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# Investigating the active phase of Ca-based glycerol polymerization catalysts: On the importance of calcium glycerolate

Negisa Ebadi Pour, Franck Dumeignil, Benjamin Katryniok, Laurent Delevoye, Bertrand Revel, Sébastien Paul\*

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## Abstract

Ca-based catalysts are of strong interest for glycerol polymerization reaction due to their high catalytic performances, their wide availability and the absence of any toxicity. In the present study, we investigated the active phase of CaO, Ca(OH)<sub>2</sub>, CaCO<sub>3</sub> and calcium diglyceroxide used as catalysts for this reaction. The solids were analyzed by XRD, solid-state <sup>13</sup>C-NMR and TGA-DSC. XRD evidenced the presence of calcium glycerolate in the spent catalysts when CaO, Ca(OH)<sub>2</sub> and calcium diglyceroxide were used as starting materials. This was corroborated by the TGA-DSC results. Further, the SS NMR results showed that the as-formed calcium glycerolate is a mixture of linear Ca(C<sub>3</sub>H<sub>7</sub>O<sub>3</sub>) and cyclic-branched Ca(C<sub>3</sub>H<sub>6</sub>O<sub>3</sub>). Moreover, the recycled catalyst issued, *e.g.*, from CaO was more efficient than the initial catalyst with a glycerol conversion of 47% (*vs.* 22% initially for CaO) and a 70% (*vs.* 55%) selectivity to polyglycerols higher than tetraglycerol at 245 °C after 4 h in the presence of 3.5 mol.% of catalyst. As the main outcome, we have shown that Ca-glycerolate is the actual *solid* active phase, which is formed *in situ* from CaO and Ca(OH)<sub>2</sub> playing the role of catalyst precursors. A mechanism involving the dissolution of CaO and Ca(OH)<sub>2</sub>, the formation of Ca-glycerolate and its precipitation followed by crystallization, supported by characterization studies, is proposed.

**Keywords:** Glycerol, Polyglycerol, Ca-glycerolate, Active phase, Mechanism.

## 1 Introduction

Polyglycerols (PGs) are water soluble highly functionalized compounds (*i.e.*, containing many hydroxyl groups), biocompatible and with a high thermal stability. These properties make them highly desirable for many applications in the food, cosmetics, plastic or biomedical sectors [1,2]. While polyglycerols are currently produced from biosourced epichlorohydrin, the change in customer demand - more particularly for cosmetics and food - require products derived from nontoxic and preferably natural ingredients. This strongly encourages the manufacturers to produce PGs directly from glycerol [3].

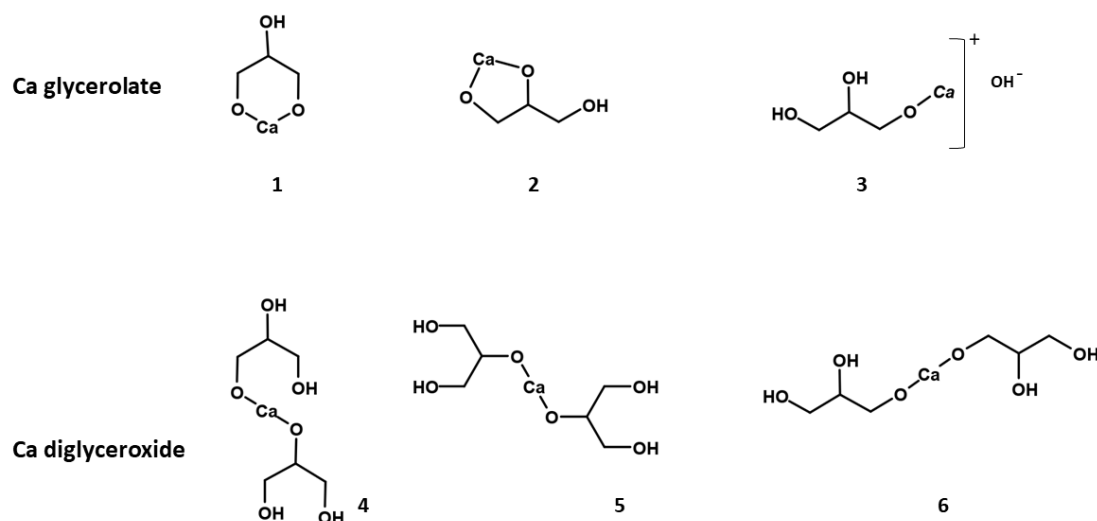
In the last two decades, attention was paid to glycerol polymerization over alkaline earth oxides-based catalysts such as CaO, BaO and SrO due to their higher catalytic activity [4–6] compared to other catalysts such as alkali-modified zeolites [7] or MgAl mixed oxides derived from layered double hydroxides [8,9]. For instance, CaO, SrO and BaO have shown a conversion of nearly 80% with 90%

selectivity to di- and triglycerol at 220 °C [4], while 96 % glycerol conversion with a 88% selectivity to acrolein was obtained with MgAl-CaAl layered double hydroxides as catalysts at 235 °C [10].

Among alkaline earth oxides catalysts, Ca-based catalysts such as bulk CaO, CaO supported on carbon nanofibers [11], dolomite (CaO-MgO mixed oxides) [12] exhibited a higher catalytic activity towards oligomers production. Such higher performances were explained by the possible *in situ* formation of Ca-glyceroxides [13–15] during the glycerol polymerization reaction but without any direct evidence.

Ca glyceroxides may present various structures. Potential structures of calcium monoglyceroxide, described by  $\text{Ca}(\text{C}_3\text{H}_6\text{O}_3)$  and  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)$  formulas, and calcium diglyceroxides (CaDG) with the formula  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2$ , are represented in Scheme 1. However, in the literature CaDG is referred generally as Ca glyceroxides (plural form) [16] or for sake of simplicity as Ca glyceroxide (singular form) [17–19]; calcium monoglyceroxide being similarly referred as Ca glycerolate [20].

Thus, to avoid any confusion, in the present work, we will use CaG for Ca glycerolate (*i.e.*, monoglyceroxide) and CaDG for Ca diglyceroxide.



Scheme 1. Potential structures of Ca glyceroxides, 1) cyclic CaG with  $\text{Ca}(\text{C}_3\text{H}_6\text{O}_3)$  formula; 2) cyclic-branched CaG with  $\text{Ca}(\text{C}_3\text{H}_6\text{O}_3)$  formula; 3) linear CaG with  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)$  formula; and Ca diglyceroxides with  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2$  formula, 4,5) branched CaDG and 6) linear CaDG.

Synthesis of Ca-glyceroxides was first reported using a CaO-glycerol system at temperatures from 10 to 150 °C by Grün and Bockish [21] and Fujii and Kondo [22]. Fujii and Kondo reported the formation of 4 types of crystalline glyceroxides depending on the temperature range, namely CaG ( $\text{CaC}_3\text{H}_6\text{O}_3$ ) (Scheme 1(1-3), further noted CaG(1), CaG(2) and CaG(3)); CaDG ( $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2$ ) (Scheme 1 (4-6) , further noted CaDG(4), CaDG(5) and CaDG(6)); tricalcium octa-glyceroxide ( $\text{Ca}_3(\text{C}_3\text{H}_7\text{O}_3)_6.(\text{C}_3\text{H}_8\text{O}_3)_2$ ) and calcium hexa-glyceroxide ( $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2.(\text{C}_3\text{H}_8\text{O}_3)_4$ ) using a mass ratio calcium oxide:glycerol of 3:100 at > 100 °C, 40-100 °C, 20-60 °C, < 20 °C, respectively. They reported that different Ca crystalline glyceroxides structures can be formed and interconverted depending on the temperature. For instance, calcium hexa-glyceroxide could be transformed into tricalcium octa-glyceroxide at 18-30 °C, tricalcium octa-glyceroxide to CaDG at 44 °C, while the decomposition of CaDG into CaG was observed in the 130-160 °C temperature range [22].

Similarly, Taylor *et al.* [20] synthesized CaG ( $\text{CaC}_3\text{H}_6\text{O}_3$ ) as a pharmaceutical product, by heating calcium hydroxide and glycerol above 180 °C in a microwave oven. The exact structure of the as-obtained CaG obtained was not discussed in this paper.

Later, Kouzu's group demonstrated that CaDG was formed *in situ* during the transesterification reaction to produce biodiesel starting from CaO as the catalyst precursor [23,24]. Although CaDG was reported to be an active catalyst itself for the synthesis of biodiesel by several groups, CaO showed slightly higher catalytic activity compared to that of *in situ* formed CaDG [24] or to that of CaDG synthesized prior to the reaction [18,25]. To the best of our knowledge, except its catalytic role clearly identified in the transesterification reaction, no study has been conducted so far to elucidate the formation of CaG during the glycerol polymerization reaction.

In the present work, we investigate the nature of the active phase in the glycerol polymerization reaction when the catalyst precursors were CaO,  $\text{Ca}(\text{OH})_2$ ,  $\text{CaCO}_3$  or CaDG. Besides, to explain the *in-situ* CaG formation, a mechanism based on a characterization study using X-ray diffraction (XRD), solid-state  $^{13}\text{C}$  NMR, thermal analysis and scanning electron microscopy is proposed. Furthermore, a mechanism for PGs formation is also proposed based on the mechanism of CaG formation.

## 2 Method and Materials

### 2.1 Materials

Calcium hydroxide was purchased from Alfa Aesar. Glycerol (99% purity), calcium nitrate tetrahydrate, calcium carbonate, and HPLC grade methanol (99.9% purity) and ethanol (99.5% purity) were purchased from Sigma-Aldrich. All the chemicals were used as such without any pre-treatment or purification.

### 2.2 Catalyst preparation

Calcined calcium oxide (CaO) was freshly prepared from calcium nitrate tetrahydrate ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ) treated under static air in a calcination oven from room temperature to 700 °C during 2 h with a ramp of 10 °C.min<sup>-1</sup>.

CaDG was prepared by a modified procedure previously described in the literature [17,26]. Namely, a mixture of methanol, glycerol and commercial CaO (molar ratio 38 : 4.2 : 1) was prepared and heated at 60 °C for 4 h. Then, the obtained yellowish precipitate was washed with methanol to remove unreacted glycerol before the remaining solvent was evaporated under vacuum at 90 °C. A yield of 91% to CaDG was obtained.

### 2.3 Catalytic test

Catalytic tests were performed with 218 mmol (20 g) of pure glycerol in a 100 mL Schlenk tube maintained at 245 °C and stirred at 800 rpm with a magnetic bar under N<sub>2</sub> atmosphere in the presence of 3.5 mol.% of catalyst (based on moles of glycerol) including  $\text{Ca}(\text{OH})_2$ ,  $\text{CaCO}_3$  and CaDG (loadings of catalysts in wt.% are given in Table 1). After 4 h of reaction, the catalyst was separated by centrifugation and washed with ethanol. The collected catalysts in pasty form were characterized by XRD, before drying at 80 °C in an oven for 4 h prior to further uses or analyses.

### 2.3.1 Glycerol and polyglycerol analyses

The glycerol analyses were carried out by high performance liquid phase chromatography (HPLC) using a Phenomenex column (organic acid H+) 300 x 7.8 mm and equipped with a refractive index detector, where the mobile phase was 5 mM H<sub>2</sub>SO<sub>4</sub> fed at 0.6 mL/min. The glycerol conversion was calculated by Equation (1):

$$\text{Glycerol conversion}(\%) = 100 * \frac{\text{initial mol of glycerol} - \text{mol of unreacted glycerol}}{\text{initial mol of glycerol}} \quad (1)$$

Polyglycerols analyses were conducted by direct infusion Electrospray Ionization Mass Spectrometry (ESI-MS) in a Waters ESI-MS/MS SYNAPT G2-Si HDMS (High Definition Mass Spectrometer) set in the positive ion mode. ESI source conditions were as follows: heated capillary temperature 300 °C, spray voltage 3 kV and capillary voltage of 60 V. By this technique, PG2 to PG6 were detected.

As a quantitative analysis would have required a pure PG standard for each product, whereas the available standards were mixtures of PGs, a relative PG selectivity has been chosen to evaluate and compare the catalysts performances.

Hence, as indicated in Equations (2) and (3) a relative polyglycerol selectivity was defined as being the ratio of the desired polyglycerol (PG<sub>x</sub>) peak intensity divided by the sum of the peaks intensities of all the PGs observed by direct ESI-MS:

$$\text{PG}_{2-3} \text{ selectivity} = 100 * \frac{\text{Sum of PG2 and PG3 peak intensities}}{\text{Total PGs peak intensities}} \quad (2)$$

Where PG2 and PG3 are di- and tri- glycerols respectively.

$$\text{PG}_{4+} \text{ selectivity} = 100 * \frac{\sum_{i=4}^6 \text{PG}_i \text{ peak intensities}}{\text{Total PGs peak intensities}} \quad (3)$$

Where PG<sub>4+</sub> represent the polyglycerols including tetra-, penta- and hexaglycerols.

## 2.4 Characterization of the catalysts

### 2.4.1 XRD

X-ray diffraction patterns of the catalysts were recorded on a D8 Discover X-Ray Diffractometer from Bruker using an X-Ray tube in Cu (K $\alpha$ ) radiation ( $\lambda = 1.54060 \text{ \AA}$ ). The diffraction angle  $2\theta$  was taken in the 10-60° range with steps of 0.01° per second.

### 2.4.2 Thermal Analyses

Thermo Gravimetric and Differential Scanning Calorimetry (TGA and DSC) were performed using a Setaram Labsys instrument. A continuous heating was applied from room temperature to 900 °C with a heating rate of 10 °C min<sup>-1</sup> under a flow of nitrogen of 30 mL/min.

### 2.4.3 Solid state-NMR

<sup>13</sup>C solid-state NMR spectra were recorded using a 400 MHz Bruker BioSpin spectrometer equipped with AVANCE-III consoles at a spinning rate of 10 kHz.

### 2.4.4 SEM

To study the morphology of the catalysts, scanning electron microscopy (SEM) pictures were recorded on a Hitachi S3600N electron microscope equipped with a Thermo Ultradry EDS detector using an acceleration voltage of 15 kV.

## 3 Results and discussion

### 3.1 Catalytic performances

The catalytic performances were evaluated in presence of 3.5 mol% of CaO, Ca(OH)<sub>2</sub>, CaCO<sub>3</sub> and of freshly prepared CaDG catalysts. The results are presented in Table 1. CaO, Ca(OH)<sub>2</sub> and CaDG all led to ~ 22 % glycerol conversion at 245 °C after 4 h of reaction with a selectivity to diglycerols (linear, branched and cyclic) of 12.5, 8 and 19 %, respectively; whereas the glycerol conversion was lower in the presence of CaCO<sub>3</sub> compared to other catalysts (10%) and the selectivity to PG2 was very high (83%). Higher polyglycerols (PG4+) including tetra-, penta- and hexaglycerol were obtained in the presence of CaO, Ca(OH)<sub>2</sub> and CaDG.

Table 1. Catalytic performance of glycerol in the presence of 3.5 mol% of CaO, Ca(OH)<sub>2</sub>, CaCO<sub>3</sub> and CaDG.

<i>Catalyst</i>	<i>Catalyst amount (wt.%)</i>	<i>Glycerol conversion (%)</i>	<i>PG2 Selectivity (%)</i>	<i>PG3 Selectivity (%)</i>	<i>PG4+ Selectivity (%)</i>
<i>CaO</i>	2.13	22	12.5	32	55.4
<i>Ca(OH)<sub>2</sub></i>	2.8	22	8	37	55
<i>CaCO<sub>3</sub></i>	3.8	10	83	17	-
<i>CaDG</i>	8.4	23	19	43	38

The eye-catching similar catalytic activity observed for CaO, Ca(OH)<sub>2</sub> and CaDG suggests that the polymerization reaction was most probably catalyzed by the same *in-situ* formed active phase. Thus, to investigate the actual nature of this active phase, a characterization study was performed on all the used catalysts.

### 3.2 Performance of recycled catalysts

The catalytic performance of used catalysts obtained from CaO (CaG-O) was assessed by its reutilization in the reaction. The results revealed that, in the same reaction conditions, 47% of glycerol conversion and 70% of selectivity to PG4+ could be reached when recycled CaG-O was used as catalyst, while conversion and selectivity were only 22% and 55%, respectively, when starting initially from CaO (Figure 1). This increase can be explained by the dissolution of CaG in the new reaction medium where the reaction is then catalyzed homogenously. This dissolution of CaG in the 2<sup>nd</sup> run, which is not observed in the 1<sup>st</sup> test can be explained by the mechanism of CaG formation proposed in Section 3.4.

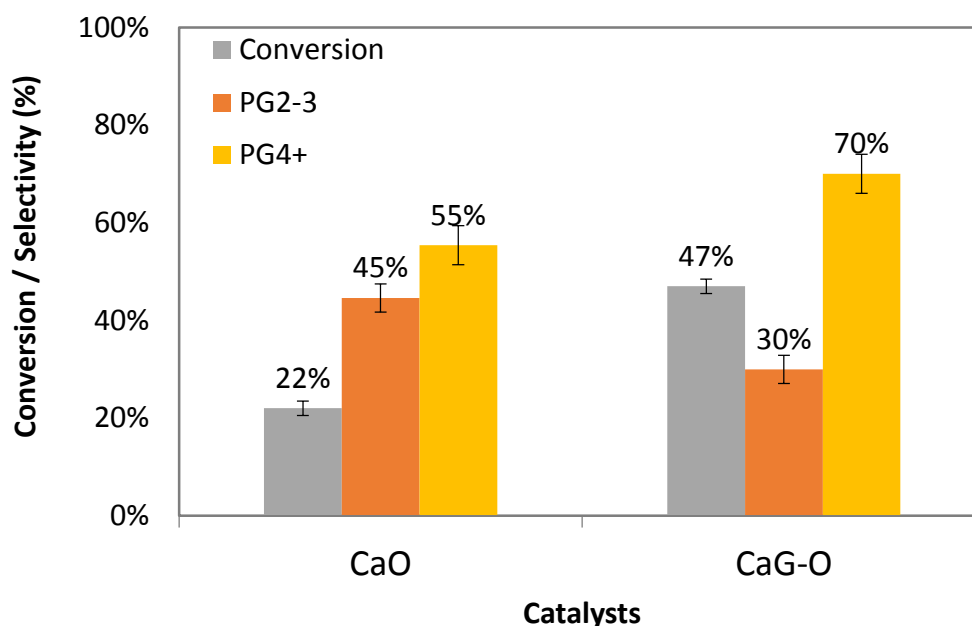


Figure 1. Catalytic performances of CaO and CaG-O in glycerol polymerization reaction

### 3.3 Catalyst characterization

#### 3.3.1 XRD

First, XRD analyses were carried out over the collected spent materials recovered after the reaction when CaO, Ca(OH)<sub>2</sub>, CaCO<sub>3</sub> and CaDG were used initially as catalysts. To verify the structural transformation of the active phase without affecting the latter, the collected catalysts were analyzed in the pasty form without any intermediate washing and drying steps.

The XRD diffractograms evidenced structural modifications of calcium oxide, calcium hydroxide and CaDG under test conditions. Figure 2(e-g) exhibits XRD patterns of the used catalysts. A sharp peak at  $2\theta = 10.4^\circ$  (200) (main peak) was observed for spent CaO, Ca(OH)<sub>2</sub> and CaDG after 4 h of reaction. This diffraction pattern was similar to those previously reported in the literature [20,22] for CaG with a cubic lattice (001) and also for other crystallized glycerolate metal complexes such as Zn (Zn(C<sub>3</sub>H<sub>6</sub>O<sub>3</sub>)) with a cubic lattice (100) [27]. Moreover, no peaks attributed either to CaO (Figure 1-c) with  $2\theta$  at 32.2, 37.4 and 53.9 (PDF- 99-0070) nor to Ca hydroxide (Figure 1-b) with  $2\theta$  at 18.14°, 28.7°, 34.2°, and 50.8° (PDF-00-087-0673) were observed for the used catalysts, suggesting that the latter was transformed quantitatively to CaG. On the other hand, the XRD pattern of the used catalyst CaCO<sub>3</sub> clearly showed that the latter remained in its initial calcite form (PDF-01-071-3699). Thus, these results show that the higher catalytic performances of CaO, Ca(OH)<sub>2</sub> and CaDG compared to that of CaCO<sub>3</sub> could be attributed to the *in-situ* formation of CaG as an active phase.

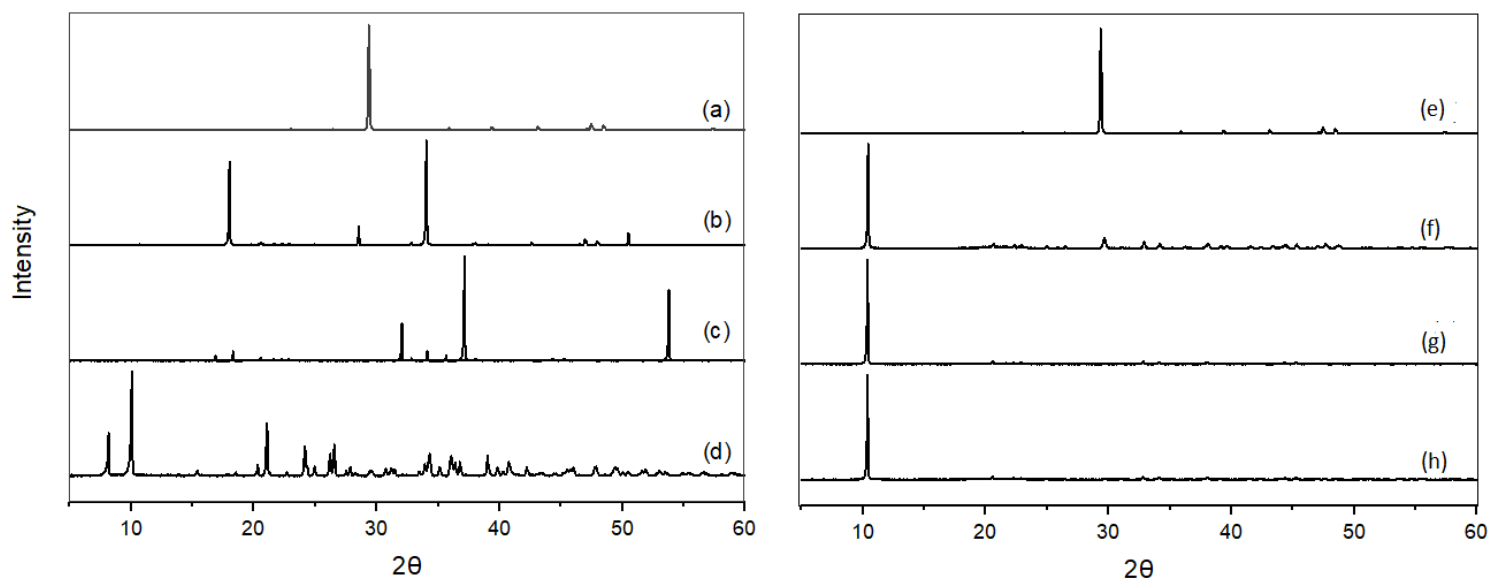


Figure 2. XRD patterns of a) fresh  $\text{CaCO}_3$ , b) fresh  $\text{Ca}(\text{OH})_2$ , c) fresh  $\text{CaO}$  and d) freshly prepared CaDG and spent catalyst issued from experiments in presence of e)  $\text{CaCO}_3$ , f)  $\text{Ca}(\text{OH})_2$ , g)  $\text{CaO}$  and h) CaDG.

The XRD patterns for the synthesized CaDG can be seen in Figure 2-d. It shows 2 main sharp peaks at  $2\theta$  of  $8.2^\circ$  and  $10.1^\circ$ , which is consistent with the theoretical diffractogram of CaDG (PDF-00-021-1544) and with the diffraction patterns previously reported in the literature [24,28,29].

XRD analysis was also carried out on the used sample issued from  $\text{CaO}$  after washing with ethanol and drying at  $80^\circ\text{C}$ . The diffractograms (not shown here) revealed only one peak at  $2\theta = 10.4^\circ$  corresponding to the CaG structure. This showed that – after all – the washing and drying steps did not affect the crystalline structure of CaG. Thus, other characterization techniques were performed on the washed and dried collected samples.

### 3.3.2 Thermal analyses

TGA was performed on the used samples to determine the thermal stability of the CaG obtained after reaction using initially  $\text{CaO}$  and  $\text{Ca}(\text{OH})_2$  as catalysts. The samples were labeled “CaG-O” and “CaG-H”, respectively.

The TGA curve for CaG-O showed multistep weight loss behavior with a first weight loss of 5 wt.% between  $130$  and  $343^\circ\text{C}$ , followed by 2 steps of mass loss of 14 wt.% and 3.5 wt.%, respectively, up to  $550^\circ\text{C}$ . According to the DSC curve, shown in Figure 3-a, each of these mass losses correspond to an exothermic peak, which could be attributed to phase transitions of the glyceroxides crystallites. A final weight loss of 34 wt.% was recorded between  $550$  and  $835^\circ\text{C}$ . The total weight loss of 56.5 wt.% for CaG-O is in good agreement with the theoretical value of 57 % for CaG, *i.e.* when it is totally decomposed to form  $\text{CaO}$  and one molecule of glycerol.

Similarly, the TGA for CaG-H curve (Figure 3-b) also showed a multistep weight loss with a first weight loss of about 5.8 wt.% between  $80$  and  $140^\circ\text{C}$  followed by 3 steps of mass losses up to  $525^\circ\text{C}$  (12 wt.%). Three main exothermic peaks in DSC curve between  $300$  and  $500^\circ\text{C}$  also correspond to these weight losses. A final weight loss of 39 wt.% was recorded between  $525$  and  $830^\circ\text{C}$ . The total



weight loss of 56.8 wt.% for the CaG-H is also very close to the theoretical value of 57% for total decomposition of CaG to form CaO and glycerol.

The TGA–DSC profiles of CaDG are shown in Figure 3-c. Four weight loss steps can be observed. The first step was observed between 100 and 260 °C with a mass loss of 31 wt.%. For this step, the DSC curve showed an endothermic peak, whereby the weight loss was attributed to the partial decomposition of CaDG to CaG where the theoretical weight loss for total decomposition is 41.5% (to form CaG and one molecule of glycerol). However, Fujii and Kondo [22] reported a decomposition of CaDG to CaG in the range of 130-160 °C and similarly León-Reina *et al.* [28] observed a peak corresponding to CaDG decomposition between 160 and 200 °C. This variation in decomposition temperatures, in the literature and our sample, can be attributed to the presence of different CaDG structures, linear and branched (Scheme 1), which can consequently affect the global thermal stability [30].

Further losses were observed in the 260-534 °C temperature range with a total loss of 21 wt.%. The final weight loss of 22.8 wt.%, which was recorded between 534 and 830 °C most likely corresponds to the formation of CaO. The total weight loss of 74.4% is very close to the theoretical one (74.8%) expected when CaDG is totally decomposed to CaO plus two molecules of glycerol.

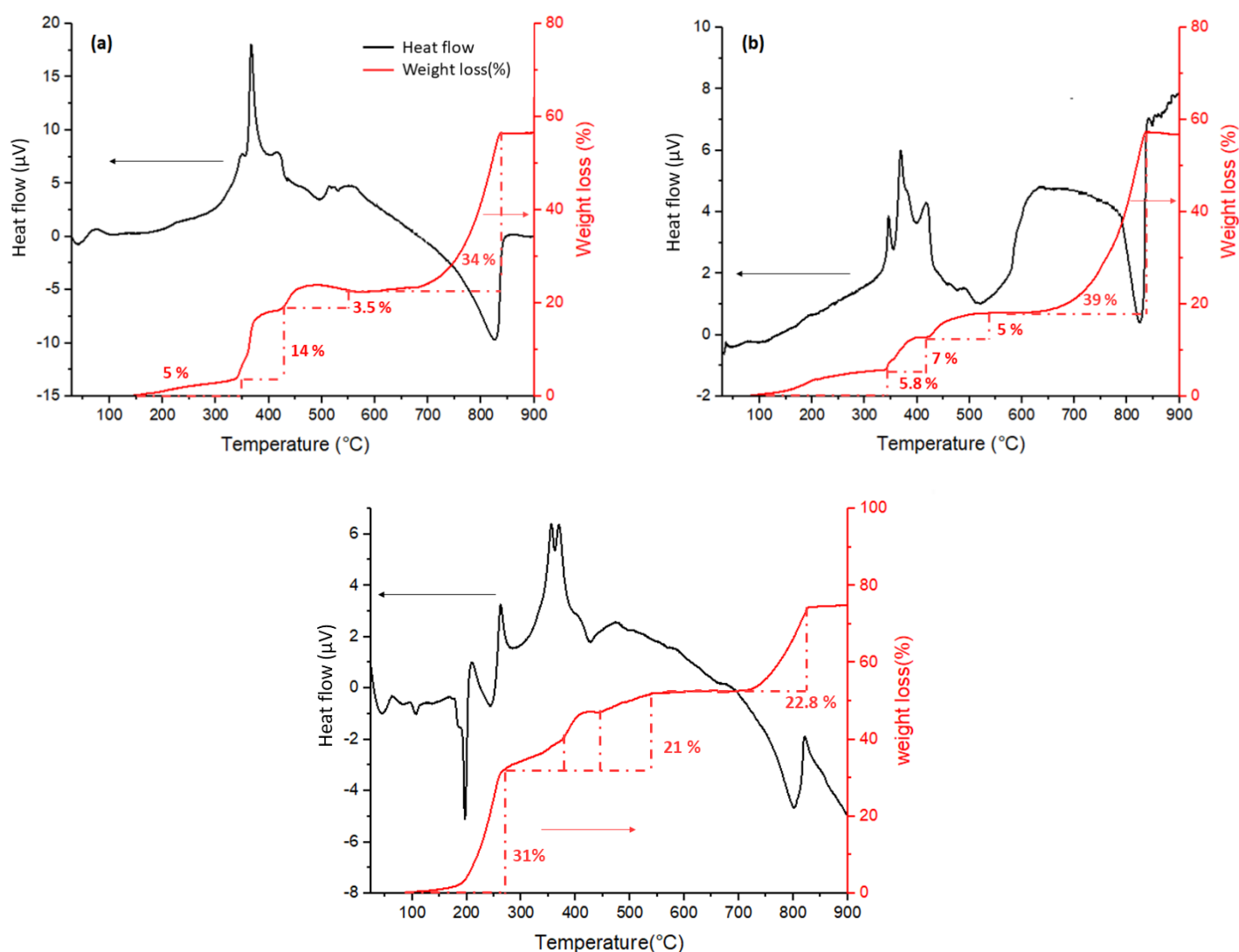


Figure 3. TGA-DSC profiles for a) CaG-O, b) CaG-H and c) CaDG

### 3.3.3 Solid state-NMR

The structures of CaG-O and CaG-H used samples were further studied by solid-state  $^{13}\text{C}$  NMR. For these compounds, three peaks were observed at 67.9 ppm, 70.2 ppm and 74.9 ppm (Figure 4 a-b).

Based on the various possible CaG structures (Scheme 1), for cyclic CaG(1) of formula  $\text{Ca}(\text{C}_3\text{H}_6\text{O}_3)$ , 2 peaks corresponding to  $-\text{CH}_2\text{OCa}$  (2 equivalent carbons) and  $-\text{CH}-\text{OH}$  are expected on the  $^{13}\text{C}$  NMR spectrum. For cyclic-branched form CaG(2), 3 peaks corresponding to  $-\text{CH}_2\text{OH}$ ,  $-\text{CH}_2-\text{OCa}$  and  $-\text{CH}-\text{OCa}$  are expected and for the linear CaG(3) of formula  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)$  also 3 peaks corresponding to the carbons in  $-\text{CH}_2\text{OH}$ ,  $-\text{CH}_2-\text{OCa}$  and  $-\text{CH}-\text{OH}$  are expected.

Thus, the three observed peaks in CaGs spectra at 67.9 ppm, 70.2 ppm and 74.9 ppm (Figure 4 a-b) could be assigned either to the  $-\text{CH}_2\text{OH}$ ,  $-\text{CH}_2-\text{OCa}$  and  $-\text{CH}-\text{OH}$  carbon chains of glycerolate, respectively, in linear form (CaG(3)); or to the  $-\text{CH}_2\text{OH}$ ,  $-\text{CH}_2-\text{OCa}$  and  $-\text{CH}-\text{OCa}$  carbon chains in CaG(2). Besides, from these spectra one can concluded that the CaGs are not in a fully cyclic conformation CaG(1) on Scheme 1.

It also should be noted that  $^{13}\text{C}$  CPMAS SS NMR is not a quantitative technique, thus, it is difficult to conclude if the CaGs are in a unique structure or a mixture of CaG(2) and CaG(3).

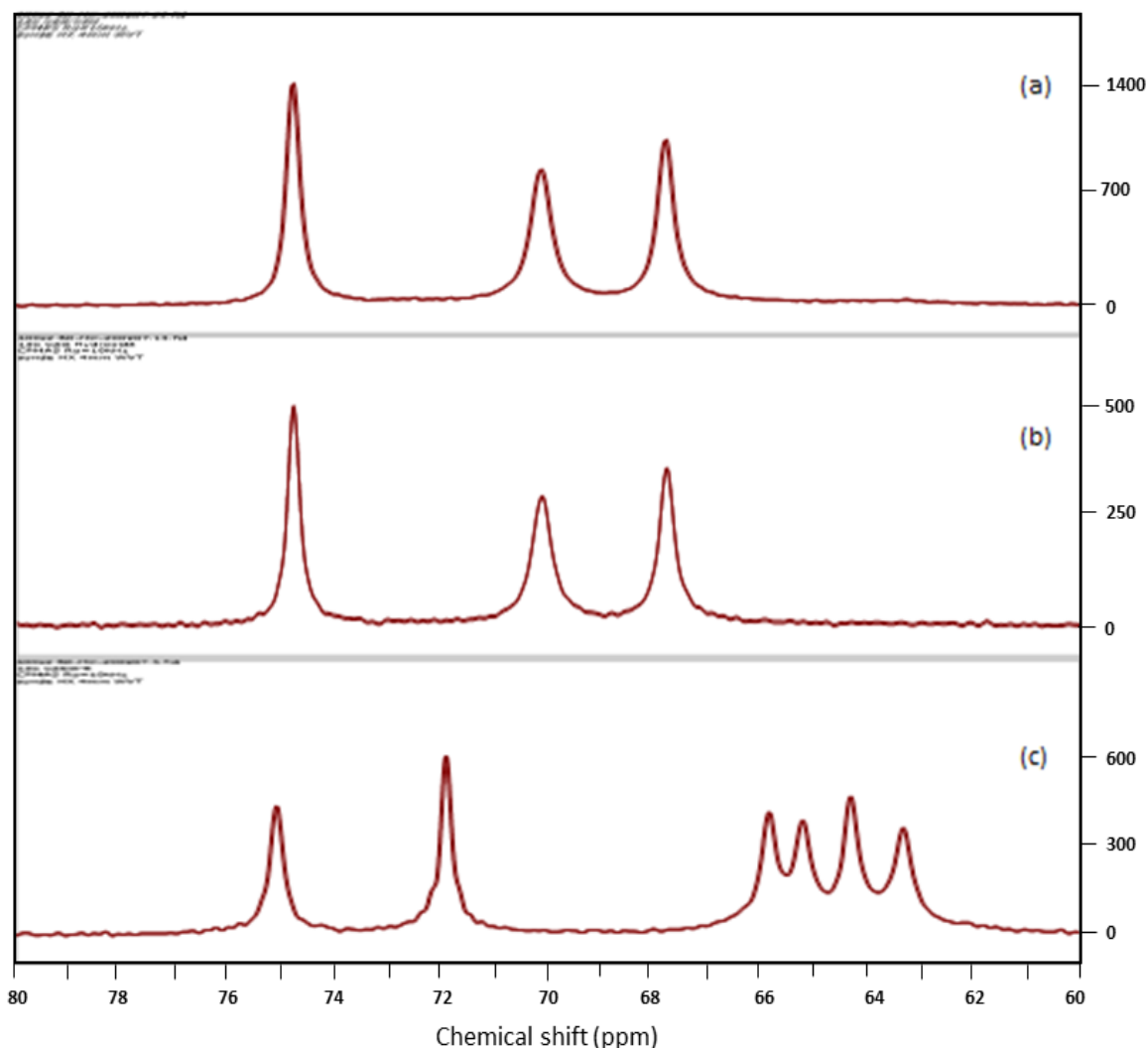


Figure 4.  $^{13}\text{C}$  SS-NMR spectra of a) CaG-O, b) CaG-H and c) CaDG.

Furthermore, for CaDG six peaks at 63.3 ppm, 64.3 ppm, 65.2 ppm, 65.8 ppm, 71.9 ppm and 75.1 ppm were observed in the  $^{13}\text{C}$  NMR spectrum (Figure 4-c). These peaks can be attributed to the carbon chains of glycerol in the different CaDG structures (Scheme 1 (4-6)). However, 6, 2 and 3 peaks are expected to be observed for CaDG(4), CaDG(5) and CaDG(6), respectively. Thus, once again due to the fact that  $^{13}\text{C}$  CPMAS SS NMR is not a quantitative technique, it cannot be concluded if CaDG is pure CaDG(4) or a mixture of CaDGs. Nevertheless, similar spectra for CaDG were previously reported by Kouzou *et al.* [17]. It could thus be concluded that CaDG is not present in the *in-situ* formed CaG.

### 3.3.4 SEM

The morphologies of the used catalysts CaG-O, CaDG and CaO were analysed by SEM (Figure 5). Fig.5a shows that CaG-O presents large “potato-shaped” particles with irregularities on the surface (Fig. 5a-left). For CaDG (Figure 5b), large particles with an angular rock shape were observed. This is in good agreement with what was previously reported in the literature for CaDG [19,24]. From Fig.4c, it can be seen that calcium oxide is in the form of large agglomerates with outgrowths.

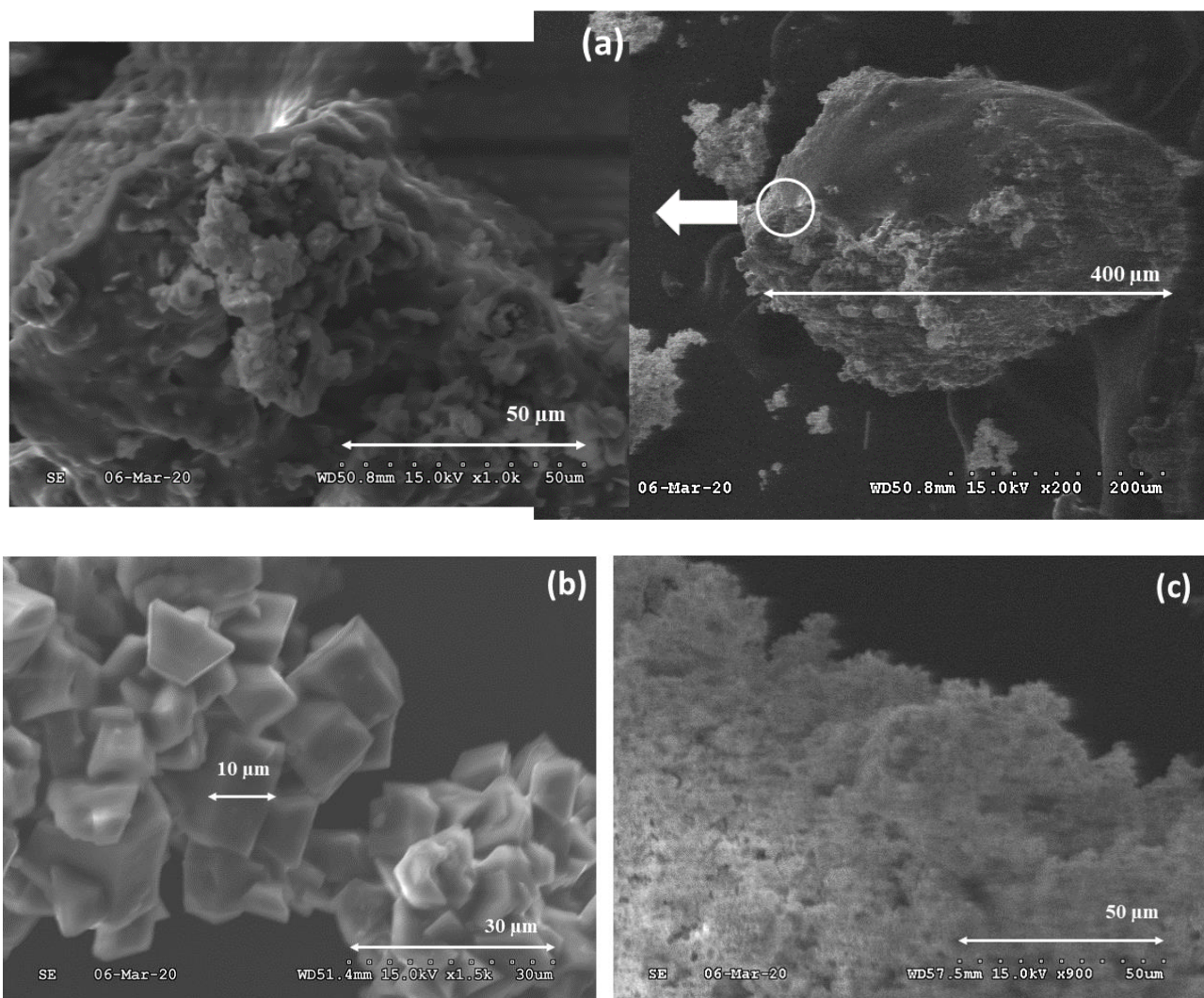


Figure 5. SEM analysis of: a) CaG-O, b) CaDG and c) CaO samples

### 3.3.5 Main conclusions on the characterization study

From the XRD results, it can be concluded that CaO and  $\text{Ca}(\text{OH})_2$  are transformed to calcium glycerolate during glycerol polymerization reaction. These catalysts also showed a similar thermal behavior with a total weight loss of 56.5 and 56.8 wt.% respectively for CaG-O and CaG-H, which agrees with the theoretical value of 57% when CaG is totally decomposed to form CaO. These results strongly suggest that CaG-O and CaG-H only contain CaGs, *i.e.*, do not contain any CaDG. However, the phase transitions observed between 350 °C and 550 °C for CaG-O and CaG-H suggest that various structures of CaGs are probably present. Solid state  $^{13}\text{C}$  NMR results were also consistent with XRD and TGA-DSC analyses, confirming that CaG-O and CaG-H contain no CaDG or other Ca glyceroxides suggesting that these samples are mixtures of the CaG(2) and CaG(3) species.

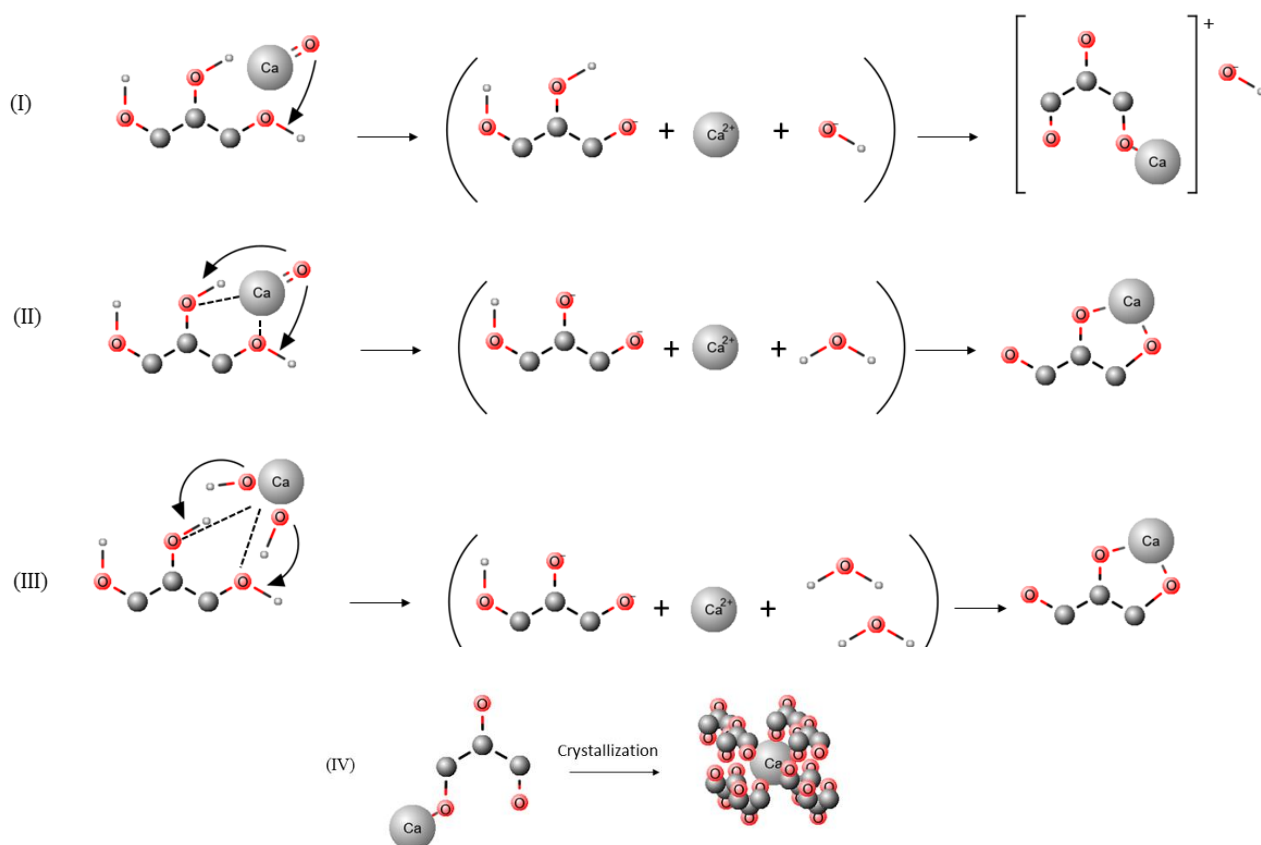
Thus, based on the characterization studies a mechanism is hereafter proposed to explain the *in-situ* CaGs formation.

### 3.4 Mechanism of CaGs formation

In order to explain the *in situ* formation of CaGs, a mechanism based on dissolution-precipitation-crystallization for CaGs formation starting either from CaO and Ca(OH)<sub>2</sub> is proposed (Scheme 2). Note that CaG can also be formed from thermal decomposition of CaDG (Figure 2-c). A similar mechanism was previously suggested [31] for the formation of CaDG from a mixture of glycerol and Ca(OH)<sub>2</sub> at 70 °C under transesterification reaction conditions.

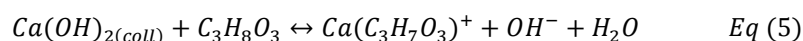
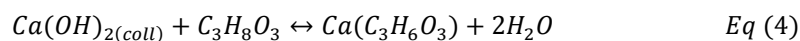
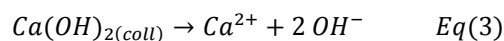
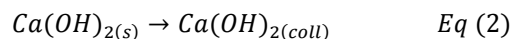
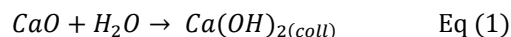
Following this mechanism CaG is formed from CaO (or Ca(OH)<sub>2</sub>) by a dissolution of the precursor; its conversion in the liquid phase is followed by a precipitation step, which allows CaG to eventually crystallize.

For the dissolution of CaO (Scheme 2 – I and II) and Ca(OH)<sub>2</sub> (Scheme 2 – III), the Ca cation interacts with the oxygen lone pair from the terminal -OH group in glycerol. In the following, the hydroxyl group of calcium hydroxide (or of CaO) abstracts the proton of the as-activated -OH group of glycerol. Consequently, a glycerolate anion and a Ca<sup>2+</sup> cation are formed, which coordinate together with OH<sup>-</sup> in a Ca-glycerolate-OH<sup>-</sup> complex. When the medium is saturated, crystallization takes place, whereby Ca coordinates with more glycerolate anions (Scheme 2- IV). Besides, , as reported previously [4], colloidal Ca(OH)<sub>2</sub> is formed due to the presence of the water concomitantly formed during the reaction.



Scheme 2. Proposed mechanism for CaG formation in the PGs synthesis reaction from glycerol.

However, when CaO and Ca(OH)<sub>2</sub> are converted to solid CaG, colloidal Ca(OH)<sub>2</sub>, Ca<sup>2+</sup> and hydroxide ions in the liquid phase (Eq. 1-3), an equilibrium takes place between CaG and colloidal Ca(OH)<sub>2</sub> (Eq(4)).



Hence, a simultaneous dissolution of CaG to Ca ion and intermediate glyceroxide species and its reformation takes place due to the presence of colloidal Ca(OH)<sub>2</sub>, as previously described.

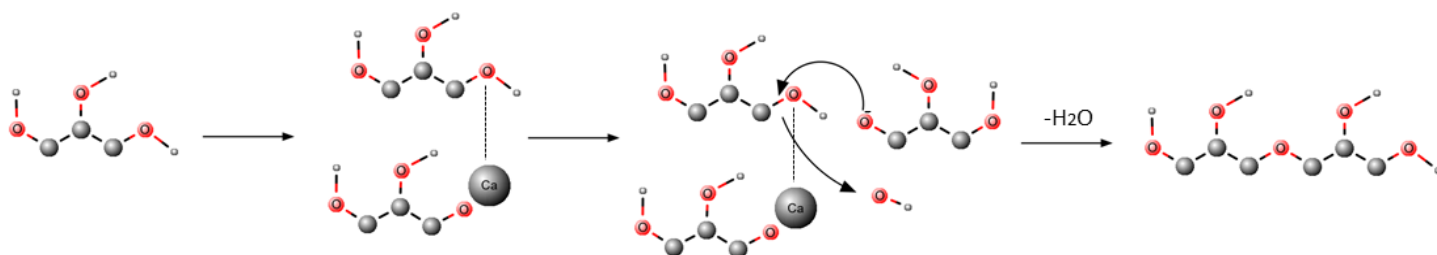
It is clear that after recovering the CaG from the first reaction medium, when CaO was the precursor, and during the washing step, the colloidal forms of Ca(OH)<sub>2</sub> were washed out. Thus, CaG in the fresh medium (glycerol) began to solubilize while it could not reform *in situ* due to the absence of protonated oxygen. This mechanism also confirms that CaG can only be formed from CaO and Ca(OH)<sub>2</sub> because of the presence of protonated oxygen in these compounds, and thus cannot form from CaCO<sub>3</sub>.

### 3.5 Polyglycerol formation mechanism

By understanding the CaG formation mechanism, the polyglycerol formation mechanism can also be explained. Based on our recent review [3], PGs could form in both homogeneously and heterogeneously catalyzed reactions even when the catalyst precursor is initially solid due to its partial solubility under the reaction conditions. As aforementioned in the CaG formation mechanism, Ca and hydroxyl ions are simultaneously present in the reaction media. Thus, at this stage the homogenous reaction can take place as described previously in the literature [1,32]. On the other hand, the heterogeneously catalyzed reaction could also take place by CaG which is formed *in situ*. The mechanism of polymerization of glycerol by CaG is presented in Scheme 3.

In this proposed mechanism, CaG activates the carbon–oxygen bond of the terminal hydroxyl group of glycerol. By decreasing its electron density through the coordination with Ca, the glycerol can undergo a nucleophilic attack by a glycerolate anion thus removing the hydroxyl group.

It should be noted that we chose here to represent linear CaG structure to simplify the mechanism.



Scheme 3. Proposed mechanism for diglycerol formation.

## 4 Conclusion

In the present paper, the nature of the active phase in glycerol polymerization reaction was investigated by characterizing the spent catalysts issued from CaO, Ca(OH)<sub>2</sub> and CaDG used as catalyst precursors. The XRD diffractograms revealed a good agreement with the glycerolate (CaG) patterns reported in the literature. Besides, while the obtained calcium glycerolate, CaG-O and CaG-H, respectively issued from CaO and Ca(OH)<sub>2</sub> showed a similar thermal behavior, namely a total weight loss close to 57 wt.%, which is in very good agreement with the theoretical value for CaG decomposition, the phase transitions observed between 350 °C and 550 °C suggested that Ca glycerolates are simultaneously present under different structures. Furthermore, the SS 13 C NMR results confirmed the XRD and thermal analyses and proved that CaG samples most probably consist in mixtures of cyclic-branched CaG(2) and linear CaG(3) and do contain any cyclic CaG or CaDG. We also showed that the similarity between catalytic performances of CaO, Ca(OH)<sub>2</sub> and CaDG is due to the *in situ* formation of CaG actually acting as the catalyst. Furthermore, 47% of glycerol conversion was obtained on CaG, vs. 22% on CaO used as the catalyst precursor. This increase in catalytic performances can be explained by a mechanism of CaG *in situ* formation, which comprises the simultaneous dissolution of the catalyst precursors and the precipitation of CaG after recombination of the intermediate with glycerol. A mechanism of glycerol polymerization reaction itself could be subsequently proposed, in which the *in situ* formed CaG and the glyceroxide ion participate in the formation of diglycerol.

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**Declaration of interests**

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: