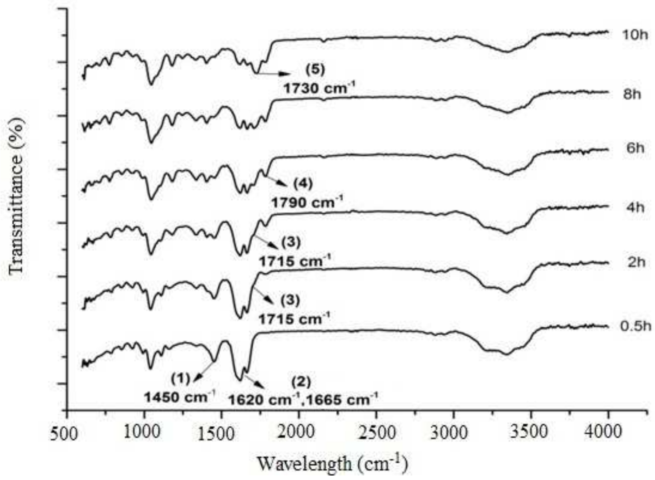


**Fig. 6.** ATR-FTIR spectra for time online analysis of Gyp800 reaction from 0.5h to 10h. Key: (1) glycerol; (2) urea; (3) 2,3-dihydroxypropyl carbamate; (4) glycerol carbonate; (5) 4-(hydroxymethyl) oxazolin-2- one

### 3.2.3. Stability and reusability of catalyst

One of the key factors that must be considered for heterogeneous catalysts operating in liquid phase systems is the possibility that active components can leach into the reaction mixture, thereby leading to catalyst deactivation or, to the formation of an active homogeneous catalyst. Therefore, the reusability of catalyst was investigated by utilizing it in four consecutive batch runs. Fig. 7 presents the results of glycerol conversion, selectivity and yield of glycerol carbonate obtained up to fourth consecutive catalytic reaction in the presence of Gyp800. The results confirm that this catalyst is reusable with no appreciable decrease in its activity and selectivity. In addition to that and as previously mentioned, the reaction solution was subjected to ICP-MS and CHNOS analysis in order to determine the possibility of metal leach-out. The insignificant amount of leaching confirms the stability of the catalyst. The reusability of Gyp800 catalyst is expected since the $\gamma$-$CaSO_4$ structure was reported to be an insoluble phase by Rolnick [19].

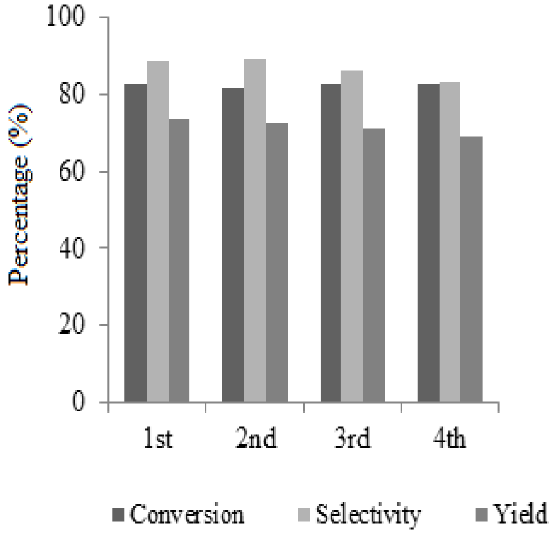


Fig. **7.** Reusability study of Gyp800 on glycerol conversion, glycerol carbonates selectivity and yield. Reaction conditions: Temperature, 150˚C; Gas, $N_2$; Glycerol: Urea, 1: 1.5 (Molar ratio); Catalyst mass 0.25g; Time: 4h; Standard stirring rate, 340 rpm.

To further validate the stability of gypsum based catalyst, the used catalyst was subjected to different characterization techniques (XRD, FTIR and Hammett test) in order to inspect the changes in its physico-chemical properties. XRD diffractogram (Fig. 8) revealed that similar diffraction peaks were detected for both fresh and used catalyst. Table S2 shows that the average crystallite size for the used catalyst was very similar compared to the fresh catalyst, which shows agglomeration did not occur.

The XRD data was further supported by FTIR analysis of both fresh and used catalyst. It is clear from FTIR spectra (Fig. 9) that the characteristic peak was almost similarly presented for the both Gyp800 and GypR catalyst. However, additional IR peak was observed at 2919cm$^{-1}$ and peak at 3448cm$^{-1}$, broader than Gyp800 which is attributed to the presence of OH- functional group. Additional peak also observed at 1717cm$^{-1}$ due to the presence of carbonyl group C=O functional group. The presence of O-H and C=O can be explained by the excess of glycerol and products molecule that were not totally removed during washing step.

Besides, Hammett test analysis for used catalyst also shows similar observation of fresh catalyst counterpart. Therefore confirm the stability and reusability of gypsum (Gyp800) toward producing glycerol carbonate from glycerol and urea.

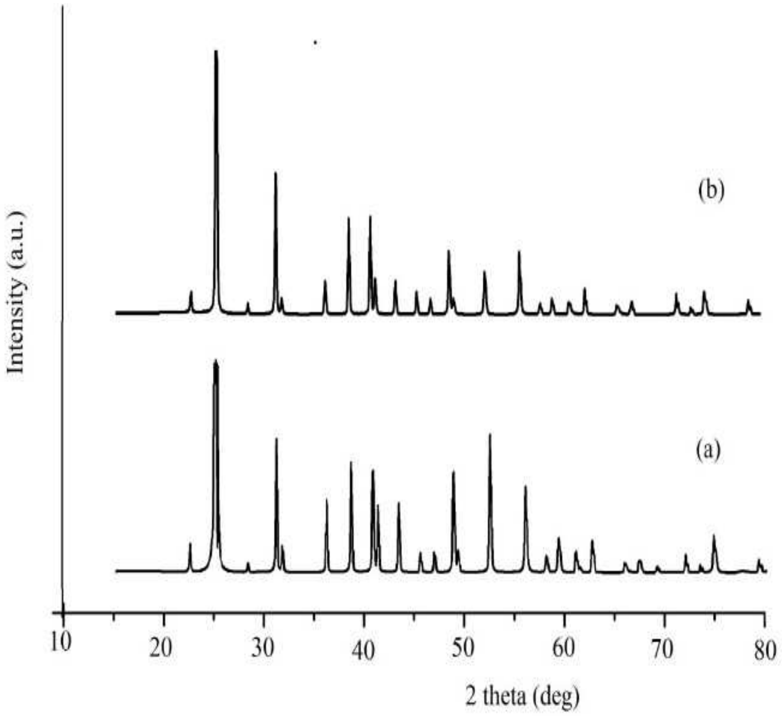


Fig. **8.** XRD pattern of a) Gyp800 b) GypR

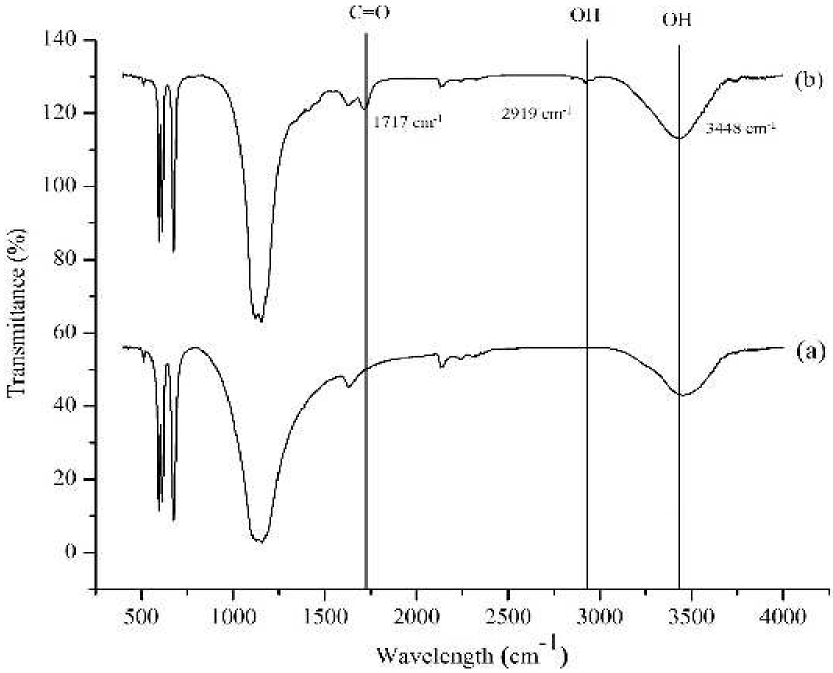


Fig. **9.** FTIR Spectra of a) Gyp800 b) GypR

## 4. Conclusion

It is clear from the work details in this study that gypsum based catalyst is efficient and reusable for the synthesis of glycerol carbonate from glycerol and urea. The reaction is environmental friendly and also introduces a proper and an alternative way for disposal of gypsum. Simple pre-treatment techniques were shown to successfully produce different physico-chemical properties of gypsum based catalysts. The ß-$CaSO_4$ structure was identified as the most active phase where it produced 92.8% conversion of glycerol, 90.1% of selectivity and 83.6% yield of glycerol carbonate, respectively. However, the slightly less productive γ-$CaSO_4$ phase is essentially important where it shows true heterogeneous catalyst characteristics with a similar catalytic performance at consecutive cycles of reaction. The presence of $Ca^{2+}$ as Lewis acid sites with $(SO_4)^{2-}$ as conjugate base sites in gypsum based catalyst is believed to responsible for the catalytic activity and selectivity. As a final point, the stability of sulphur inside the catalyst structure shall add to the viability of the glycerol carbonate to be utilised in different broad applications without causing extra issues.

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## LIST OF TABLE

### Table 1

The effect of gypsum pre-treatment on glycerol conversion, glycerol carbonate selectivity and yield.

| **Entry** | **Catalyst** | **Temp. heat treatment (°C)** | **Gly. Conv. %** | **Selectivity %** | | | | **GC yield %** | **TOF** (mmol $g^{-1}$ cat. $h^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | **GC** | **(3)** | **(5)** | **(6)** | | |
| 1 | Blank | - | 78.7 | 32.8 | 24.0 | 43.1 | - | 25.8 | - |
| 2 | CaO800 | 800 | 89.5 | 57.0 | 4.5 | 26.7 | 7.3 | 51.0 | 76.3 |
| 3 | GypF | - | 92.5 | 64.8 | 9.0 | 18.1 | 5.4 | 59.9 | 89.7 |
| 4 | Gyp150 | 150 | 92.8 | 90.1 | 0.6 | 8.4 | 0.9 | 83.6 | 110.5 |
| 5 | Gyp800 | 800 | 89.1 | 82.8 | 5.1 | 10.3 | 1.7 | 73.8 | 125.4 |
| 6 | GypH | 110 | 91.0 | 43.8 | 14.8 | 29.6 | 11.8 | 39.8 | 59.6 |

Reaction conditions: Temperature, 150°C; Gas, $N_2$; Glycerol: Urea, 1: 1.5 (Molar ratio); Catalyst mass 0.25g; Time: 4h; Standard stirring rate, 340 rpm, TOF: calculated based on the glycerol carbonate yield per gram catalyst per total reaction time (h). RSD: <5%. Note: Gly. is Glycerol; GC : Glycerol carbonate; (3) is 2,3-dihydroxypropyl carbamate; (5) is 4-(hydroxymethyl)oxazolin-2-one; (6) is (2-oxo-1,3-dioxolan-4-yl) methyl carbamate.

The effect of gypsum pre-treatment on glycerol conversion, glycerol carbonate selectivity and yield.

| **Entry** | **Catalyst** | **Temp. heat treatment (°C)** | **Gly. Conv. %** | **Selectivity %** | | | | **GC yield %** | **TOF** (mmol $g^{-1}$ cat. $h^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | **GC** | **(3)** | **(5)** | **(6)** | | |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Blank | - | 78.7 | 32.8 | 24.0 | 43.1 | - | 25.8 | - |
| 2 | CaO800 | 800 | 89.5 | 57.0 | 4.5 | 26.7 | 7.3 | 51.0 | 76.3 |
| 3 | GypF | - | 92.5 | 64.8 | 9.0 | 18.1 | 5.4 | 59.9 | 89.7 |
| 4 | Gyp150 | 150 | 92.8 | 90.1 | 0.6 | 8.4 | 0.9 | 83.6 | 110.5 |
| 5 | Gyp800 | 800 | 89.1 | 82.8 | 5.1 | 10.3 | 1.7 | 73.8 | 125.4 |
| 6 | GypH | 110 | 91.0 | 43.8 | 14.8 | 29.6 | 11.8 | 39.8 | 59.6 |