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ORIGINAL PAPER

Glycerol Oligomerization Using Low Cost Dolomite Catalyst

Fernando José S. Barros[1] · Juan A. Cecilia[2] · Ramón Moreno-Tost[2] · Matheus F. de Oliveira[1] · Enrique Rodríguez-Castellón[2] · Francisco Murilo T. Luna[1] · Rodrigo S. Vieira[1]

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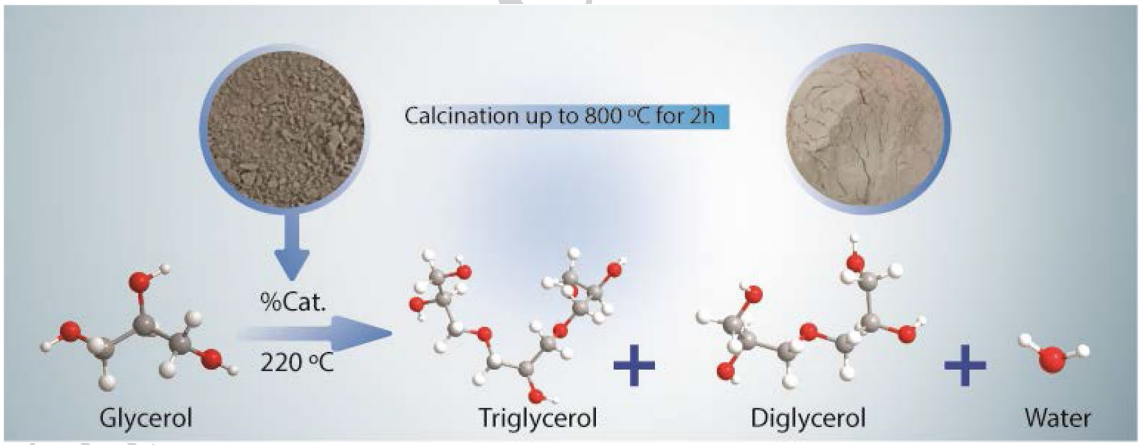
Abstract

Production of glycerol oligomers by heterogeneous catalysis is being studied as an option for valorization of this biodiesel by-product. In this study, the catalytic activity of dolomite and the effects of parameters such as catalyst loading, reaction temperature, and reaction time were evaluated. Reusability and stability test were also performed. The material was tested as-received and after a thermal treatment, being characterized by XRD, FTIR, N_2 adsorption–desorption, SEM, CO_2-TPD and TG/DTG. Reaction products were analyzed by GC-FID for oligomers composition and ICP to verify metallic species leaching. The thermal treatment led to a decrease of the particle size, increase of the specific surface area and improved basicity. Calcined dolomite showed better catalytic performance than natural dolomite, leading to almost 80% glycerol conversion and selectivities for diglycerol and triglycerol of 51% and 3%, respectively. Kinetic test revealed that the reaction is slow along the first hours and later the reaction rate increases. Ca and Mg are leached to the reaction medium but the catalyst could be reused up to 2 cycles, with similar diglycerol yield. The reaction conditions for this material are less severe than those reported previously, which added to the low cost and reusability capacity turns suitable for glycerol oligomerization process.

Graphical Abstract



Keywords Glycerol · Etherification · Dolomite · Diglycerol · Triglycerol

Statement of Novelty

To the best of our knowledge, a profound study including the characterization and evaluation of dolomite as catalyst for valorization of glycerol, a by-product of biodiesel industry, in oligoglycerols has not been addressed yet. The change from a homogeneous industrial catalytic process to

✉ Rodrigo S. Vieira
rodrigo@gpsa.ufc.br

Extended author information available on the last page of the article

a heterogeneous one will turn it into more sustainable one. Moreover, the abundancy, worldwide distribution and the low cost of dolomites are important features to make it also economically viable. In this manuscript, the influence of both basicity and textural properties will be evaluated in the reaction. The thermally modified solid showed good activity and reusability, under reaction conditions lower than those reported for commercial catalysts, what are interesting features for the development of a new process.

Introduction

Several energy sources have been proposed to gradually replace the traditional fossil fuels. Among them, the use of biomass seems to be a sustainable source to obtain chemicals and fuel through catalytic processes. In the last decades, the synthesis of biodiesel from vegetable oils, like soybean oil, palm oil, etc., and short-chain alcohols has gained wide interest as alternative fuel [1].

The synthesis of biodiesel also forms glycerol as by-product. The increasing production of this fuel worldwide has led to a surplus of glycerol, causing a decrease in the price. In fact, glycerol was initially discarded or stored without specific purposed [2]. This compound is a colorless, viscous, and non-toxic liquid, which is frequently used in the food, cosmetics, soaps and toothpastes, sweetener and pharmaceutical industries [2–4]. The presence of three hydroxyl groups provides to its molecule a diverse reactivity to obtain a large amount of valuable compounds by diverse chemicals reactions. Therefore, one major challenge on this topic is to find a way to take advantage of glycerol potential, enhancing its market value through low-cost chemical routes [5].

Thus, the glycerol conversion into high-added value products by dehydration to obtain acrolein has been reported in the literature [6, 7], hydrogenolysis to obtain propanediols [8], oxidation [9, 10] as well as conversion to syngas [11] or the synthesis of fatty esters [12]. The glycerol etherification is another reaction to valorize this by-product obtained in the biodiesel industry. Previous authors have carried out the glycerol etherification with alkenes [13], with other alcohols [14] or even solventless [15–17].

Glycerol can react with itself to form short-chain oligomers (di- and triglycerol). The production of those compounds has motivated the scientific community due to its wide range of applications, such as in cosmetics, polymers, food additives, plastic coating industry, biomedical and drug administration systems [18]. One feature that has made increase the interest for these compounds is their potential to replace petrochemical-based glycol, used as coalescent in paints, solvents, and inks or in cleaning formulations, however, some of them are toxic such as short ethylene glycols [19]. On cosmetic applications, diglycerol is used to enhance fragrance, flavor impact and longevity in products such as toothpastes, mouthwashes and deodorant sticks [20]. Di- or triesters of glycerol oligomers can be synthesized via esterification with carboxylic acids or transesterification with carboxylic acid methyl esters [3]. Previous works have reported that lower amounts of diglycerol monooleate can achieve an antifogging effect in food packages [21].

The glycerol oligomerization reaction has been approached from homogenous catalysis point of view, using both acid and basic catalysts such as H_2SO_4 and $CsHCO_3$ [22, 23]. The use of heterogeneous catalysts has emerged as alternative to the traditional homogenous catalysts since the heterogeneous catalysts can be easier purified and reused. Several solid acid catalysts, such as cationic exchange resins and zeolites have shown activity in solventless glycerol etherification [20, 24, 25]. The use of heterogeneous base catalysts is also reported in this reaction. Thus, Ruppert et al. [26] evaluated the use of different alkaline-earth metal oxides (MgO, CaO, SrO and BaO) in the glycerol etherification, establishing that the glycerol conversion is closely related with the strength of the basic sites of the catalysts. In this sense, Barros et al. [17] used eggshell as natural and inexpensive source as catalytic precursor to obtain CaO with high activity in the glycerol etherification reaction. In the same way, Clacens et al. [27] using Cs^+ as active phase supported on silica MCM-41 to disperse the active phase, achieved a good activity and selectivity. In addition, these authors reported that an increase of the glycerol conversion also leads to a loss of the selectivity towards di- and triglycerols. Recently, layered double hydroxides (LDHs) have been used as catalytic precursors to obtain mixed-oxides catalysts ($MgO–Al_2O_3$, $CaO–Al_2O_3$ and $MgO–Fe_2O_3$), which display high specific surface area and high availability of active sites [15, 16, 28].

Considering that solid basic catalysts with high basicity have reached interesting yields to di- and triglycerols, dolomite could be considered a natural source with high potential to obtain solid basic catalysts after a thermal treatment. This double carbonate of calcium and magnesium ($CaCO_3{\cdot}MgCO_3$) is a recurring mineral in the nature, formed by dolomitization process from magnesium substitution on calcite, and has a theoretical content of 45.7% $MgCO_3$ and 54.3% of $CaCO_3$. Dolomite has found different applications, such as a refractory material, as well as a fluxing agent in metallurgical, glass and ceramic industry; and filling material in paper, rubber and plastic production. Large amounts of dolomite are also used in building industry and agriculture [29].

In addition, this material has been used as precursor in several catalytic processes such as the production of biodiesel from canola or sunflower oil with short-chain alcohols, achieving excellent conversion rates in all cases [30–32]. Dolomite was used as catalyst in the reaction

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between glycerol and dimethyl carbonated (DMC) to obtain glycerol carbonate, reaching a glycerol conversion of 97% and glycerol carbonate yield of 94% [33]. The material has also been tested as catalytic support in Ni/dolomite catalysts in the H_2 production from the pyrolysis gasification of waste tires, achieving a yield of 49.1% [34].

The aim of this research is the use of dolomite as catalytic precursor in the glycerol etherification without solvent. For this purpose, dolomite is thermally activated to obtain their respective metal oxides (CaO–MgO), considered as active phase in the etherification reaction. The present research evaluates the influence of catalyst loading, temperature and reaction time. In addition, the stability and reusability tests have been also performed with the catalyst with the highest yield under the best catalytic conditions.

Experimental Section

Catalysts Preparation

Dolomite was provided by a local industry (Itamil Itaoca), the as-received sample was labeled as ND (natural dolomite). The material was activated by calcination at 800 °C for 2 h in a muffle furnace (EDG equipment), being labeled as CD (calcined dolomite). The activation conditions were chosen considering previous research on calcium natural sources [31].

Catalyst Characterization

The chemical composition was measured with an X-ray fluorescence spectrometer Rigaku brand, model ZSX mini II, operating at a voltage of 40 kV and a current of 1.2 mA in the tube coupled to Pd.

The crystalline phases of natural and calcined dolomite were determined by X-ray diffraction (XRD) using an X'Pert Pro MPD diffractometer with Co Kα radiation ($\lambda = 1.788965$ Å) operating at a voltage of 40 kV and a current of 40 mA. To perform the analysis, sample powders were placed in the cavity of the support used as the sample holder. The diffractograms were obtained by sweeping in the range 10–70° at a scan rate of 0.5 min^{-1}.

Thermal decomposition of the catalysts was evaluated by thermogravimetric analysis/differential thermal analysis (TG/DTG), carried out on a STA 449 F3-JUPITER/NETZSCH analyzer operating under the following conditions: flow N_2 (50 mL min^{-1}); heating rate, 10 °C min^{-1}; temperature, from room temperature 40–1000 °C.

FTIR was used to follow the functional group transformation during the thermal process on dolomite (IR-PRESTIGE 21 SHIMADZU FTIR). Samples were analyzed in the range of 400–4000 cm^{-1}, with spectral resolution of 4.0 cm^{-1}. The textural analyses of catalysts were performed with Autosorb 1-MP equipment (Quantachrome Instruments). The nitrogen adsorption–desorption measurements were carried out at − 196 °C with a sample previously treated at 300 °C for 12 h with N_2. Pore diameter and pore volume were determined from the adsorption branch of the isotherms by the Barrett–Joyner–Hallenda (BJH) method. The surface area was determined according to the Brunauer–Emmett–Teller (BET) method (S_{BET}).

The surface morphology of precursor and catalyst was observed using a JEOL JXA-840A scanning electron microscope (20 kV) under a vacuum of 1.33×10^{-6} mbar (Jeol, Japan), both samples were initially covered with a thin layer of gold (10 nm) using a sputter coater (SCD 050; Baltec, Liechtenstein).

The basicity of the calcined dolomite was studied by temperature-programmed desorption of CO_2, where approximately 100 mg of sample was pretreated in helium flow (60 mL min^{-1}) at 800 °C for 30 min (10 °C min^{-1}). The reaction temperature was lowered to 100 °C and pure CO_2 stream (60 mL min^{-1}) was subsequently introduced into the reactor for 30 min. The reaction of CO_2-TPD was conducted between 100 and 800 °C helium flow (10 °C min^{-1} and 30 mL min^{-1}) and the amount of CO_2 evolved was analyzed using a quadrupole mass spectrometer (Balzer 02 GSB 200) equipped with a Faraday detector (0–200 U) that monitored the weight of CO_2 (44 U) during the experiment.

Reaction Procedure

Glycerol etherification was carried out in batch reactor (Parr model), using 100 g of glycerol under nitrogen flow. First, the reactor was loaded with glycerol and the temperature was raised up to the set point, then the catalyst was added under nitrogen flow and this time was considered as time zero. The reactions were carried out in a range of temperature between 200 and 245 °C, with catalyst loading of 0.5–2 wt% for 24 h.

Kinetic reaction was accomplished and monitored at the intervals of time of 1, 2, 3, 4, 5, 6 and 24 h, the test was started when the temperature of the reactor was stabilized. Sampling occurred through a tube inserted into the middle of the reaction medium and a valve allowed the withdrawal of aliquots during the reaction without opening the reactor.

For the first reusability study, the catalyst was separated from the mixture of reaction by decantation. Then, the recovered solid was used on the next test, carried out in the same reaction conditions. On the second set of tests, the catalyst was separated of the reaction medium by vacuum filtration on a porous plate after being diluted on deionized water, finally, the recovered solid was calcined at 800 °C for 2 h prior the new reaction cycle.

The reaction medium was analyzed by means of gas chromatography with a flame ionization detector GC-FID

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(Agilent) following the same methodology for products silylation with BSTFA as well analysis of reaction parameters reported on Barros et al. [17] in terms of glycerol conversion (X_{gly}), selectivities for diglycerol (S_{di}), triglycerol (S_{tri}), high oligomers and other products (S_{ho}) and oligomers yielding (Y_{di} and Y_{tri}).

The determination of Ca leaching in the reaction medium was carried out by ICP using an ICP-OES (Thermo Fisher Scientific—Model iCAP 6000) equipment. Reaction mixture and catalyst were separated by filtration; 1 mg of sample was diluted on 10 mL of ultrapure water and then filtrated through a syringe filter with a pore diameter of 0.45 µm. A calibration curve was prepared by using an aqueous multi-elemental standard solution of Ca and Mg.

Results and Discussion

Dolomite Characterization

The chemical composition of dolomite was determined by X-ray fluorescence (XRF) (Table 1). Taking into account that several elements such as carbon and oxygen, which are present in dolomite, cannot be determined by XRF, the data reveal that dolomite is mainly composed by calcium (81.28%) and magnesium (15.30%), with minor proportions of iron and silicon species. These data also show that the substitution of Ca^{2+} by Mg^{2+} species is relatively low. As it was expected, the thermal activation does not cause significant changes in the elemental composition of the material.

Figure 1 shows Thermo-XRD patterns of dolomite. The experiment started with natural dolomite (ND) at 30 °C. The material exhibited the characteristic peaks of tremolite, a member of the calcic amphibole group of silicate minerals with the chemical formula $Ca_2Mg_5Si_8O_{22}(OH)_2$. From 100 to 600 °C, the solid exhibited peaks at 2θ = 29.6 and 30.9°. Less intense peaks between 35–55° are consistent with dolomite (33.28, 35.37, 41°, 43.75, 44.86, 50.25, and 50.79°). At 700 °C, the peaks ascribed to $CaCO_3$ and MgO increased their intensity and also the shrinkage of dolomite peaks takes place, even after that, some dolomite phase still remains, in accordance with results observed by Engler et al. [35]. At 800 °C, the characteristic peaks ascribed to dolomite and calcite decrease in intensity and new crystalline phases arise which can be attributed to

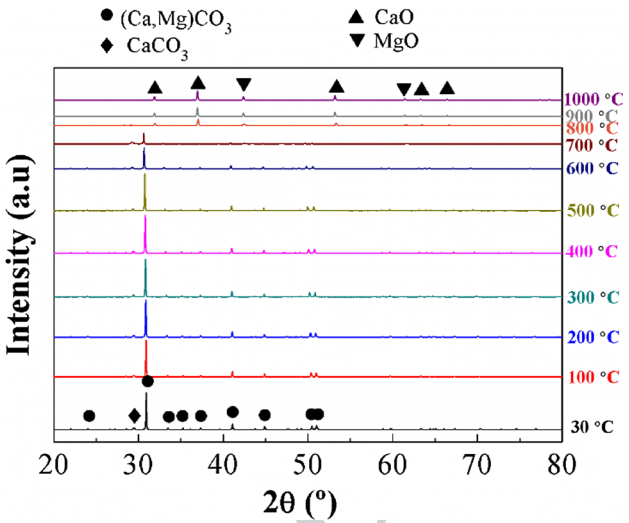

Fig. 1 Thermo-X-ray diffraction of natural dolomite

MgO (48.47°) and CaO (32 and 38°), in agreement with the findings reported by Shahraki et al. [29]. Moreover, reflection peaks ascribed to $CaCO_3$ (37 and 42.5°) can be still observed. Finally, at 900 °C, $CaCO_3$ is still detected and the crystallinity of both MgO and CaO phase is slightly increased [35].

The crystal size was determined using the Scherrer's equation from the main diffraction peak of each crystallographic phase. These data reveals that dolomite displays a crystal size of 297 nm, while calcite exhibits a crystal size of 153 nm. After the thermal treatment, it is obtained lime and periclase with a crystal size of 134 and 58 nm, respectively.

The thermal analysis of the natural dolomite is shown in Fig. 2. The TG curve of the raw dolomite hardly suffers mass loss below 650 °C, only 1.49%. From these temperatures the DTG curve shows an endothermic event between 650 and 840 °C, in which the sample displays a mass loss of 42.28 wt%, being attributed to the decomposition of the carbonate species. These data are in agreement with those obtained by thermo-XRD where the diffraction peaks attributed to carbonate species decrease from 600 °C. The obtained values in the decarbonation step are close to the theoretical value of the dolomite decomposition (47.7 wt%). The small differences could be attributed to the presence of impurities in the natural dolomite, as indicated the XRF data (Table 1).

Table 1 XRF data and textural parameters for ND and CD

XRF (wt%)					Textural properties		
Sample	Ca	Mg	Fe	Si	S_{BET} ($m^2\ g^{-1}$)	V_p ($cm^3\ g^{-1}$)	D_p (nm)
ND	81.28	15.30	1.27	1.51	1.57	0.01	16.16
CD	80.73	16.34	1.43	1.14	37.7	0.22	23.41

ND natural dolomite, *CD* calcined dolomite (800 °C, 2 h)

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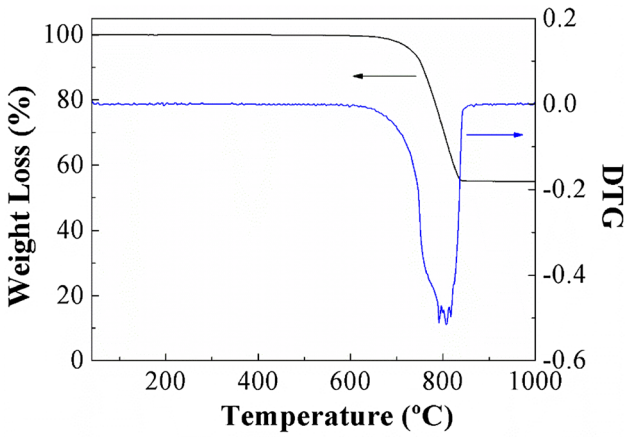

Fig. 2 TG-DTG profiles of natural dolomite

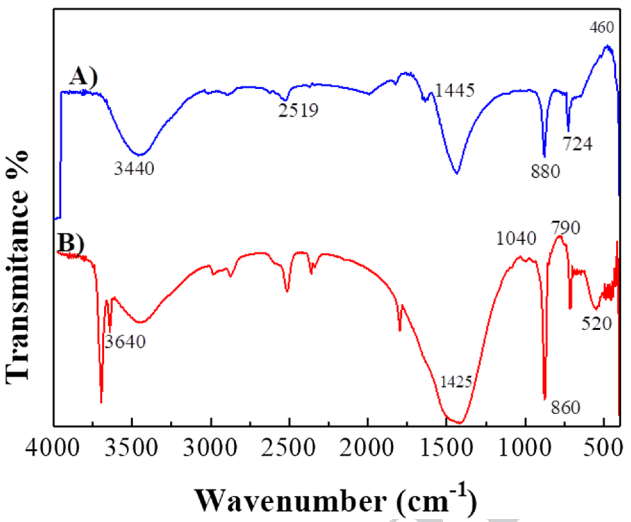

Fig. 3 Dolomite FTIR spectra **a** ND **b** CD (800 °C, 2 h)

The FTIR spectrum of natural dolomite (Fig. 3a) contains the main absorption bands of dolomite: 2519, 1445, 880 and 724 cm^{-1}. Sample shows intense bands relate to the presence of absorbed water at around 3440 cm^{-1}, since the material was not thermally treated and it was analyzed as received. A weak band due to quartz is also visible around 465 cm^{-1} [29, 36]. Weak bands due to silicate phase (1040, 790, 520 and 460 cm^{-1}) are also observed, which is according to data from X-ray fluorescence [29].

The CD sample shows new bands at 720, 860 and 420 cm^{-1} (Fig. 3b) and the bands due to dolomite phase are missing. These features point out the structural change from dolomite to calcite. It must be highlighted that the CD sample was not preserved from the atmosphere contact before FTIR analysis. The narrow band observed at around 3640 cm^{-1} and the bands at higher wavelengths indicate that after calcination at 800 °C the dolomite is transformed into CaO–MgO mixed oxides. The presence of bands at 3640 and 1425 cm^{-1} points out that the solid is hydroxylated, giving rise the formation of $Ca(OH)_2$ in accordance with the information obtained from XRD analysis. According to Granados et al., the solid is hydrated very fast during the first minutes of contacting with air [37]. The bands at around 1425, 1074 and 860 cm^{-1} can be assigned to carbonate species on the surface of the CaO, indicating that the material is readily carbonated after calcination and air exposition [37]. There is also the appearance of a peak at 450 cm^{-1} due to the formation of MgO [29, 30].

The textural properties of both ND and CD are summarized in Fig. 4 and Table 1. From N_2 adsorption–desorption isotherms, it can be deduced that both materials display low porosity. Considering the IUPAC classification, the isotherms of both ND and CD can be considered as type-II, which are typical of macroporous materials [38]. Both materials are solid structures without intrinsic porosity.

The specific surface values (S_{BET}), reported in Table 1, are only attributed to the N_2-filled of the interparticle voids. The thermal treatment causes an increase of the surface area and the pore volume. This data is in agreement with the XRD data where the decarbonation of the dolomite leads to structures with lower crystallinity, which generates higher proportion of interparticle voids and porosity in comparison to the starting dolomite. ND and CD pore size distribution plot shows meso and macropores, the thermally treated material presents a broader distribution, in accordance with previously reported results [39, 40].

The morphology of ND and CD was analyzed from their SEM images (Fig. 5). Figure 5a shows that ND displays a smooth and irregular surface with heterogeneous particle size. After the thermal process (Fig. 5b), the material exhibits a greater proportion of fine particles with roughness as a consequence of the exothermic process of the decarbonation, which can even form micropores by the CO_2 liberation [31].

The strength of the basic sites was evaluated by CO_2-TPD (Fig. 6) from the CaO–MgO catalytic system obtained after the thermal treatment. The graph shows the presence of two basic sites with different strengths. The peak between 100 and 200 °C with maximum desorption near to 140 °C, can be attributed to the interaction of CO_2 with weak basic sites associated with the oxygen in the Mg^{2+}–O^{2-} pairs [41]. The peak located between 400 and 700 °C with maximum at about 560 °C is related to sites with strong basicity and corresponds to basic sites ascribed to CaO. The high temperature required to the CO_2 desorption suggests the presence of strong basic sites after the thermal activation.

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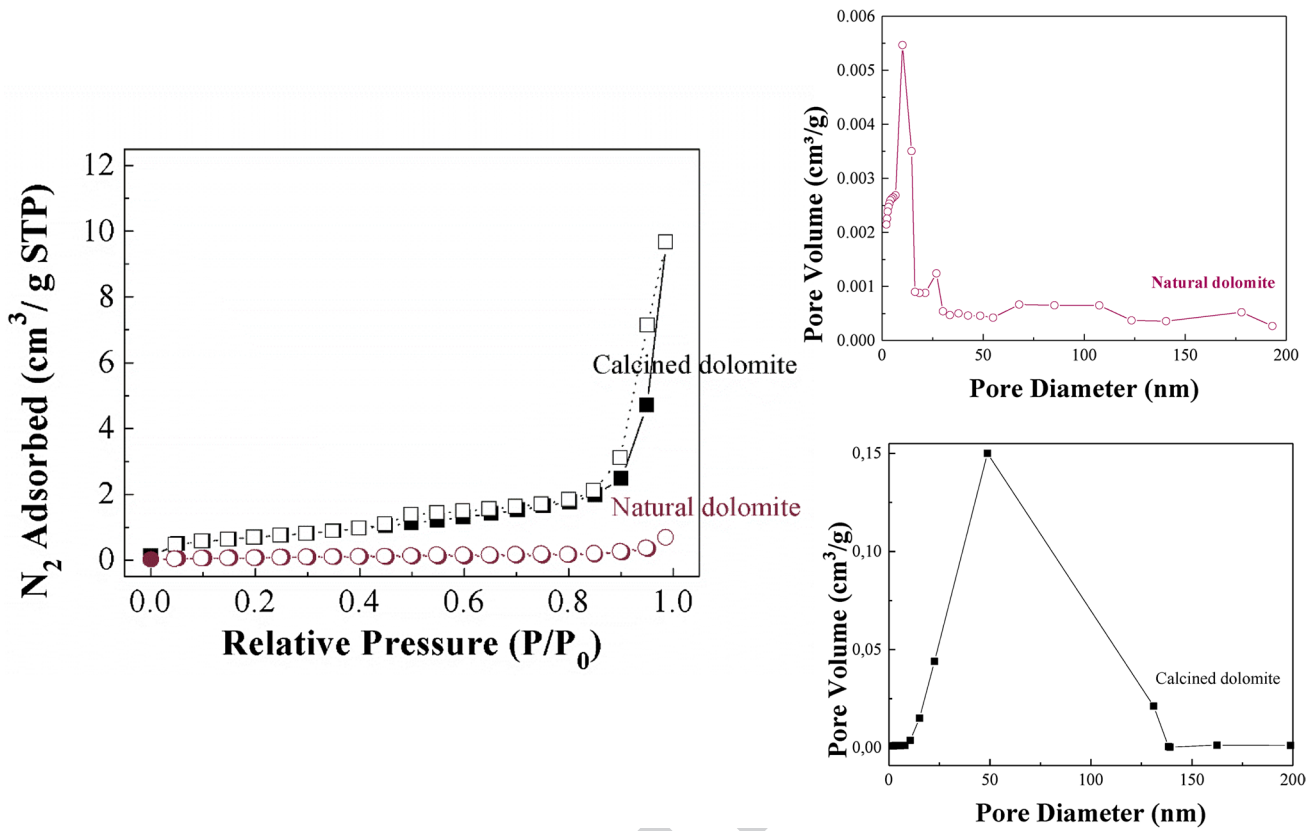

Fig. 4 Nitrogen adsorption/desorption isotherms and pore size distribution of ND and CD (800 °C, 2 h)

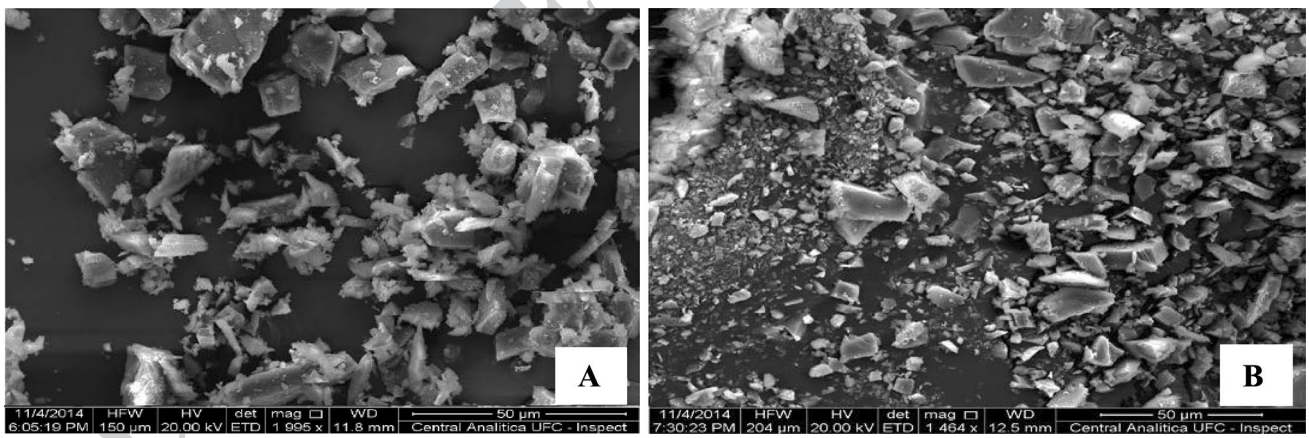

Fig. 5 SEM images **a** ND ×1995 **b** CD ×1464

Catalytic Results

Blank Test

In order to evaluate the promotional effect of dolomite (Fig. 7), it was performed an experiment without catalyst and compared with the catalytic performance of both ND or CD catalysts. The reaction was carried out at 245 °C and 6 h of time on stream and catalyst loading of 2 wt%.

It is observed that in absence of catalyst, glycerol conversion ($X_{gly} = 23\%$) is similar to that with ND (22%) and lower than the one with the presence of CD (37%). Both catalysts increased diglycerol selectivity, from $S_{di} = 29\%$ for the blank test to 52% on ND case and 55% for CD, leading the calcined

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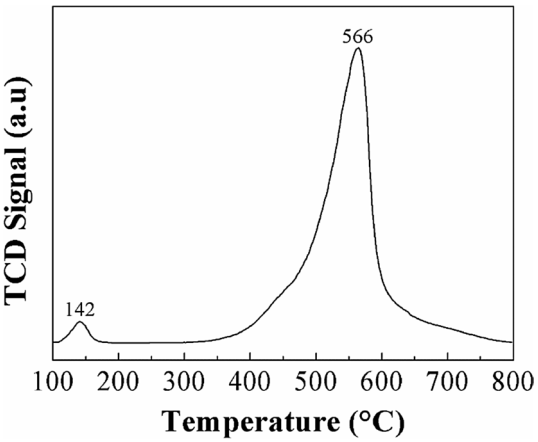

Fig. 6 CO_2-TPD of the calcined dolomite at 800 °C for 2 h

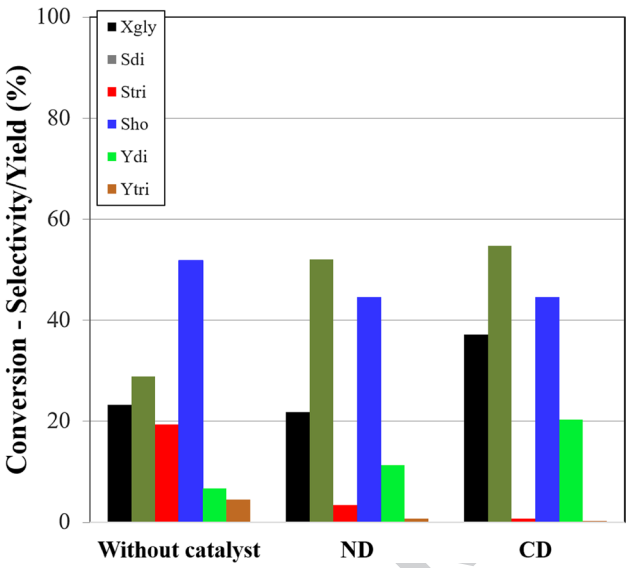

Fig. 7 Glycerol conversion (X_{Gly}), selectivities to diglycerol (S_{di}), triglycerol (S_{tri}), high oligomers and other products (S_{ho}), diglycerol yield (Y_{di}) and triglycerol yield (Y_{tri}) for tests without catalyst, with 2 wt% of natural dolomite and 2 wt% of calcined dolomite (reaction conditions: 245 °C, 6 h)

material to the highest Y_{di}, 20%. Regarding the dolomitic material, it was observed that the activation of the catalyst was effective in increasing the glycerol conversion as well as diglycerol yield, reaching higher values than those obtained without thermal treatment of the solid.

XRD and FTIR analysis have pointed to the presence of CaO–MgO mixed oxides as major constituents of calcined dolomite. However, XRD also confirmed that $CaCO_3$ remains after thermal treatment. Garti et al. [42] has compared several base catalysts on glycerol polymerization at lower reaction times (4 h), finding the following order of activity:

$$K_2CO_3 > Li_2CO_3 > Na_2CO_3 > KOH > NaOH > CH_3ONa > Ca(OH)_2 > LiOH > MgCO_3 > MgO > CaO > CaCO_3 = ZnO$$

In which $CaCO_3$ had lower activity than MgO and CaO, due to lack of solubility and basicity [42]. According to Salehpour et al. [43], for the calcium carbonate catalysis, the reaction can proceed by the same mechanism as the calcium hydroxide but it would start differently. The carbonate can deprotonate the primary hydroxyl of the glycerol. The bicarbonate ion generated from the first reaction would quickly decompose into carbon dioxide and hydroxide at elevated temperatures. Thus, the carbonate is not recovered and the reaction is actually catalyzed by calcium hydroxide.

The influence of this remaining $CaCO_3$ present on CD in the catalytic activity could be considered negligible, due to solubility.

The higher catalytic conversion in the etherification reaction of the calcined material is associated with the thermal treatment of dolomite. Due to the structure of dolomite, the basic properties are originated from the calcination, probably ND shows negligible basic sites. This process provokes the increasing of textural properties (specially $S_{BET,}$ which is 30 times higher than ND) removes carbonate species and also acts forming alkaline-earth mixed oxides (CaO–MgO), which are the active phases. In this sense, Ruppert et al. have pointed out that the glycerol conversion increases with the amount of basic sites as well as the strength of Lewis acid centers, which facilitate the removal of hydroxyl groups by the presence of O^{2-}–M^{n+} acid-base pairs, as was indicated for CaO-based catalysts [26]. TPD-CO_2 data, reported in Fig. 6, showed that CaO–MgO system displays strong basic sites that are the active sites in the etherification reaction, which are in agreement with that reported in the literature [17, 26, 27, 44, 45]. Previously, Ruppert et al. [26] have proposed a mechanism in the glycerol etherification where Lewis acid sites (metal oxide coordinates unsaturated metal cations) and Lewis basic sites (oxygen anions) are involved (Scheme 1). These authors established that a basic site attacks a hydroxyl group of a glycerol molecule, extracting a proton. On the other hand, an unsaturated metal site located on the surface of the alkaline earth oxide is able to activate a hydroxyl group of another glycerol molecule, which is attacked by the nucleophilic oxygen obtained in the first step, leading to a diglycerol molecule. The further formation of triglycerol and heavier polymers are consecutive reactions.

Effects of Reaction Temperature

After confirming that calcined dolomite exhibits the highest activity in the synthesis of polyglycerols in comparison to

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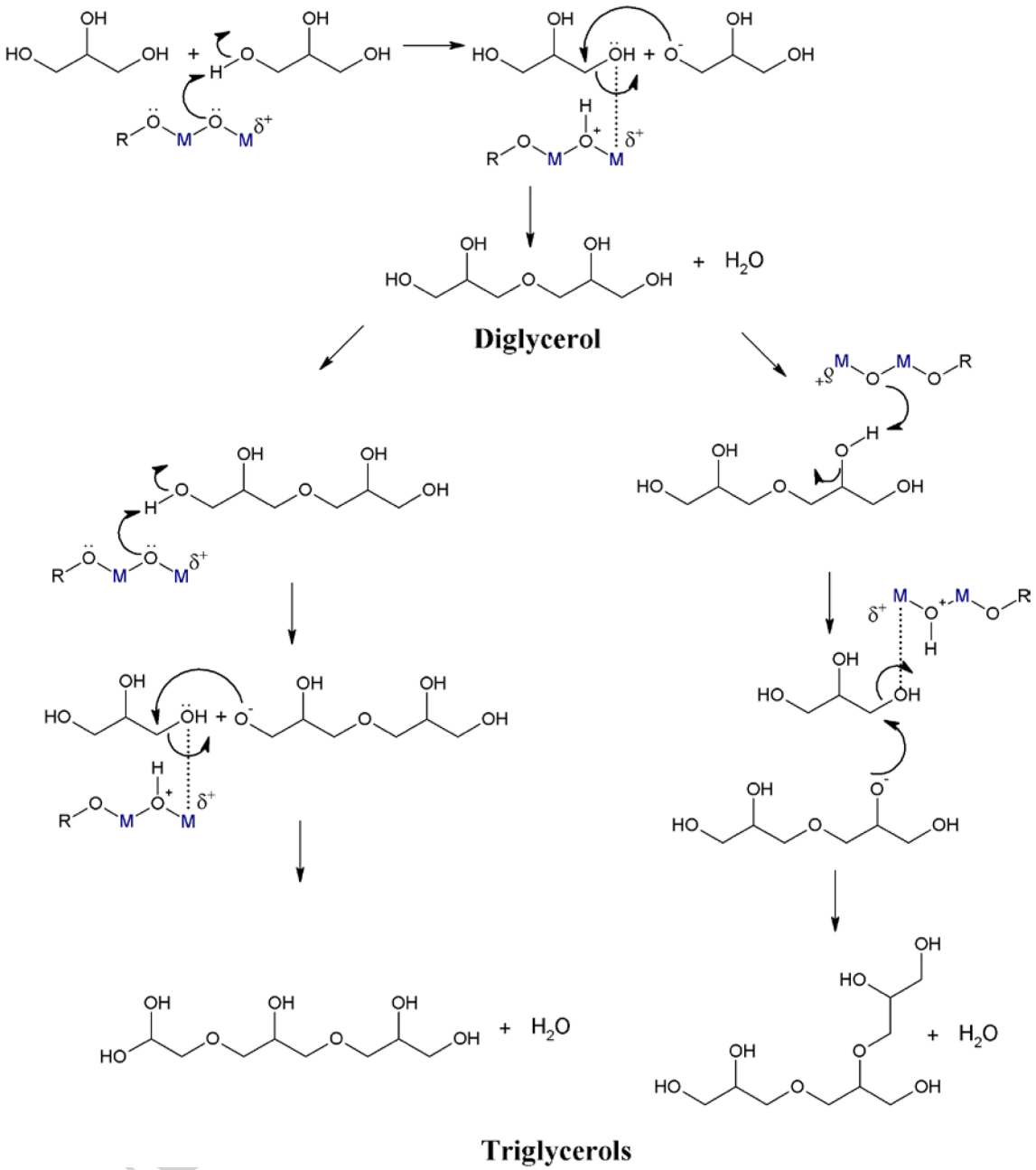

Scheme 1 Mechanism proposed by the glycerol etherification, according to Ruppert el al. (2012)

the as-received dolomite, the influence of the reaction temperature was ranged between 200 and 245 °C, maintaining constant the catalyst loading on 2 wt% and 24 h of time of stream (Fig. 8).

Even with a longer reaction time, at the lowest temperature (200 °C), CD exhibited a lower glycerol conversion, only 9%; although good selectivity to diglycerol, close to 50%. The increase of the temperature caused a clear increase in the conversion, obtaining a glycerol conversion of 77%, maintaining high selectivity towards to diglycerol, nearly 51%, which leads to higher diglycerol yield to that obtained by Barros et al. under similar reaction conditions (X_{gly} = 85% S_{di} = 40%), using CaO as active phase coming from eggshell [17].

When the temperature is raised to 245 °C, although the catalyst showed high glycerol conversion, a decrease on diglycerol selectivity was observed (X_{gly} = 91% S_{di} = 23% and S_{tri} = 22%). Another important feature highlighted on Fig. 9 is that color and viscosity of obtained products were directly related with the reaction temperature. Thus, a very

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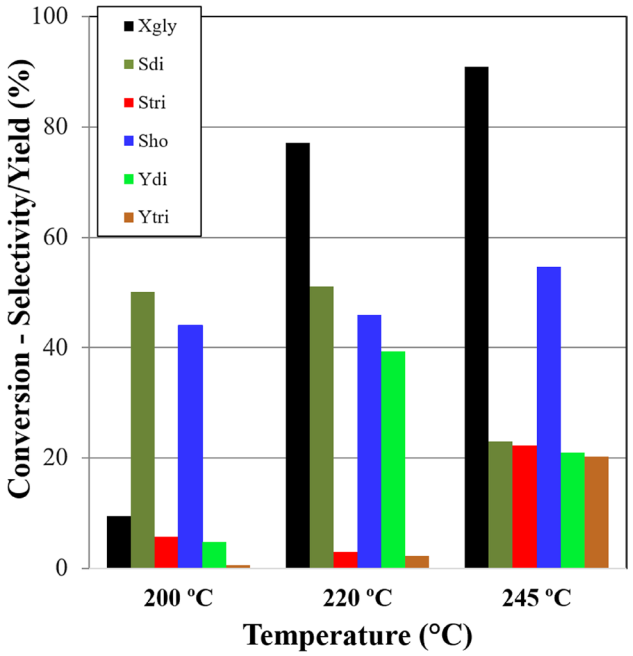

Fig. 8 Influence of the reaction temperature in the glycerol etherification. (Reaction conditions: 2 wt% of calcined dolomite, 24 h). Glycerol conversion (X_{Gly}), diglycerol selectivity (S_{di}), triglycerol selectivity (S_{tri}), high oligomers and other products (S_{ho}), diglycerol yield (Y_{di}) and triglycerol yield (Y_{tri})

clear product, similar to the unreacted glycerol was obtained at 200 °C; while the product obtained at 245 °C was darker and very viscous.

At higher temperature, the polymerization of glycerol increases, with the appearance of oligomers greater than tetraglycerol. The separation of the oligoglycerol mixtures into their components is difficult by direct distillation [20]. Therefore, lower temperature conditions allow the synthesis of the desired products (di- and triglycerol) and it would involve fewer separation steps for the purification of the final product. The content of the glycerol oligomer mixture is regulated by specific laws, according to the European Community legislations, for example, polyglycerol polyricinoleate, used as food additive, was considered, the content of di-, tri- and tetraglycerol should be predominated (not less than 75%), whereas the amounts of polyglycerols equal to or greater than heptaglycerol should not be greater than 10% [12, 46].

Evaluation of Catalyst Loading

Since reaction temperature of 220 °C led to more diglycerol selectivity and lower formation of higher oligomers and other products, this temperature was used for the catalyst loading evaluation. A trend of increasing the conversion with increasing of catalyst loading (Fig. 10) is observed, reaching 77% X_{gly} for CD, with Y_{di} ca. 40% and ca. 2% for Y_{tri}. For this maximum catalyst loading, calcined eggshell (mainly composed by CaO) led to higher glycerol conversion (85%), but slightly lower Y_{di} (34%), probably due to diglycerol oligomerization [17].

These data are in agreement with those reported in the literature, where the catalytic activity using basic catalysts and mainly alkaline-earth oxides increases directly with the catalyst loading, obtaining the maximum value for 2 wt% [20, 45]. The use of a higher loading caused a decrease of the glycerol conversion, probably due to the back-scissions of diglycerol to glycerol [20].

In addition, it is also noteworthy that the selective pattern is similar in all cases so an increase in catalyst loading only causes an improvement in catalytic activity by an increase in available active centers, while the selectivity pattern must be attributed to the reaction temperature. The increase of the glycerol conversion with the catalyst loading together with the similar values in the selectivity pattern leads to a diglycerol yield of 40%, while the triglycerol yield is only of 2%. These values are slightly higher to those exposed by Barros et al. [17] for the calcined eggshell thermally treated, where a glycerol conversion of 85% was obtained with a diglycerol yield slightly lower (34%) to that shown for the calcined dolomite.

These temperature and catalyst load conditions are interesting in comparison with previously published results. Using MgAl mixed oxides as base catalysts for glycerol etherification, Garcia-Sancho et al. [15], working at same temperature (220 °C) found a highest conversion of 50.7% for a catalyst loading of 2 wt%. Pouilloux et al. [47] studied

Fig. 9 Obtained product after the reaction at 200, 220 and 245 °C for 24 h with 2 wt% of calcined dolomite

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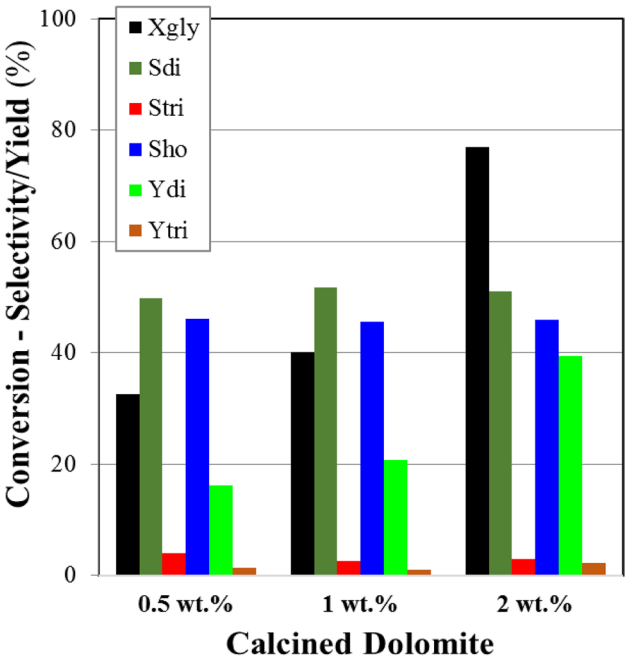

Fig. 10 Effect of catalyst loading in the glycerol etherification. (Reaction conditions: 220 °C and 24 h). Glycerol conversion (X_{Gly}), diglycerol selectivity (S_{di}), triglycerol selectivity (S_{tri}), high oligomers and other products (S_{ho}), diglycerol yield (Y_{di}) and triglycerol yield (Y_{tri})

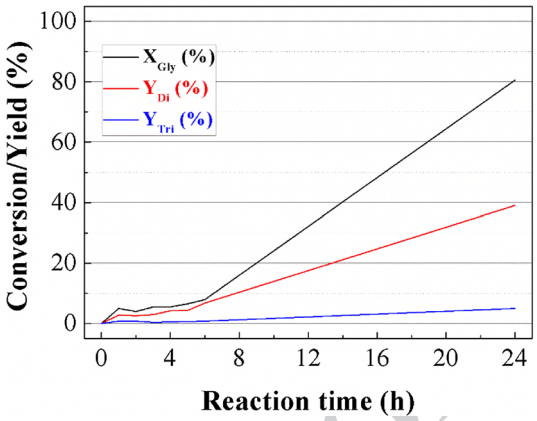

Fig. 11 Kinetic study in the glycerol etherification. (Reaction conditions: 2 wt% of calcined dolomite, 220 °C). Glycerol conversion (X_{Gly}), diglycerol yield (Y_{di}) and triglycerol yield (Y_{tri})

this reaction with Cesium catalysts impregnated in MCM-41 and SBA-15, using 1% catalyst, 260 °C, and 24 h of reaction, obtaining glycerol conversions of 72% for Cs/SBA15 and 74% for Cs/MCM-41. For 2 wt% of calcined dolomite, a much more cheap material, similar X_{gly} was obtained at a temperature 40 °C lower.

Effect of Reaction Time

Once the parameters of the glycerol etherification have been optimized (100 g of glycerol, 2 wt% of calcined dolomite, 220 °C and 24 h), the influence of the reaction time was studied (Fig. 11). It has been observed that the glycerol conversion as well as the di- and triglycerol yield increase with the reaction time. In the first hours, it is observed that the glycerol conversion is lower, only 8% after 6 h of reaction time. This fact could indicate that it is necessary an activation step to accelerate the glycerol etherification since a conversion close to 80% is obtained after a reaction time of 24 h. Considering the mechanism proposed by previous authors, the glycerol etherification takes place in two steps [26, 44]. In a first step, a basic site extracts a proton of the glycerol molecule, while in a second step, an unsaturated site favors the attack of the deprotonated glycerol to another glycerol molecule (Scheme 1). From the obtained data in Fig. 11, it can be inferred that the formation of the deprotonated glycerol species could be limited requiring higher reaction temperature or higher reaction time than the second step.

The catalytic data also show how diglycerol is formed at shorter reaction times in comparison to triglycerol molecules. Later, from diglycerol molecules can be obtained triglycerol molecules or polyglycerols with higher chain following the same mechanism shown in Scheme 1 [26]. The increase of the polyglycerol chain is in agreement with the literature, where the use of prolonged reaction time favors the condensation of higher proportion of glycerol molecules or other side reactions. In the present study, the use of relatively low temperature (220 °C) limits the existence of undesired side reactions, which can generate toxic products such as acrolein or glycidol [19, 27, 48].

Reusability and Stability

The use of inexpensive and reusable catalysts is key to obtain sustainable and competitive catalysts. For this purpose, the product mixture (reaction with 2 wt% of dolomite, 24 h at 220 °C) and catalyst was separated by decantation. In order to maintain a similar catalyst loading, the glycerol-catalyst weight ratio was maintained. The catalytic data (Fig. 12) show a decrease of the glycerol conversion from 80 to 35% after the first reuse and 40% after second reuse, indicating that the conversion in more or less constant after the first cycle. Regarding the selectivity, all reactions maintain approximately the same pattern, confirming that selectivity is directly related with the reaction temperature.

The decay of glycerol conversion could be assigned to several factors. It is difficult to know if the Mg and Ca species detected by ICP (Table 2) come from the partial leaching of the calcined dolomite or can be attributed to the loss of small particle in the filtration step since the obtained product has high density. Previous researches have established

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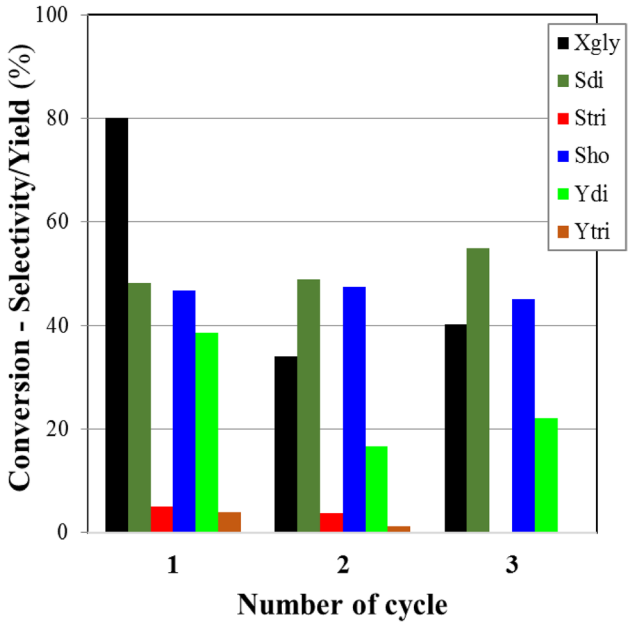

Fig. 12 Reuse tests (calcined dolomite, 2 wt%, 220 °C and 24 h) (filtration between each cycle)

Table 2 Ca and Mg amounts determined by ICP-OES on reaction mixture obtained with 2 wt% of commercial CaO, 2 wt% CD (220 °C, and 24 h of reaction) and from reusability tests

Sample	Concentration (g/L)	
	Ca	Mg
Glycerol (reactant)	–	–
Commercial CaO	13.68 ± 0.364	–
220 °C, 2% CD	7.03 ± 0.09	0.19 ± 0.01
First run	9.97 ± 0.05	0.16 ± 0.01
Second run	1.78 ± 0.24	0.19 ± 0,004
Third run	0.85 ± 0.02	0.24 ± 0.03

CD calcined dolomite

the loss of Ca^{2+} species [16, 23, 40] or Cs^{+} species in the glycerol etherification, which suggests that the reaction could be partially homogeneous [47]. Previous studies have pointed out that the homogeneous contribution is related to the formation of a calcium glyceroxide phase that exhibits high activity in basic reactions such as glycerol etherification [26] or synthesis of biodiesel [49, 50].

Table 2 shows the leaching of calcium and magnesium for CD catalyst after different catalytic cycles and compared with commercial CaO. It has been remarked that the Ca^{2+} leached from CD tests was much lower than that observed with commercial CaO (test performed on our previous study) even though the test with CD was performed up to 24 h. Considering dolomite composition, determined by XRF, and that 2 g of catalyst were used in each test for 100 g of glycerol (density: 1.26 g mL^{-1}), there would be initially 20.41 g L^{-1} of Ca and 4.03 g L^{-1} of Mg, considering that Ca^{2+} and Mg^{2+} were completed lixiviated to glycerol. Therefore, analyzing the remaining metal amounts in the products, it can be noticed that for the first run, both calcium and magnesium leaching was of 49% and 4%, respectively. Considering the decreasing on metal content on the catalyst due to leaching, for second run Ca leaching is of 17% and 5% for Mg; and finally for third run, 10% Ca and 7% Mg. These data confirm that the decrease on glycerol conversion is due to the lower amount of basic sites remaining on the catalyst, being the most active site those related to calcium species.

Calcined dolomite was previously used as solid basic catalyst in the synthesis of biodiesel. Several authors have reported that the complete recovery of the active phase was not possible by the partial leaching of Ca^{2+} and Mg^{2+} species, although this leaching did not cause a pronounced decrease of the fatty acid methyl ester (FAME) yield [32, 44, 51]. Jaiyen et al. [52] evaluate dolomite and waste seashell as catalysts for methanolysis of palm oil to biodiesel observing that the calcined dolomite was more tolerant to deactivation than calcined seashells by the reaction of CaO active phase with glycerol to form $Ca(C_3H_7O_3)_2$.

For other base catalyzed reactions, such as aldol-condensation of furfural with acetone, the catalyst derived from dolomite also presented leaching processes, although the deactivation was very low and attributed to the formation of carbonaceous deposits [53]. The synthesis of glycerol carbonate from glycerol and dimethylcarbonate also revealed a decline of the catalytic activity after several cycles by a progressive loss of the CaO–MgO phases [33]. Galadima and Muraza [54] summarized a series of works on glycerol carbonate production and associated resistancy to deactivation with mass transfer properties. Catalysts with poor mass transfer properties were subject to quick deactivation with time.

Other cause of the loss of the activity can be ascribed to the alkaline earth mixed oxides (CaO–MgO) obtained from the thermal treatment of the raw dolomite that have high susceptibility to retain CO_2 molecules, causing a superficial carbonation and therefore the loss of the available basic sites provoking a decrease of the catalytic activity. Thus, Ilgen et al. [51] regenerated the active phase by calcination to remove the carbonate species and the carbonaceous deposits formed on the surface for the synthesis of biodiesel. Nonetheless, the FAME yield decreased in comparison to the first run.

For the second set of reusability tests (Fig. 13), after the first cycle (reaction at 220 °C, 2% CD and 24 h) after dissolution in ultrapure water followed by filtration, the catalyst was calcined at 800 °C and 2 h, moreover, the amount of glycerol was adjusted to maintain the catalyst/glycerol ratio.

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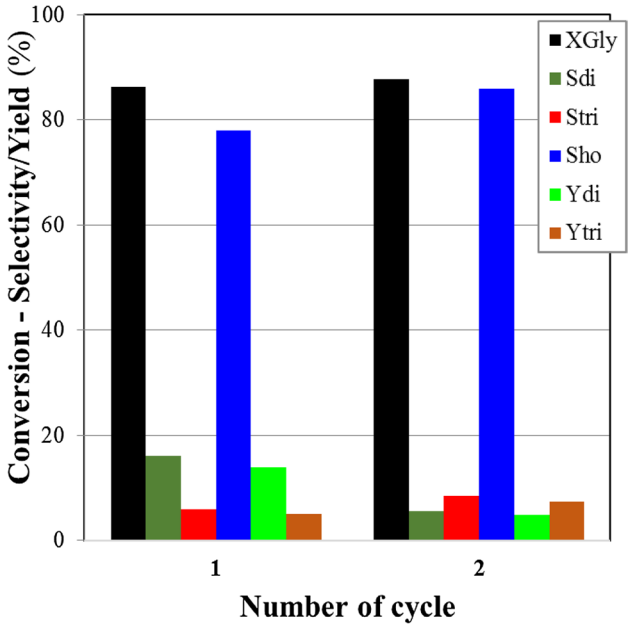

Fig. 13 Reuse tests (calcined dolomite, 2 wt%, 220 °C and 24 h) (calcination at 800 °C for 2 h before new cycle)

Despite similar glycerol conversions (86% on first run and 88% on second run), there was a drop on diglycerol selectivity, reaching half of the previous value, and a slightly increase on triglycerol selectivity (from 6 to 8%). Catalyst from second run could not be separated from the mixture to run another cycle, pointing to a considerable dissolution on the reaction medium, what could have contributed to the similar conversion and the differences on oligoglycerols yields.

The first set of reusability tests (Fig. 12) presented a drop on conversion after the first cycle, however kept similar selectivity. On the other hand, the second set of tests (Fig. 13) had a lower yield due to the drop on selectivity. Washing the catalyst with water probably changed the catalyst, being very likely that the surface was hydroxylated, modifying the catalytic properties. The washing step eliminated the adsorbed glycerol or oligomers and hot spots during the calcination were avoided. However, the thermal process also reduced the amount of material and probably consumed actives species such as calcium glyceroxide, decreasing it selectivity to the oligomers. Therefore, the first procedure for catalyst reusability is more interesting since it leads to more cycles and diglycerol yielding.

Conclusions

Dolomite was used as catalytic precursor to obtain a catalytic system (MgO–CaO) for the glycerol etherification. The characterization data reported that it is necessary 800 °C to convert dolomite in MgO–CaO. The thermal treatment is an exothermic process, which causes a decrease of the particle size and an increase of the specific surface area. The TPD-CO_2 experiment reported that the obtained sample displays basic sites with great strength.

For the parameters covered on this study, calcined dolomite features lead to the following set of best conditions: catalyst load of 2%, temperature of 220 °C and 24 h of reaction time. Under these conditions, there was glycerol conversion of 77%, and di and triglycerol selectivities of 51% and 3%, respectively.

The influence of reaction time reveals that the reaction is slow along the first hours and later the reaction rate increases probably due to the first etherification step being thermodynamically or kinetically limited.

Reusability and stability tests showed loss of catalytic activity from the first reuse, as well as significant differences in the selectivity to the diglycerol due to active phase leaching to the reaction mixture, suggesting some homogeneous contribution.

Calcined dolomite catalytic performance allows us to conclude that it has potential to be used on glycerol oligomerization, reaching significant glycerol conversions when used in smaller amounts and temperatures than those previously reported on other reaction routes. Dolomites application as catalyst on glycerol oligomerization is promising considering that this material has low price, reusability capacity and large availability world widely.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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Affiliations

Fernando José S. Barros[1] · Juan A. Cecilia[2] · Ramón Moreno-Tost[2] · Matheus F. de Oliveira[1] · Enrique Rodríguez-Castellón[2] · Francisco Murilo T. Luna[1] · Rodrigo S. Vieira[1]

[1] Grupo de Pesquisa em Separações por Adsorção–GPSA, Departamento de Engenharia Química, Universidade Federal do Ceará, Campus do Pici, 709, Fortaleza, CE 60.455-760, Brazil

[2] Facultad de Ciencias, Departamento de Química Inorgánica, Mineralogía y Cristalografía (Unidad Asociada ICP-CSIC), Universidad de Málaga, Campus de Teatinos s/n, 29071 Malaga, Spain

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