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A New Approach to High Value Conversion of Phosphogypsum from Phosphate Rock to Catalyst for Glycerol Carbonate Synthesis

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Abstract. This paper reports a new process of using phosphate rock as the precursor to prepare a high performance catalyst for glycerol carbonate synthesis. The reported technical route will create a new opportunity to synthesis the active chemical intermediate that can be used for energy generation. Three important preparation parameters were investigated to find out both singular and binary effects upon the statistical significances of prepared glycerol carbonate conversion using response surface methodology (RSM) approach. The optimal condition with the goal of maximizing the glycerol carbonate was set and achieved. The obtained catalyst prepared at the optimal condition was characterized. The proposed process offers a rosy prospect for high value conversion of colossal by-product phosphogypsum generated from phosphorous acid manufacturing industry.

1. Introduction

Phosphorite, phosphate rock or rock phosphate is a non-detrital sedimentary rock that contains high amounts of phosphate minerals. It is regarded as one of the most paramount precursor for industrial phosphoric acid manufacturing. Simultaneously, huge amounts of by-product (phosphorous contained gypsum) was produced. Because of existences of highly soluble phosphor, fluorite etc, the phosphogypsum (PG) will become a major environmental hazardous substance that jeopardizes the fragile ecosystem. In the meanwhile, from material recycling and utilization perspective, stockpiling such substance without further high value conversion is a gigantic waste [1]. Therefore, the gap lies in the alternatives for high value conversion of PG. With an increase of renewable energy productions and utilization, the by-products such as glycerol, which is one of the main products generated during trans-esterification reaction for biodiesel synthesis, need to find more channels to be consumed [2, 3]. Glycerol carbonate (GC) is a new and emerging material in the chemical industry. Inexpensive GC could serve as a source of new polymeric materials for the production of polycarbonates, polyurethanes, important fine chemicals, and intermediates for energy productions. In addition, GC synthesis route also offers the flexibility for CO_2 sequestration and conversion, which is critical for carbon capture storage and utilization (CCSU) for short and middle term global climate change mitigation strategy [4-6]. Coupling these two processes together would open a new door for economical synthesis GC and high value conversion of by-product (gypsum) from phosphoric acid industry [7]. And more importantly, a

potential technical route for carbon capture storage and utilization (CCSU) process could be proposed for large scale utilizations for the by-product (phosphogypsum) generated from phosphorous acid industry [8]. This initiates our interests for exploring directly using PG produced from phosphate rock as a catalyst to catalyze GC synthesis via glycerol and urea. Although there are reports for using gypsum to catalyst, very few attempts have been made to directly use PG, therefore, in this paper, we report a new route for catalyst preparations using PG produced from phosphate rock.

2. Experimental

Acid leaching is one of the most practical approach to liberating elements from ore matrix and catalyze hydrolysis [9]. In this work, we employ a binary system which contains the phosphorous acid and sulfuric acid. The phosphate rock (collected from Guizhou province) was processed by a so-called 'two-water process', which uses ternary system H_2O-H_2SO_4 (18wt%)-H_3PO_4 (22wt%) as reaction leaching media to $CaSO_4.2H_2O$. The leaching media was adjusted by adding 98% H_2SO_4 and 85% H_3PO_4, respectively. The amount of solid residue ($CaSO_4$-phosphogypsum) obtained was based on stoichiometry of reactions. Then the produced phosphogypsum was further pretreated (calcination and hydrogen peroxide processing) and used as a catalyst to catalyze glycerol carbonate (GC) synthesis. The schematic diagram for this catalytic reaction is shown in Figure 1:
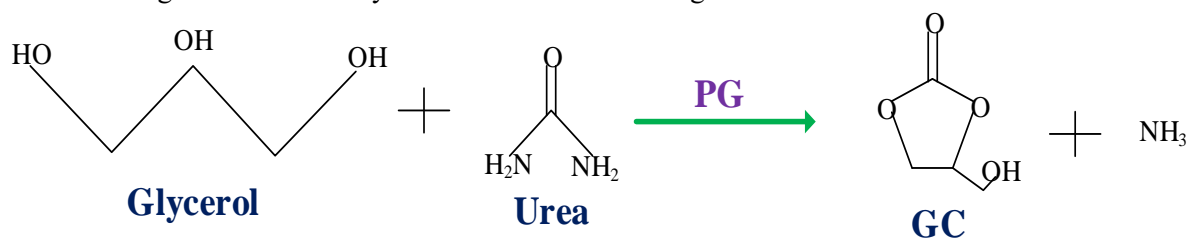

Figure 1. Schematic diagram of glycerol carbonate catalytic synthesis via glycerol and urea route, where GC refers to glycerol carbonate.

The glycerol conversion was calculated as the following:

$$Conversion\ /\% = \frac{c_{gly_0} - c_{gly_t}}{c_{gly_0}} \times 100 \tag{1}$$

where c_{gly_0} refers to the glycerol concentration at the beginning of reaction (mol.m^{-3}), c_{gly_t} refers to final glycerol concentration at time of t (h). Different characterization techniques were deployed to characterize the catalyst with the optimal catalytic performance. X-ray diffractometer (XRD) analysis was conducted using Empyrean PAN B.V. (50 kV) following by the conditions that reported from literature reports [10]. The morphological observation of catalyst samples was performed using ZEISS Sigma300 VP (UK), while scanning electron microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDX) analyses were conducted, for morphological imaging and elementary mapping [11]. Once gypsum was obtained, it was further calcined at different temperature (from 100 to 900 ºC) with different durations (1 to 5 hours) to enhance its catalytic performance. After calcination, the gypsum was treated with H_2O_2 with different ratios (1 to 3). The experimental plans were carried out using Box-Behnken Design (BBD) shown in Table 1 and the corresponding results were shown in Table 2.

Table 1. Box-Behken design (BBD) for glycerol conversion, where X_1 refers to calcination temperature/ºC, X_2 refers to roasting duration/h, and X_3 refers to H_2O_2 addition ratio/-

Variables	symbol	-β	-α	0	α	β
Calcination temperature/ºC	X_1	100	300	500	700	900
Calcination duration/h	X_2	1	2	3	4	5
H_2O_2 addition ratio/-	X_3	1	1.5	2	2.5	3

Table 2. Experimental results using Box-Behken design

Runs	Code values			Conversion/-
	X_1	X_2	X_3	
1	500	3	2	0.8622
2	500	5	1	0.8548
3	900	1	2	0.7660
4	100	3	1	0.8004
5	500	3	2	0.8622
6	100	1	2	0.8339
7	500	5	3	0.9808
8	900	3	3	0.9224
9	500	3	2	0.8622
10	500	1	3	0.9136
11	100	5	2	0.9371
12	900	5	2	0.8944
13	500	3	2	0.8622
14	900	3	1	0.7298
15	500	1	1	0.7163
16	500	3	2	0.8622
17	100	3	3	0.9598

The experimental results were analysed by analysis of variance (ANOVA), the response surface methodology (RSM) analysis was performed through software (Design Expert V.11 ® USA). Each experimental conditions were run for triplicates and experimental data were taken average. Table 2 was used to optimize the process to find out the optimal condition in GC production.

3. Results and discussion

There are various factors affecting the final performances of GC conversion. In this preliminary study, three major parameters namely calcination temperature, calcination duration and hydrogen peroxide addition ratio were selected to investigate their impacts (singular and binary) upon the response (GC conversion). The output in responding to three outputs using a quadratic second order expression is calculated using response surface methodology (RSM):

$$Y_{conversion} = 0.8622 - 0.0273X_1 + 0.0547X_2 + 0.0844X_3 + 0.0063X_1X_2 + 0.0083X_1X_3 - 0.0178X_2X_3 - 0.0088X_1^2 + 0.0045X_2^2 - 0.0003X_3^2 \tag{2}$$

And the corresponding ANOVA analysis of the investigated three process operational parameters are shown in Table 3.

Table 3. ANOVA with the Predicted r² of 0.9664 is in reasonable agreement with the adjusted R² of 0.9952

Source	DF	Sum of squares	Mean square	F-value	Prob>F
Model	9	0.0890	0.0099	369.44	< 0.0001
X_1	1	0.0060	0.0060	223.23	< 0.0001
X_2	1	0.0239	0.0239	892.98	< 0.0001
X_3	1	0.0570	0.0570	2130.22	< 0.0001
X_1X_2	1	0.0002	0.0002	5.96	0.0447
X_1X_3	1	0.0003	0.0003	10.30	0.0149
X_2X_3	1	0.0013	0.0013	47.49	0.0002
X_1^2	1	0.0003	0.0003	12.19	0.0101
X_2^2	1	0.0001	0.0001	3.17	0.1181
X_3^2	1	2E-07	2E-07	0.0106	0.9209
Residue	7	0.0002	0.0000		
Lack of fit	3	0.0002	0.0001	15.56	0.0002
Pure Error	4	0.0001	0.0000		
Cor total	16	0.0892			

Assuming the null hypothesis is to be true, the *p*-value and *F*-value are the probability value and statistic distribution of the null hypothesis in the statistical model [9, 10]. Among the investigated parameters (with higher *F*-value and lower *p*-value), the singular variable (X_1, X_2, X_3) and the interactive X_2X_3 are found to be significant in the catalytic conversion. This indicates that selected parameters in this work are statistical critical in determining GC conversion.
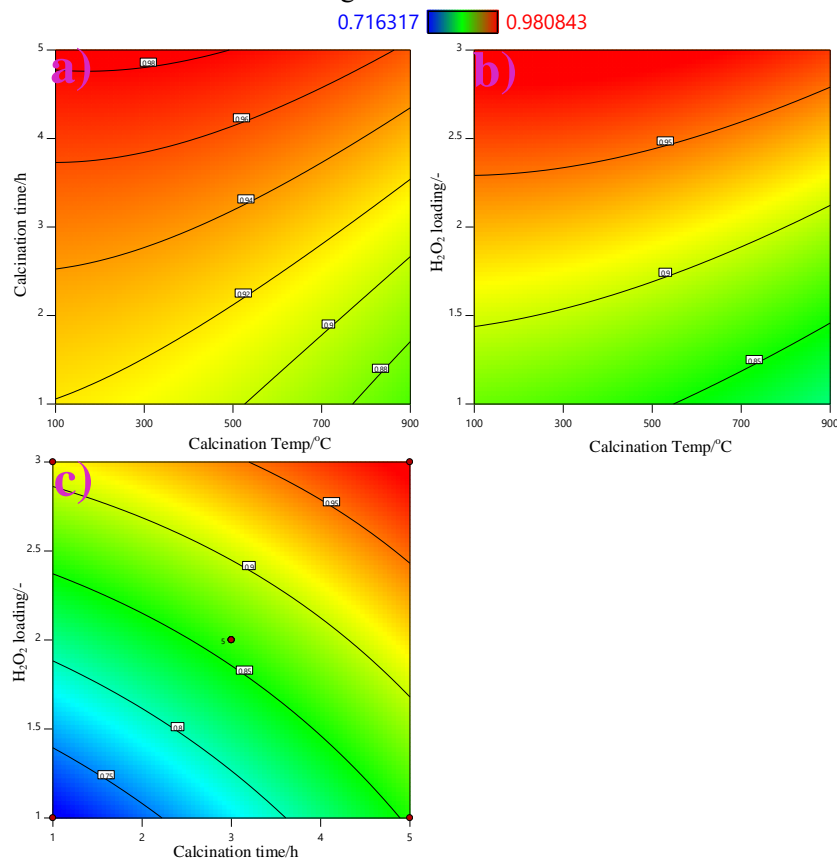

Figure 2. Contour plot of the combined variables to the response during catalytic synthesis, where a) is calcination temperature and calcination duration versus GC conversion, b) calcination temperature and H_2O_2 addition ratio versus GC conversion, c) calcination duration and H_2O_2 addition ratio versus GC conversion.

The contour plot of binary parameters is shown in Figure 2. The effects of calcination temperature and calcination duration versus GC conversion are shown in Figure 2a. Clearly, the GC conversion is found to be favorable at low calcination temperature and longer calcination duration. The effects of calcination temperature and hydrogen peroxide addition ratio versus GC conversion is shown in Figure 2b. It indicates the hydrogen peroxide needed to be high, for instance, the favorable range of hydrogen peroxide ratio should be over 2. The effects of hydrogen peroxide addition ratio and calcination duration versus GC conversion is shown in Figure 2c. Apparently, the relative higher GC conversion is found at the region with high hydrogen peroxide addition ratio and calcination duration. The advantage of RSM is that it offers a visual tool to investigate the binary effects of the parameters towards the variations of response.
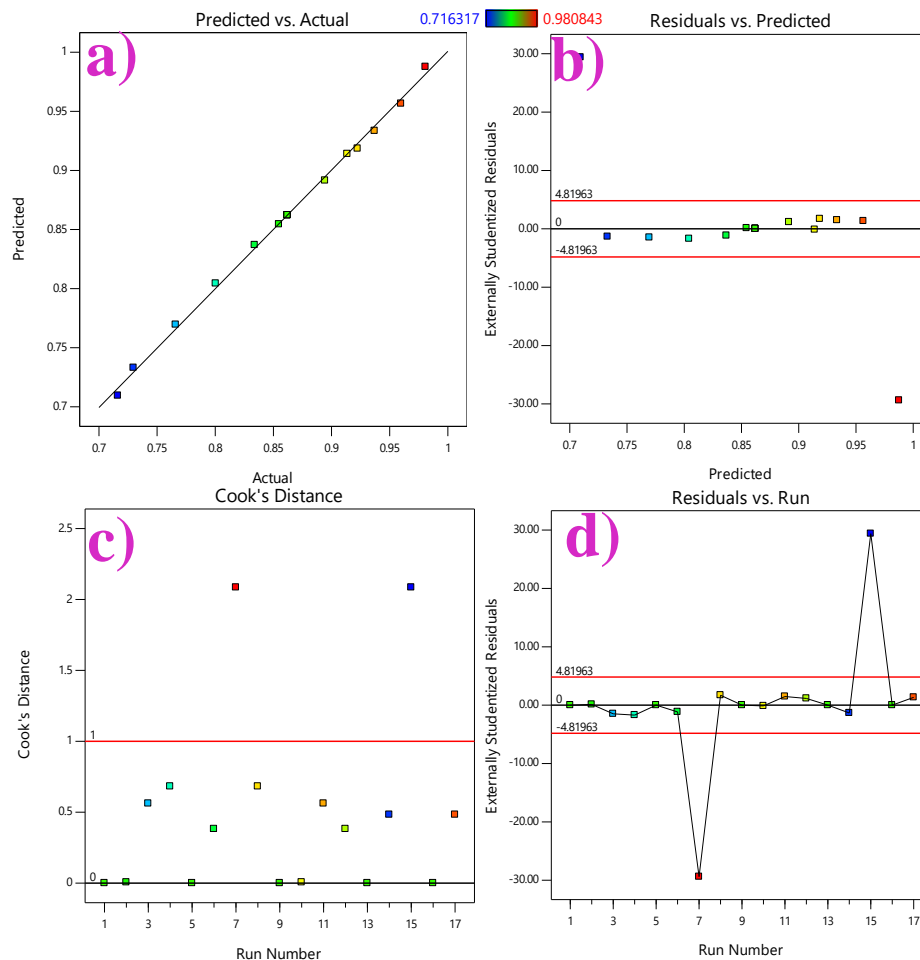
Figure 3. Statistical analysis of experimental data sets, where a) is parity plot, b) externally studentized residues analysis of residues versus predictions, c) Cook's distance analysis, d) studentized residues analysis of residues versus runs.

The statistical analysis of the three investigated parameters towards the variations of response is shown in Figure 3. The parity plot between actual experimental values and calculation values that were established from the RSM model is shown in Figure 3a. The good distribution of the data points along linear straight line indicates a well agreement between the experimental data and model predictions. The externally studendized residues analysis is shown in Figure 3b. All data points are well located within ±4.81963 range, except a one (GC conversion around 0.98) that is far out of that range reaching almost -30. It indicates that this relative higher GC conversion presents a relatively big experimental uncertainties in BBD data matrix. The Cook's Distance were also investigated and results are shown in Figure 3c. With detailed expanding experimental runs and their corresponding Cook's Distance, it is identified that run 7 and 15 are two experimental works that are falling out of the range of normal unit Cook's Distance, which will lead to a relative bigger experimental uncertainties. The studentized residues analysis of residues versus runs are shown in Figure 3d. Large residues of discrepancy for run 7 and 15 are captured, which agrees well with Cook's Distance analysis. With this analysis, among all experimental runs in Table 2, only 2 out of 17 experimental runs leads to a relatively bigger experimental uncertainties, indicating the validity of the BBD. With the established RSM model, the optimal condition to produce GC with a relatively larger conversion is determined as the following: $X_1=110$, $X_2=4$, and $X_3=4$, respectively, with GC conversion at 0.98. Once the optimal condition is determined, a validation experiment is conducted using the obtained optimal conditions, the resultant conversion of GC is 0.955, indicating a -2.55% experimental errors.

4. Characterization of catalyst prepared at optimal conditions

The catalyst prepared at the optimal condition is further characterized. The SEM morphology of prepared catalyst is shown in Figure 4.
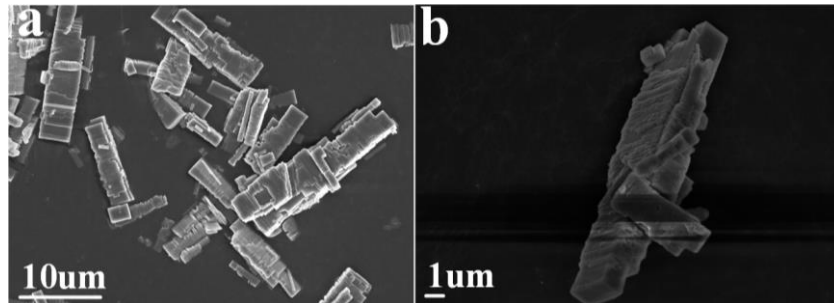

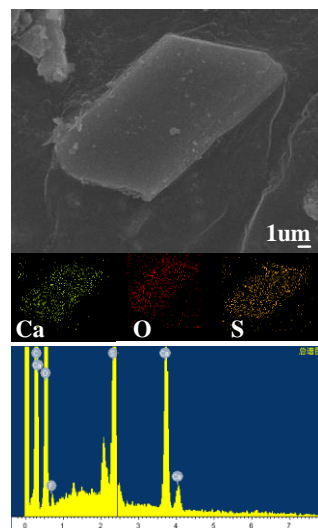**Figure 4.** SEM morphology of prepared catalyst at the optimal condition.

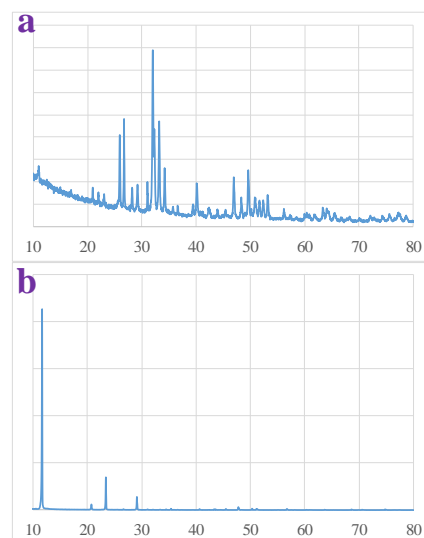**Figure 5.** EDX mapping of the catalyst prepared at the optimal conditions

Figure 6. XRD spectra a) Phosphorite, b) the catalyst prepared at the optimal conditions

The morphologies of the prepared catalyst presents the rhombohedral shape crystals with (1 μm in

width and 10 μm in length), which are typical to the process crystallization when rhombohedral crystal seeds are added at the beginning of the process [12]. The elementary mapping using SEM-EDX is shown in Figure 5. The elementary distributions suggest an even distribution of calcium, oxygen and sulphur element of the investigated sample. By comparing with energy spectra, the majority of sample is gypsum with the existence of trace amount of fluorite, which is accompanied contaminates during phosphorous acid production. The XRD spectra of the original phosphorite or phosphate rock and catalyst prepared the optimal condition is shown in Figure 6. Clearly, the original phosphate rock presents the complicated structures in crystallite matrix, which was reflected from many small broad scattering peaks in Figure 6a [13, 14]. The catalyst prepared the optimal condition presents the typical $CaSO_4.2H_2O$ with characteristic peaks at 020, 021 and 041 planes [15, 16]. By combining characterization information, it is clear that the GC synthesis is catalysed by crystal gypsum produced from phosphate rock. This prepared PG presents very similar peaks pattern to that of PDF-00-033-0311.

5. Conclusions

This paper proposed a new process of utilizing phosphate rock as precursor to prepare high performance catalyst for glycerol carbonate synthesis using glycerol and urea as reagents. Three main process parameters namely calcination temperature, calcination duration and hydrogen peroxide addition ratio were selected to investigate their impacts (both singular and binary) upon the response (GC conversion). The response surface methodology (RSM) results indicate that the investigated three parameters together with the combination of interactive X_2X_3 (calcination duration and hydrogen peroxide addition ratio) are found to be significant to the catalytic conversion. The characterization of the catalyst prepared at the optimal condition shows that the prepared catalyst is a crystallite high purity gypsum. The proposed process shows a promising prospect for high value conversion of the by-product generated from phosphate rock in phosphorous acid manufacturing industry. The produced glycerol carbonates open the opportunities of converting glycerol into other important chemical intermediates for energy chemical production.

Acknowledgements

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