

Article

Glycerol Carbonate Production via Transesterification: The Effect of Support Porosity and Catalyst Basicity

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Abstract: Glycerol transesterification with diethyl carbonate (DEC) using catalysts with different porosities as support for CaO was performed, seeking the evaluation of how textural properties influence glycerol conversion and product selectivity. A total of 20% CaO was supported on ZSM-5, K-10, MCM-41, SiO₂, and γ -Al₂O₃. Catalysts showed a well-dispersed active phase of CaO in all the supports and no changes in the support crystalline structure were noticed. Reactions were performed in dimethyl sulfoxide (DMSO), 10 wt.% of catalyst in relation to glycerol, at 130 °C, and 1:3 glycerol/DEC molar ratio. According to our results, the higher the pore volume and pore size, the higher the glycerol conversion. On the other hand, concerning selectivity, higher glycerol carbonate selectivities were reached when strong basic sites were present. A total of 86% glycerol conversion and 91% glycerol carbonate selectivity were found using 60% CaO supported on γ -Al₂O₃ after 5 h of reaction.

Keywords: glycerol; diethyl carbonate; glycerol carbonate; CaO



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1. Introduction

In the growing search for fuels that are not derived from fossil resources, biodiesel appears as a renewable alternative fuel that can be produced from the transesterification reaction of vegetable oils or animal fats with alcohols [1], generally methanol or ethanol [2]. However, biodiesel production entails the generation of glycerol as a coproduct and an excessive amount of this chemical implies a fall in the commercialization price [3] and environmental issues. Due to the versatility of glycerol, several compounds can be produced to avoid saturation of the glycerol on the market, for example, 1,3-propanediol, 1,2-propanediol [4], glyceric acid, and glycerol carbonate [5], among many others [6].

Glycerol carbonate (GlyC) is a high-value glycerol derivative with several applications [7]. GlyC has excellent interaction with polar and apolar compounds, low toxicity, volatility, and flammability. As a direct application, it can be used in the cosmetics industry as a humectant and a transepidermal water controller, in the agriculture industry, it can be used as a fertilizer when combined with surfactants. It can also act as an electron carrier in lithium batteries [3,8]. As an indirect application, GlyC can be used as a chemical intermediate to synthesize surfactants, polymers, and glycidol [3].

Several works in the literature report the use of dimethyl carbonate (DMC) as a reactant for synthesizing GlyC by glycerol transesterification using as catalysts hydrotalcites, hydrocalumites, zeolites, and magnesium lanthanum, among others [9–12]. Considering this reaction with DMC, two methanol molecules are produced for each transesterified glycerol molecule under mild reaction parameters [13]. The production of glycerol carbonate by transesterification using DMC is the most explored route due to higher conversion in shorter reaction times; in this way, other carbonic acids, like diethyl carbonate (DEC), are being explored for this reaction [14–16].

Souza Júnior et al. [17] evaluated the use of hydrocalumites to synthesize GlyC. The catalyst calcined at 700 °C reached high conversion (90%) and selectivity (92%) using a 1:3 glycerol/DEC molar ratio at 130 °C, pointing to the basic sites from CaO as key for the high catalyst efficiency. Álvarez et al. [18] performed continuous reactions using glycerol, DEC, and dimethyl sulfoxide (DMSO) as solvents, and hydrotalcites of MgAl rehydrated supported on α and γ -Al₂O₃. The authors obtained high conversion and selectivity values for catalysts with a high concentration of Brønsted basic sites, which favors transesterification reactions. The same research group [19] studied the use of hydrotalcites rehydrated in a batch system using excess DEC as solvent under an argon atmosphere and obtained 98% glycerol conversion with 65% selectivity for the desired product associated with the capacity of absorption of the Brønsted basic sites of the catalyst. Wu et al. [20] assessed several mixed oxide catalysts of Ce_{1-x}Cd_xO in a batch system with a 1:3 proportion of glycerol/DEC. The catalyst Ce_{0.7}Cd_{0.3}O calcined at 500 °C showed high conversion (96.84%) and was selective for the synthesis of GlyC. The authors conclude that high activity is associated with the catalyst's moderate and strong basic sites.

Li et al. [21] evaluated a series of Mg-Zr composite oxides in glycerol carbonate production from a reaction between glycerol and dimethyl carbonate. The authors conclude that an increase in basic sites and highly dispersed active phase favors glycerol conversion. Pradhan and Sharma [22] investigated the use of mixed nickel and magnesium oxide for the synthesis of glycerol carbonate (GC). The optimal metal ratio identified by the authors was 3:1 for Mg/Ni. The highest conversion and selectivity values were obtained using a feed ratio of 4:1 for DMC/glycerol, with the catalyst mass being 4% of the glycerol mass, at 90 °C for 1.5 h. The catalyst remained active during recycling tests, showing only a slight loss of activity, which was attributed to catalyst leaching. Praikaew et al. [23] employed calcium oxide (CaO) for the production of glycerol carbonate. The authors achieved a glycerol conversion of 96% and a yield of 94% for the desired product in a short operational time of 3 h. This was accomplished with a CaO/glycerol ratio of 0.08, a glycerol/DMC molar ratio of 1:2.5, and a temperature of 60 °C. Saiyong et al. [24] investigated heterogeneous catalysts for the transesterification of glycerol with DMC at 70 °C. Both CaO and SrO exhibited comparable selectivity, which can be attributed to the similar basicity of these catalysts in the transesterification process. Chotchuang et al. [25] evaluated glycerol carbonate production with the utilization of glycerol and DMC. The authors observed that the strong basicity of CaO and SrO promotes transesterification; however, the high number and strength of their basic sites tend to decompose the formed glycerol carbonate (GlyC) into glycidol.

In contrast to the referenced studies, which largely focused on optimizing catalyst composition and reaction parameters to enhance glycerol conversion and selectivity in the transesterification process, the present work provides an in-depth investigation into the role of catalyst textural properties and basicity in glycerol transesterification using diethyl carbonate (DEC). While Li et al. [21] and Pradhan and Sharma [22] highlighted the importance of basic sites and metal ratios, their research did not address the impact of the catalyst's textural characteristics, such as pore volume and size, on the reaction results. Similarly, the investigations conducted by Praikaew et al. [23], Saiyong et al. [24], and Chotchuang et al. [25] demonstrated the role of strong basic sites in promoting transesterification but did not explore the influence of support porosity on the reaction mechanism or product distribution. The present study differentiates itself by assessing the effects of various support materials for calcium oxide with distinct porosity levels. This approach elucidates the interplay between support textural properties and catalyst basicity, revealing their combined influence on glycerol conversion and glycerol carbonate selectivity.

Glycerol transesterification using carbonic acid esters is challenging, especially concerning its immiscibility with glycerol. This is due to the polar nonprotic nature of the carbonic acid esters and the polar protic nature of glycerol, resulting in a liquid–liquid biphasic reaction mixture [16]. In a heterogeneous catalytic reaction, the system complexity increases to a triphasic liquid–liquid–solid system.

Non-inert supports, like clays (e.g., montmorillonite K-10) and zeolites, also play an essential role in enhancing the basicity of the supported oxides. These materials possess inherent acidic or amphoteric properties that, when combined with basic oxides such as CaO and SrO, create a synergetic effect that enhances the catalytic activity. Saiyong et al. [24] and Chotchuang et al. [25] observed that CaO and SrO supported on these materials exhibit not only increased basicity but also improved selectivity toward the desired product (glycerol carbonate). Additionally, the use of clays and zeolites can modulate the strength of the basic sites, preventing excessive decomposition of intermediate products like glycerol carbonate into glycidol.

In the present work, the performance of three alkaline earth metal oxides (MgO, CaO, and SrO) was investigated as basic catalysts for glycerol transesterification with diethyl carbonate (DEC). The choice of catalyst is crucial for the viability of the process, as catalyst properties directly influence the reaction mechanism and the yield of the desired products. In glycerol transesterification to glycerol carbonate, catalyst basicity plays a significant role. After selecting CaO as the active catalyst phase, this study focused on understanding the impact of textural properties on this reaction by supporting calcium oxide on various porous materials, including ZSM-5, MCM-41, K-10, SiO₂, and γ -Al₂O₃. The novelty of the present work lies in a comprehensive investigation of key parameters, such as support porosity and catalyst basicity, in the efficiency of glycerol carbonate production.

2. Materials and Methods

2.1. Chemicals

Anhydrous diethyl carbonate (DEC) (99%), fumed SiO₂, and montmorillonite K-10 were purchased from Sigma-Aldrich (Merck, Rio de Janeiro, Brazil); glycerol (99.5%) and magnesium nitrate hexahydrate (99.9%) from ISOFAR (Isofar, Rio de Janeiro, Brazil); dimethyl sulfoxide (DMSO) (99.9%), calcium nitrate tetrahydrate (99%), and strontium nitrate tetrahydrate (99.9%) from VETEC Fine Chemistry Ltd. (VETEC, Rio de Janeiro, Brazil); boehmite from Sasol (Sasol, South Africa); MCM-41 from Tianjin Chemist Scientific Ltd. (Tianjin, China); and HZSM-5 zeolite (CBV 8014) from Zeolyst (Zeolyst International, Conshohocken, PA, USA).

2.2. Catalyst Preparation

Catalysts of MgO, CaO, and SrO were prepared by the calcination of the nitrate precursors as follows: magnesium nitrate was calcined and decomposed at 500 °C in a synthetic air flow of 60 mL·min^{−1} for 3 h (at a rate of 10 °C·min^{−1}); calcium and strontium nitrates were calcined using the same conditions, but at 700 °C.

CaO-supported catalysts were prepared by the wet impregnation method. Before CaO impregnation, all the supports were calcined at 700 °C in a synthetic air flow at 60 mL·min^{−1} for 3 h, at a heating rate of 10 °C·min^{−1}. In a typical impregnation procedure, calcium nitrate solution (100 g·L^{−1}) was prepared in deionized water and transferred to a 250 mL round-bottom flask along with the support. This mixture was stirred at 100 rpm at room temperature. After 3 h, the system was vacuumed and heated at 70 °C. The samples were dried overnight at 100 °C, macerated, and calcined at 700 °C for 3 h with 60 mL·min^{−1} air flow and a heating rate of 10 °C·min^{−1} to produce xCaO/support catalysts, where x is the weight percentage of CaO.

2.3. Catalytic Tests

In a typical reaction, 19.5 mmol of glycerol, 58.5 mmol of DEC, and 128 mmol of DMSO were mixed in a 50 mL two-neck round-bottom flask coupled with a reflux condenser on a stirring and heating plate. The use of DMSO as a solvent in the reaction was necessary due to the immiscibility of glycerol and DEC. The solvent facilitates a homogeneous reaction medium, ensuring better interaction between the reactants and the catalyst. Reactions were performed at 130 °C with 10 wt% of catalyst in relation to glycerol. The experimental conditions used were as previously described by Souza Júnior et al. [17]. Aliquots

were withdrawn during the reaction and analyzed in Shimadzu HPLC (model LC-20A Prominence) equipped with an Aminex HPX-87H (Biorad) and a refractive index detector (RID-10A). An aqueous solution with 10 mM of H₂SO₄ was used as a mobile phase at 0.6 mL min^{−1} flow and 30 °C. Calibration curves were performed with standards of all reactants and products to evaluate glycerol conversion and glycerol carbonate selectivity. *Glycerol conversion*, *GlyC selectivity*, and *yield* were calculated using Equations (2), (3) and (4), respectively, where *n* represents the number of moles of components considering the stage of reaction (e.g., initial and final):

$$\text{Conversion (\%)} = \frac{(n_{\text{initial}}^{\text{glycerol}} - n_{\text{final}}^{\text{glycerol}})}{n_{\text{initial}}^{\text{glycerol}}} \times 100 \quad (1)$$

$$\text{GlyC selectivity (\%)} = \frac{n_{\text{final}}^{\text{GlyC}}}{(n_{\text{initial}}^{\text{glycerol}} - n_{\text{final}}^{\text{glycerol}})} \times 100 \quad (2)$$

$$\text{Yield (\%)} = \frac{\text{conversion} \times \text{GlyC selectivity}}{100} \quad (3)$$

2.4. Characterization Methods

The chemical composition of the catalysts was determined by X-ray fluorescence (XRF) using a Rigaku Primini spectrometer equipped with a palladium tube as a radiation source.

X-ray diffraction (XRD) was performed in a Rigaku Miniflex II equipment with a graphite monochromator using CuK α radiation (30 kV and 15 mA). The phases were evaluated based on the JCPDS database (Joint Committee on Powder Diffraction Standards, Swarthmore, PA, USA). The analysis was performed from 5 to 90° in 0.05° increments using a 1 s counting time per step. The average crystallite size was calculated using the Scherrer equation (Equation (1)):

$$D_{hkl} = \frac{k\lambda}{\beta \cos(\theta)} \quad (4)$$

where D_{hkl} is the average diameter of the crystals (Å), k is a constant that depends on the particle shape (for sphere, $k = 0.94$), λ is the wavelength of the X-ray source (for CuK α , $\lambda = 1.5488$ Å), β is the full width at half maximum (FWHM) in radians, and θ is the diffraction angle.

Textural characteristics were determined by nitrogen physisorption analysis performed at −196 °C using a Micromeritics TriStar II 3020 device. As a pretreatment, samples were outgassed for 24 h at 300 °C. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method, and pore volume/pore diameter by the Barrett–Joyner–Halenda (BJH) method.

Temperature-programmed desorption of CO₂ (CO₂-TPD) was performed in a device coupled to Prisma Plus (Pfeiffer) mass spectrometer to identify and quantify the basic sites of the catalysts. In a typical method, samples were pretreated at calcination temperature for 1 h with 30 mL·min^{−1} of He. CO₂ adsorption was carried out under 30 mL·min^{−1} flow of 10% CO₂/He for 30 min at room temperature. Then, the samples were treated under He flow of 30 mL·min^{−1} for 1 h to remove physically adsorbed CO₂. Finally, samples were heated up to 1000 °C at a heating rate of 20 °C·min^{−1} under He flow (30 mL·min^{−1}). The m/z ratios of 2, 12, 15, 16, 18, 28, 32, and 44 were monitored, and $m/z = 44$ was used for CO₂ quantification.

Scanning Electron Microscopy (SEM) was used to investigate catalyst morphology and energy-dispersive X-ray spectroscopy (EDS) was performed for elemental mapping and to determine surface chemical composition of catalysts before and after recycling tests, respectively. SEM analysis was conducted in a Jeol (JSM-IT700HR) microscope using secondary electrons (SED). EDS measurements were performed in the same microscope using

a backscattered detector (BED) with 10 kV and an EDS detector (SDD Jeol-74212U4L2Q, London, UK).

3. Results

3.1. Catalytic Tests

3.1.1. Alkaline Earth Metal Oxides

Catalytic reactions were performed in batch mode for 6 h. Three different alkaline earth metal oxides (CaO, MgO, and SrO) were tested as catalysts and the results are depicted in Figure 1. CaO and SrO were the most active catalysts, presenting 92% and 87% of conversion after 6 h, respectively, against just 29% of MgO. CaO and SrO were the most basic oxides (as observed in Section 3.2.4), and basicity is the main parameter for measuring success in glycerol transesterification [26]. Specifically, SrO achieved its highest conversion during the fourth hour of the reaction, maintaining stability in the fifth and sixth hours. In contrast, the conversion profile for CaO displayed a steady increase throughout the reaction.

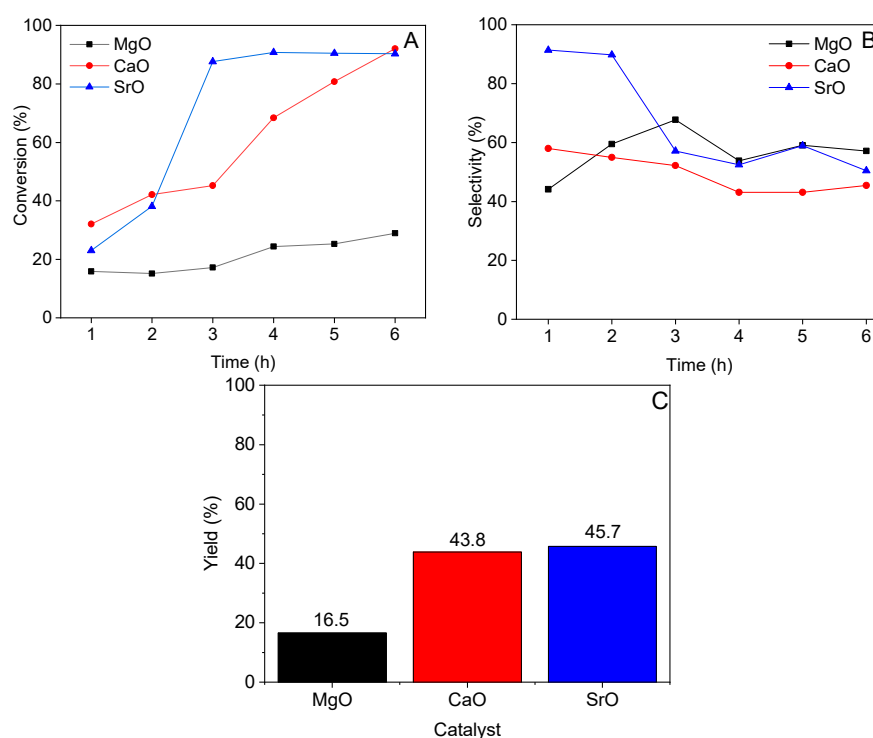


Figure 1. Conversion (A), GlyC selectivity (B), and GlyC yield after 6 h of reaction (C) of oxides. Reactions were performed at 130 °C, 1:3 for gly/DEC, and 10 wt% of catalyst.

Except for SrO in the first 2 h of the reaction, only moderate GlyC selectivity was reached with alkaline earth metal oxides (Figure 1B). After 6 h of reaction, higher GlyC selectivity was obtained for the MgO catalyst (57%), followed by SrO and CaO exhibiting selectivities of 50 and 45%, respectively. SrO was highly selective for 2 h, but, probably due to its strong basicity, it dropped as the reaction advanced. The strong basicity of CaO and SrO favors transesterification; however, the high number and strength of basic sites tend to decompose the formed GlyC into glycidol [25]. Saiyong et al. [24] evaluated homogeneous and heterogeneous catalysts, such as K_2CO_3 , NaOH, CaO, and SrO, for glycerol transesterification with DMC at 70 °C. Comparing homogeneous and heterogeneous catalysts, similar conversions were reached; nonetheless, heterogeneous catalysts were more selective. CaO and SrO presented similar selectivity values due to the similar basicity of both catalysts (analyzed by Hammett).

GlyC yield was calculated for the three different catalysts after 6 h of reaction (Figure 1C). As expected, MgO presented the lowest GlyC yield (16.5%) due to its lower conversion among the tested catalysts and the closer selectivity to CaO and SrO. CaO and SrO showed almost the same yield (43.8 and 45.7%, respectively) after 6 h. It is worth mentioning that, according to conversion results, CaO was still active after 6 h of reaction. According to these results, and considering its lower cost, synthesizability from natural sources, and less leaching than SrO [27], CaO was chosen as the active phase to be supported.

3.1.2. Evaluation of Different Supports

The conversion and GlyC selectivity of CaO supported on different materials are shown in Figure 2. The porosity of the catalysts significantly affects the accessibility of reactants to active sites. Mesoporous materials tend to facilitate higher glycerol conversion due to their larger pore sizes, which allow better diffusion of the reactants into the catalytic sites. This enhanced accessibility promotes more efficient catalytic activity compared to microporous materials, which have smaller pore sizes that may restrict reactant mobility. Consequently, the mesoporous catalysts demonstrated higher glycerol conversions. The relationship between glycerol conversion and pore size can be better visualized by observing the descending order of conversion: $20\text{CaO}/\text{SiO}_2 > 20\text{CaO}/\gamma\text{-Al}_2\text{O}_3 > 20\text{CaO}/\text{K}-10 > 20\text{CaO}/\text{MCM}-41 \approx 20\text{CaO}/\text{ZSM}-5$ (37%, 30%, 24%, 18% and 16%, respectively); this is in accordance with the descending order of pore size (as presented in 3.2.3): $20\text{CaO}/\text{SiO}_2 > 20\text{CaO}/\gamma\text{-Al}_2\text{O}_3 > 20\text{CaO}/\text{K}-10 > 20\text{CaO}/\text{MCM}-41 \approx 20\text{CaO}/\text{ZSM}-5$. GlyC yield is also influenced by the nature of the catalyst's porosity, as presented in Figure 3. There is a trend that suggests the higher the pore volume, the higher the GlyC yield, except for K-10 as support. This is probably due to the nature of the K-10 porous system that counts mostly with external area contribution.

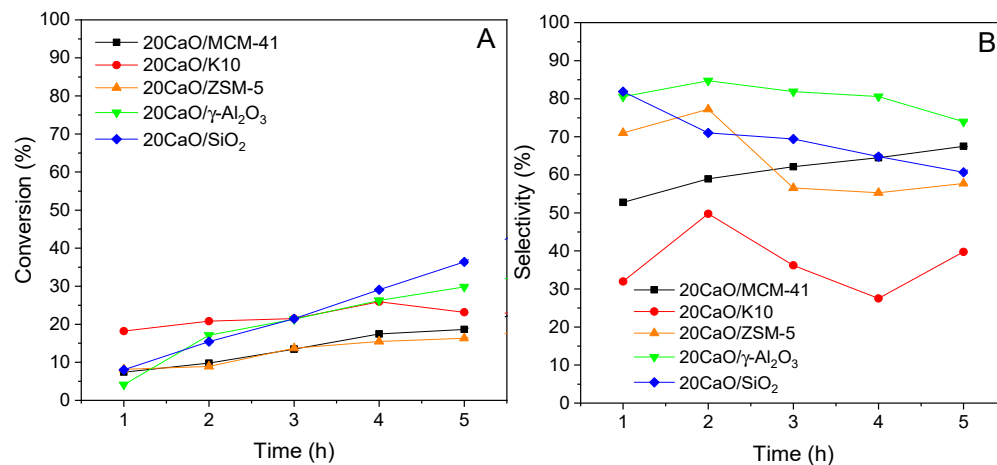


Figure 2. Conversion (A) and GlyC selectivity (B) of supported catalysts with 20% CaO. Reactions were performed at 130 °C, 1:3 for gly/DEC, and 10 wt% of catalyst.

When evaluating glycerol transesterification to glycerol carbonate, it is of major importance to take into account the basicity of the catalyst, and it is well established that glycerol conversion and GlyC production are directly related to the basicity, with the higher and stronger the basicity, the higher the glycerol conversion [28]. Zhang et al. [29] evaluated glycerol conversion with DMC using $x\text{CaO}-\text{ZrO}_2$ as a catalyst, where x ranged from 0 to 0.8 $\text{Ca}^{2+}:\text{Zr}^{4+}$ atomic ratio. The authors concluded that an increase in the CaO amount of up to 0.6 contributed to the increase in the number of basic sites on the catalyst surface, promoting an increase in glycerol conversion and a slight decrease in GlyC selectivity. Bai et al. [30] tested different amounts of NaOH supported in $\gamma\text{-Al}_2\text{O}_3$ in glycerol transesterification with DMC and reached 98% conversion with 80% NaOH/ Al_2O_3 , which was associated with the catalyst basicity provided by sodium aluminate. Wu et al. [20] evaluated $\text{CeO}_2\text{-CdO}$ as

a catalyst to produce glycerol carbonate via a reaction between glycerol and DEC. They concluded that glycerol conversion was promoted by the presence of moderate and strong basic sites.

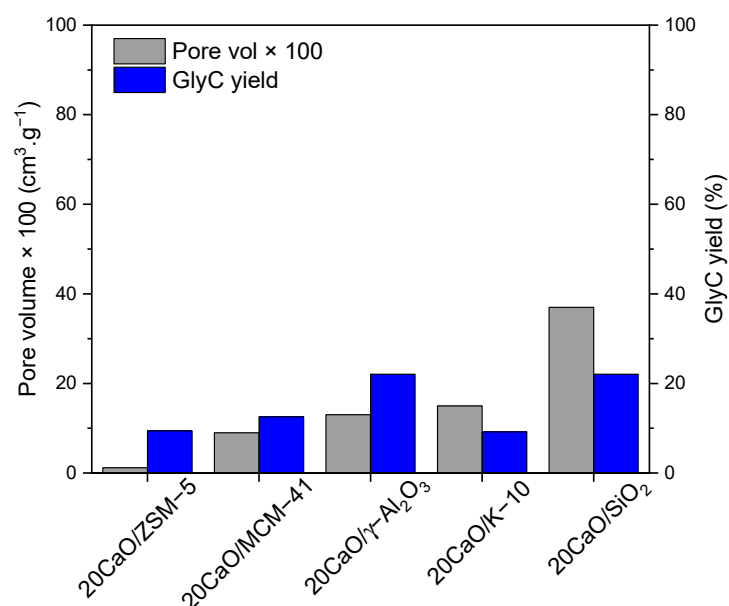


Figure 3. Comparison of pore volume × GlyC yield. Reactions performed at 130 °C, 1:3 for gly/DEC with 10 wt% catalyst after 5 h of reaction.

In the present work, different catalysts with different porous systems and basic profiles were tested in glycerol transesterification to glycerol carbonate. It was found that not only do basic profiles drive glycerol carbonate production, but the porous system also plays an important role. This idea is supported by the results, especially when textural properties (Section 3.2.3) and CO₂-TPD of the catalysts (Section 3.2.4) are analyzed. 20CaO/SiO₂ presented a total basicity of 25 μmol.g⁻¹, with a predominance of strong basic sites (82%—20.5 μmol.g⁻¹) and glycerol conversion of 48%; this is a mesoporous catalyst. On the other hand, 20CaO/ZSM-5 presented higher total basicity (44 μmol.g⁻¹), also with a predominance of strong basic sites (61%—26.8 μmol.g⁻¹), but the glycerol conversion was only 18,6%; this is a predominantly microporous catalyst. The catalytic performance of ZSM-5 in glycerol transesterification can be significantly influenced by the effects of nanoconfinement and pore accessibility. Due to its microporous structure, ZSM-5 may present limitations regarding the diffusion of larger organic molecules like glycerol and glycerol carbonate. The narrow pore size (typically around 0.55 nm) of ZSM-5 restricts the movement of bulky reagents, which can lead to partial or total blockage of active sites within the micropores, limiting the overall catalytic efficiency [31]. The phenomenon of nanoconfinement, where reactants are constrained within narrow pores, can lead to significant changes in reaction pathways and kinetics. While nanoconfinement can improve selectivity by favoring particular reaction mechanisms, it may also hinder the accessibility of reactants to internal active sites, as seen in the case of ZSM-5. In reactions involving glycerol and its derivatives, the kinetic diameter of glycerol (approximately 0.6 nm) approaches or exceeds the pore size of ZSM-5, further exacerbating mass transport limitations. Kosawatthanakun et al. [32] evaluated micro and nano BPH zeolite with potassium and cesium and observed that the nano-sized materials presented better catalytic performance compared to micro-sized materials and associated the shorter diffusion path and larger specific area as key factors for glycerol transesterification. Delesma et al. [33] performed a theoretical DFT study concerning glycerol conversion in glycerol carbonate in the presence of dimethyl carbonate. The authors concluded that pore diameters varying from micro to mesopores are beneficial for the reaction.

Concerning the selectivity of the evaluated catalysts, an increase in GlyC selectivity was observed for the 20CaO/K-10 catalyst at 5 h of reaction. This may be related to GlyC formation through an intermediate. Paula et al. [16] observed an increase in GlyC selectivity with the advancement of reaction time for the synthesis of GlyC from DEC, using CTA/MCM-41 catalyst, as observed in our work. Thus, it was suggested that glycerol carbonate is a secondary product formed from another intermediary product, identified as glycerol monocarbonates.

3.1.3. Influence of CaO Loading

Since 20CaO/ γ -Al₂O₃ presented, among the evaluated catalysts, the best results concerning conversion and selectivity, the influence of CaO content in γ -Al₂O₃ support was evaluated. According to the results presented in Figure 4, the higher the CaO content, the higher the glycerol conversion. GlyC selectivity can be considered stable around 5 h of reaction. 60CaO/ γ -Al₂O₃ reached nearly 85% of glycerol conversion at 5 h of reaction, with almost 100% of GlyC selectivity. This increase in glycerol conversion with CaO content is related to the increase in catalyst basicity, as is well represented in Figure 5.

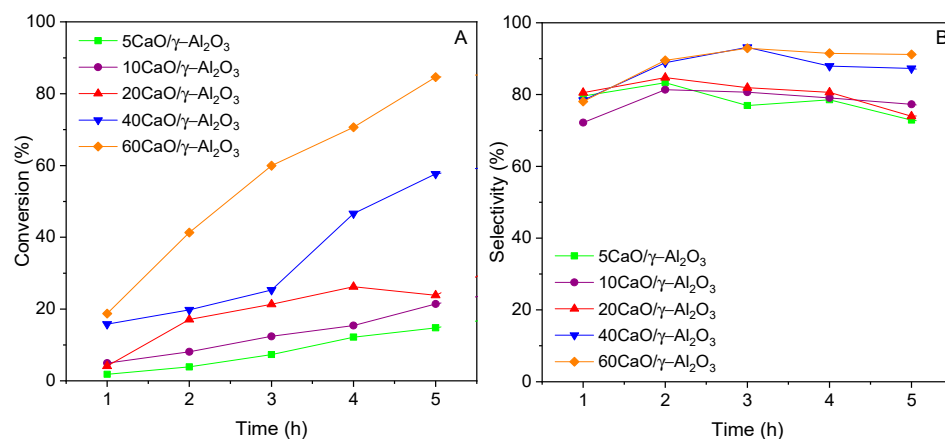


Figure 4. Glycerol conversion (A) and GlyC selectivity (B) of CaO supported on γ -Al₂O₃. Reaction performed at 130 °C, 1:3 for gly/DEC, and 10 wt% of catalyst.

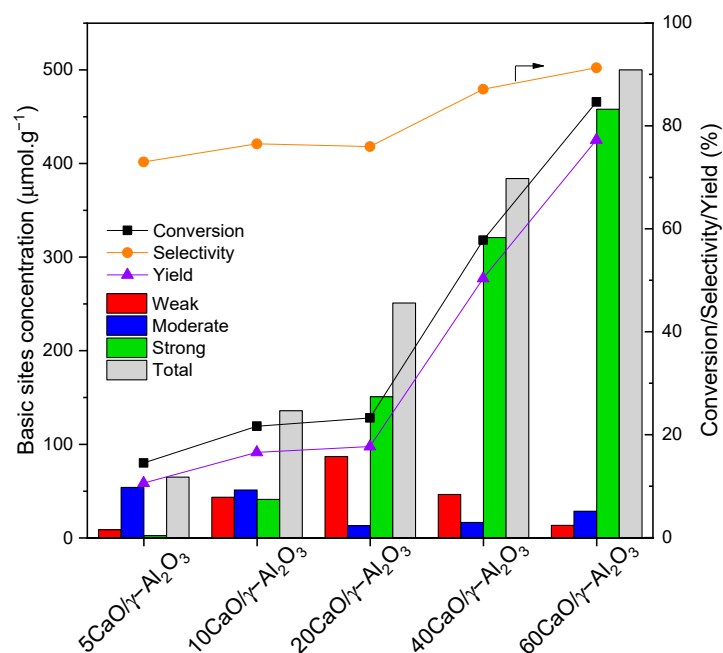


Figure 5. Comparison of basic sites $\times$ conversion $\times$ selectivity $\times$ yield. Reactions performed at 130 °C, 1:3 for gly/DEC with 10 wt% catalyst for 5 h of reaction.

As already mentioned, the basic strength of a catalyst is the most important factor in the transesterification reaction for glycerol carbonate production [30,34]. Figure 5 shows a comparison between the number and distribution of basic sites and glycerol conversion and GlyC selectivity for the CaO/ γ -Al₂O₃ catalyst series. As expected, the higher the CaO amount, the higher the basicity of the catalyst (shown in Section 3.2.4). This progressive increase in basicity promotes increased catalyst activity for glycerol transesterification. The increase in CaO content from 5 to 60% promotes a progressive glycerol conversion increase, also followed by an increase in GlyC yield, meaning the system is still selective, even at very high basicity. These results support the idea that glycerol conversion is deeply affected by the synergistic effect between the number of basic sites and their distribution, being favored at strong basic sites, in agreement with Zhang et al. [29] and Wu et al. [20].

3.2. Catalyst Characterization

3.2.1. X-ray Diffraction

Three different alkaline earth metal oxides (CaO, MgO, and SrO) were used as catalysts for glycerol transesterification to glycerol carbonate. Oxide phases were obtained after nitrate thermal decomposition, as can be seen in XRD patterns (Figure 6): MgO (JCPDS 45-0946), CaO (JCPDS 37-1497), and SrO (JCPDS 48-1477). The diffractogram of MgO displayed diffraction peaks at (2θ) 37°, 43°, 63°, 75°, and 79°, which refers to (111), (200), (220), (311), and (222) planes, where (200) is the most intense plane of diffraction [35,36]. CaO presented diffraction peaks of CaO at (2θ) 32.4° (111), 37.5° (220), 54° (220), 64.2° (311), 67.6° (222), 80° (400), and 88.7° (331) [37,38]. Peaks of calcium hydroxide with low intensity were also observed. Kumar et al. [38] associated the formation of calcium hydroxide with the high spontaneous activity of CaO in a mixture of atmospheric air, which can produce calcium hydroxide and calcium carbonate. XRD of SrO exhibited diffraction peaks at (2θ) 30°, 35°, 50°, 60°, 62.3°, 73°, 81.5°, and 84°, which refers to (111), (200), (220), (311), (222), (400), (331), and (420) planes, with (200) being the most intense peak [39].

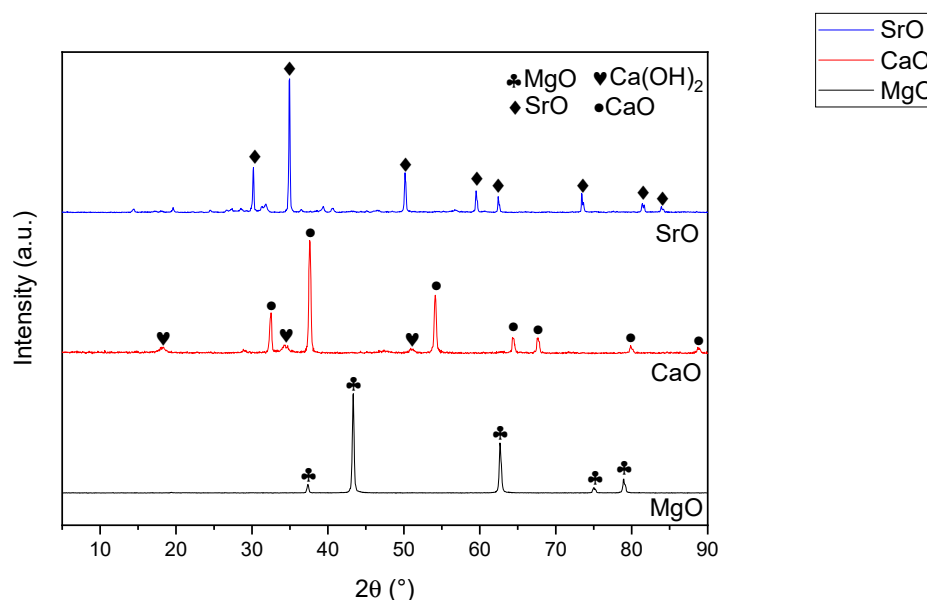


Figure 6. XRD patterns of MgO, CaO, and SrO.

The XRD of the four different supports (SiO₂, ZSM-5, K-10, and MCM-41) are depicted in Figure 7, as well as the CaO-supported catalysts. In Figure 7A, the catalyst with 20% CaO showed the same amorphous profile as the support (JCPDS 29-0085), without diffraction peaks referring to CaO; it could indicate that the active phase is well dispersed on the support [40].

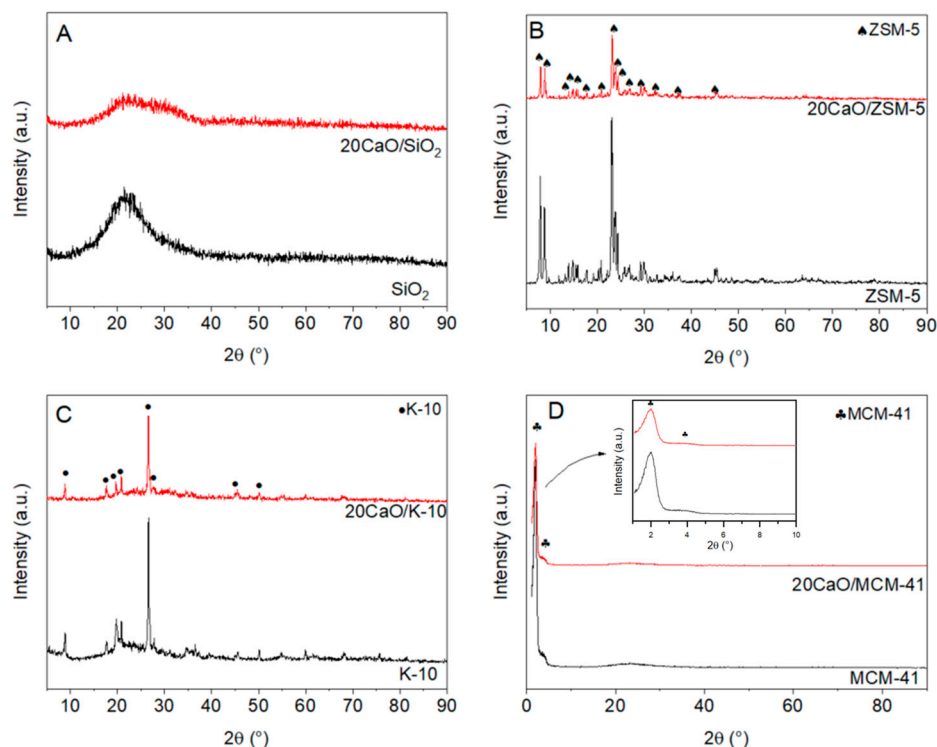


Figure 7. XRD patterns of support and supported catalysts (A) SiO_2 , (B) ZSM-5, (C) K-10, and (D) MCM-41.

In Figure 7B, it is possible to observe diffraction peaks characteristic of ZSM-5 (JCPDS 44-0003) at 2θ angles of 7.8° , 8.6° , 23° , 23.8° , and 24.2° , corresponding to the diffraction planes (011), (020), (051), (303), and (313), indicative of its crystalline nature [41]. For the catalyst impregnated with 20% CaO, no significant alteration in the crystalline structure was detected. However, a reduction in the intensity of the diffraction peaks was observed, implying a uniform dispersion of CaO within the zeolite matrix [42].

Figure 7C presents the X-ray diffractograms of montmorillonite K-10 and the catalyst impregnated with calcium oxide. K-10 is a commercial clay derived from a Bavarian bentonite that was activated with a mineral acid at high temperature, resulting in ion exchange and extraction of Fe and Mg [43]. K-10 shows diffraction peaks at 2θ angles of 20.8° , 26.6° , 36.5° , and 45.7° , corresponding to the quartz phase (hexagonal SiO_2) with crystallographic planes (100), (101), (110), and (201) (JCPDS 46-1045) [44]. It is possible to observe that the crystalline structure of K-10 remains upon impregnation with 20% CaO.

Figure 7D illustrates the X-ray diffractograms of MCM-41 and the $20\text{CaO}/\text{MCM-41}$. In the MCM-41 materials, a distinct peak is observed at a 2θ angle of 2.32° , corresponding to the (100) plane (JCPDS 29-0085), which is characteristic of the mesoporous structure of the support [45]. Furthermore, a secondary peak at 3.96° is detected, corresponding to the (110) plane, indicative of the well-ordered mesoporous framework [46]. Additionally, no peaks corresponding to the crystalline phase of calcium oxide were detected in any of the catalysts, which might be attributed to its high dispersion within the support matrix. For all the catalysts, the impregnation procedure led to a significant reduction in the diffraction peak intensities, associated with a partial covering of the corresponding structures.

The diffractograms of the catalysts with different CaO contents supported on $\gamma\text{-Al}_2\text{O}_3$ are displayed in Figure 8. $\gamma\text{-Al}_2\text{O}_3$ support exhibits broad diffraction peaks at 2θ angles of 38.0° , 46.0° , and 66.6° attributed to planes (311), (400), and (440), respectively (JCPDS 29-0063) [47–49]. Catalysts with low CaO content (5 and 10% CaO) showed the same diffraction profiles, similar to the one presented by the support, with no peak related to CaO. With the increase in CaO content in catalysts (from 20 to 60% CaO), diffraction peaks related to CaO (JCPDS 48-1467) at 32.2° , 37.4° , 54.0° , 64.1° , 67.5° , 79.6° , and 88.5°

are present. These peaks are consistent with the crystallographic planes (111), (220), (220), (311), (222), (400), and (331) [38]. Waisi et al. [50] evaluated different calcium oxide contents impregnated on γ - Al_2O_3 and observed the formation of peaks related to CaO from the 5 wt% of CaO. Zhu et al. [51] assessed the synthesis of CaO catalysts impregnated on γ - Al_2O_3 and observed that the formation of CaO occurs on the catalyst surface up to 800 °C. In contrast, at higher temperatures, the formation of calcium aluminate takes place.

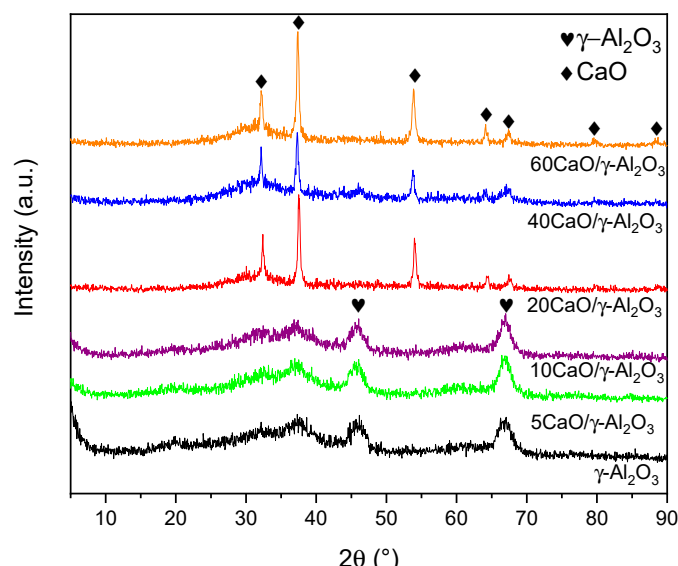


Figure 8. XRD patterns of support and catalyst supported on γ - Al_2O_3 .

3.2.2. X-ray Fluorescence

From XRF results (Table 1), it was possible to observe that the composition of the supported catalysts was close to the nominal composition. This reinforces the presence of CaO on the catalysts, although no CaO peaks were observed in the XRD analysis.

Table 1. Chemical composition (wt.%) of the supported catalysts.

Catalysts	CaO
20CaO/SiO ₂	18
20CaO/MCM-41	18
20CaO/ZSM-5	19
20CaO/K-10	20
5CaO/ γ - Al_2O_3	5
10CaO/ γ - Al_2O_3	9
20CaO/ γ - Al_2O_3	22
40CaO/ γ - Al_2O_3	41
60CaO/ γ - Al_2O_3	57

3.2.3. N₂ Physisorption

The textural properties, such as specific surface area, pore volume, and pore diameter of the supports and catalysts, are presented in Table 2. N₂ adsorption–desorption isotherms are presented in the Supplementary Material. The surface area of the catalyst, excluding the micropores, is defined as the external surface area. This includes the surface of mesopores and small macropores as well as the external surface due to small particle sizes. For the alkaline earth oxides, low values of specific area and pore volume were obtained, which is typical for these oxides [52].

Table 2. Textural properties of the supports and catalysts.

Supports/Catalysts	External Surface Area (m ² ·g ^{−1})	Micropore Area (m ² ·g ^{−1})	Pore Volume (cm ³ ·g ^{−1})	Pore Size (Å)
MgO	13	-	0.033	112
CaO	6	-	0.029	193
SrO	1	-	0.002	376
SiO ₂	136	52.0	0.238	69
MCM-41	160	435	0.209	43
ZSM-5	60	288	0.116	21
K-10	177	-	0.348	176
γ-Al ₂ O ₃	198	-	0.951	136
20CaO/SiO ₂	54	26.5	0.375	280
20CaO/MCM-41	20	70	0.090	36
20CaO/ZSM-5	58	-	0.014	48
20CaO/K-10	56	-	0.156	105
5CaO/Al ₂ O ₃	141	-	0.622	178
10CaO/Al ₂ O ₃	118	-	0.547	182
20CaO/Al ₂ O ₃	55	-	0.133	182
40CaO/Al ₂ O ₃	34	-	0.077	201
60CaO/Al ₂ O ₃	5	-	0.025	298

The five different supports for CaO were carefully chosen to reach different textural properties. N₂ adsorption–desorption isotherm of ZSM-5 (Figure S1A) shows a type I pattern, characteristic of microporous material [53]. N₂ adsorption–desorption isotherm of MCM-41 (Figure S2A) exhibits a type IV pattern, with a slight hysteresis, attributed to narrow cylindrical mesopores less than ~4 nm [54]. K-10 also presents a N₂ adsorption–desorption isotherm of type IV, but with type II characteristics, indicating a mesoporous material with a high external surface (Figure S3A); its H3 hysteresis, with the looping at P/P₀ from 0.4 to 1.0, is associated with lamellar material [43,55]. SiO₂ and γ-Al₂O₃ are mesoporous, since the N₂ adsorption–desorption isotherms (Figure S4A and Figure S5A) are type IV, related to mesoporous materials, with a hysteresis at high P/P₀. They also present some features of type III, associated with macroporous materials, which is consistent with the presence of large mesopores. All of the CaO-supported catalysts presented lower specific surface areas compared to the bare support. This is related to the high content of CaO and CaO anchorage on the support surface, decreasing the porous character of the support. The increase in pore diameter of the supported catalysts may be attributed to several factors, such as the structural alterations due to the calcination procedure and the relatively reduced resistance of mesoporous silica to the pronounced basicity of CaO [56]. For MCM-41, there was a significant decrease in total area, and especially in the micropore area associated with pore blockage by CaO, and also the partial collapse of the structure, possibly related to the high basicity of CaO and high treatment temperature.

The N₂ adsorption–desorption isotherms of CaO-supported catalysts (Figures S1–S5) are similar to the bare support ones, except for ZSM-5 and MCM-41 (Figures S1 and S2). 20CaO/ZSM-5 and 20CaO/MCM-41 presented adsorption up to high P/P₀, implying the formation of a monolayer–multilayer adsorption mode. It may be associated with the presence of some macropores or even with nonporous solids [53]. This is way more pronounced for 20CaO/ZSM-5, leading us to wonder how the deep structure was broken; this is consistent with the XRD results, which showed a decrease in peak intensity, meaning crystallinity had significantly decreased. The impregnation procedure promotes an increase in the pore size of materials, except for MCM-41 support, which indicates that the small pores are being blocked or occluded by CaO species.

Figures S17–S21 show the pore size distributions of the supports and catalysts. It can be observed that the microporous structure of ZSM-5 is altered by the presence of CaO. Since CaO has a larger pore size, its deposition on the zeolite, which originally had

smaller pores, results in an overall increase in pore size as CaO is mainly present on the external surface of the support. Unlike ZSM-5, the pore size distribution of MCM-41 is not significantly affected by the impregnation of CaO, indicating that MCM-41 mesoporous structure is more resistant to changes caused by CaO deposition. The impregnation of CaO on K-10 results in a slight change in pore distribution, with a decrease in average pore size. This effect can be associated with the deposition of CaO in the lamellar structure of K-10, partially blocking or narrowing these passages. For SiO₂, the impregnation of CaO caused an increase in pore size, which can be attributed to the deposition of CaO within the pore network of SiO₂, potentially leading to the partial blockage of smaller pores and a reorganization of the overall pore structure. It is observed that an increase in the CaO content on γ -Al₂O₃ leads to a progressive increase in pore size, which may be related to the deposition of CaO on the internal pore surfaces, causing a restructuring of the γ -Al₂O₃ porous network.

3.2.4. CO₂-TPD

CO₂-TPD analysis was performed to investigate the basicity of the catalysts. The strength of basicity is correlated with the temperature of desorption peaks. In this work, weak basic sites are associated with desorption between 100 and 250 °C, moderate basic sites at 250–500 °C, and strong basic sites with desorption above 500 °C [57]. The number of basic sites and the distribution of the basic strength were obtained by peak deconvolution performed using the multi-peak Gaussian fit (Table 3).

Table 3. Total amount and distribution of basic sites, calculated from CO₂-TPD profiles.

Supports/Catalysts	Total Amount of Basic Sites ($\mu\text{mol} \cdot \text{g}^{-1}$)	Distribution of Basic Sites (%)		
		Weak	Medium	Strong
MgO	35	27.1	19.6	53.3
CaO	310	0	0	100
SrO	650	0	0	100
SiO ₂	18	4.2	61.2	34.6
MCM-41	14	1.8	0	98.2
ZSM-5	35	4.3	18.9	76.8
K-10	21	44.5	55.5	0
γ -Al ₂ O ₃	24	7.8	52.6	39.6
20CaO/SiO ₂	25	3.0	28.2	68.8
20CaO/MCM-41	80	94.3	0.5	5.2
20CaO/ZSM-5	44	18.6	20.4	61.0
20CaO/K-10	88	7.0	82.8	10.2
5CaO/ γ -Al ₂ O ₃	65	13.2	83.0	3.8
10CaO/ γ -Al ₂ O ₃	136	32.0	37.7	30.3
20CaO/ γ -Al ₂ O ₃	251	34.7	5.2	60.1
40CaO/ γ -Al ₂ O ₃	384	12.1	4.3	83.6
60CaO/ γ -Al ₂ O ₃	500	2.7	5.7	91.6

According to the CO₂ profiles (Figure 9), MgO presented weak, moderate, and strong basic sites, while CaO and SrO showed only strong basic sites. Concerning the supports used in this work, they were used in several different reactions in our research group and, as previously published, they have an acidic nature, except γ -Al₂O₃, which has an amphoteric characteristic. The total acidity of the supports, measured by NH₃-TPD, is presented in Table S1. The presence of acid sites significantly affects the basic sites of CaO, as can be seen in CO₂-TPD profiles of the catalysts (Figure 9), and in the total amount of basic sites when compared to pure CaO (Table 3).

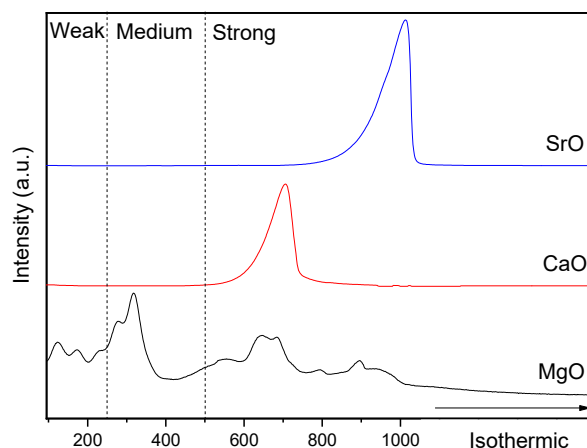


Figure 9. CO₂-TPD profiles of MgO, CaO, and SrO.

It is possible to observe deep changes in the CO₂-TPD profiles of SiO₂, ZSM-5, K-10, and MCM-41 after CaO impregnation (Figure 10), with the appearance of desorption peaks at higher temperatures (except for MCM-41), followed by increases in the total amount of basic sites ($\mu\text{mol}\cdot\text{g}^{-1}$), depicted in Table 3.

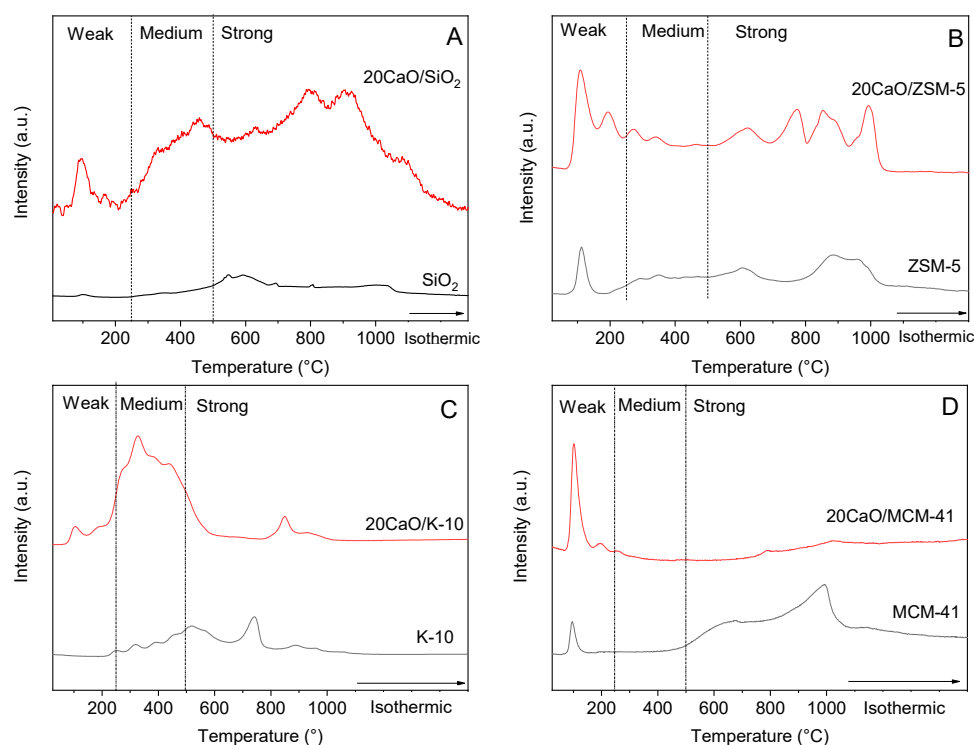


Figure 10. CO₂-TPD profiles of the supports and catalysts: (A) SiO₂, (B) ZSM-5 (C) K-10, and (D) MCM-41.

Figure 11 presents the CO₂-TPD profiles of CaO catalysts supported on $\gamma\text{-Al}_2\text{O}_3$. Since 20CaO/ $\gamma\text{-Al}_2\text{O}_3$ presented higher basicity among the evaluated catalysts, a wide range of CaO/ $\gamma\text{-Al}_2\text{O}_3$ catalysts were prepared. As expected, the higher the CaO content, the higher the number of basic sites. As the CaO content continued to rise from 5 to 60%, a progressive increase in basicity was also observed. Additionally, the strength of the basic sites was also affected, since the concentration of strong basic sites increased with the CaO content.

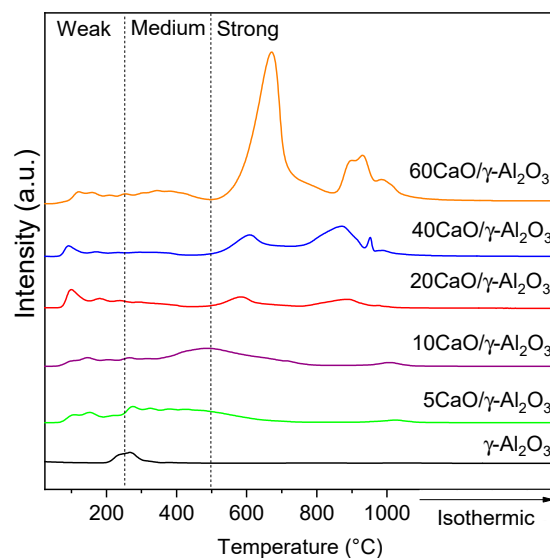


Figure 11. CO₂-TPD profiles of the catalysts supported on Al₂O₃.

3.2.5. Scanning Electron Microscopy

SEM images of the CaO catalysts are presented in Figures S6 and S7. The K-10 materials (Figure S6A,E) exhibited a lamellar structure [58] before and after impregnation with CaO, consistent with XRD data indicating no structural changes. Similarly, the other supports displayed analogous profiles. MCM-41 materials (Figure S6B,F) presented spherical particles of the support that remain after CaO impregnation [59]. ZSM-5 materials (Figure S6C,G) maintained their characteristic hexagonal structure of the zeolite matrix [60]. In contrast, amorphous SiO₂ displayed an irregular shape regardless of whether it was impregnated [61]. γ -Al₂O₃ micrographs (Figure S7A–F) presented a heterogeneous distribution showing irregular shape [62]. The EDS mapping images of elements (calcium, aluminum, silicon, and oxygen) are presented in Figures S8–S16, where each colored dot represents an atom or a cluster of atoms related to the analyzed element. These analyses show the CaO dispersed as homogenous particles in all supports. In addition, and as expected, the increment in CaO content in catalysts supported on γ -Al₂O₃ exhibits a higher density of colored dots in the image, associated with more CaO particles on the catalyst surface.

3.3. Reusability Test

Since the best results were obtained with the 60CaO/ γ -Al₂O₃ catalyst, it was tested in several sequential reactions to evaluate its stability. After each reaction, the catalyst was recovered by centrifugation, dried overnight at 100 °C, and then calcined at 700 °C to remove possible organic material deposited on the active sites. Figure 12 presents the results of the recycling tests for the 60CaO/ γ -Al₂O₃ catalyst. A significant decrease in glycerol conversion was observed over successive cycles. This decline in catalytic performance is attributed to the formation of mayenite, as shown in the XRD patterns of the used catalysts (Figure 13) and the leaching of CaO. It is well established that mayenite possesses a low specific surface area [63–65] that hinders the adsorption of reactants on the catalyst surface, thereby affecting catalytic activity. The leaching process resulted in a reduction of the CaO content to 45% after five reaction cycles, evaluated by EDS analysis. Using a hydrocalumite, Granados-Reyes et al. [66] associated the reduction in conversion and selectivity values with the leaching of the catalyst. Li and Wang [67] evaluated Ca alkali solids as catalysts to synthesize GlyC from the transesterification of glycerol and observed that the mass recovered in recycling tests was lower compared to the initial one. The change in mass was attributed to the leaching of Ca²⁺ in the reaction medium. Zheng et al. [13] evaluated the stability of mixed oxides derived from hydrocalumite as a catalyst for glycerol transesterification. They observed changes in the crystalline structure

associated with the loss of the active phase, and ICP analyses corroborated CaO leaching. Despite the conversion drop, selectivity is still stable from reaction 3. To better understand the reasons for catalyst deactivation, XRD of the used catalyst was performed and is presented as follows:

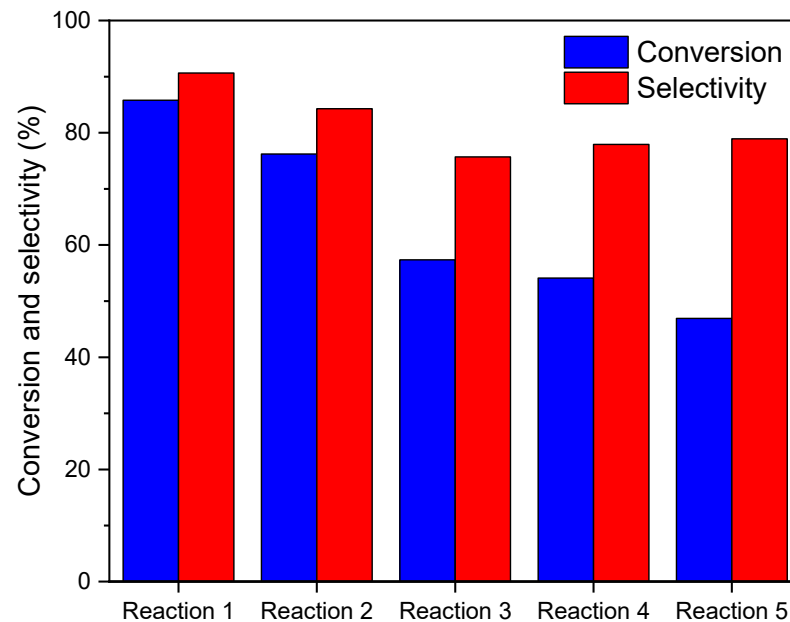


Figure 12. Recycle tests for the 60CaO/ γ -Al₂O₃ catalyst. Reactions performed at 130 °C, 1:3 for gly/DEC with 10 wt% catalyst.

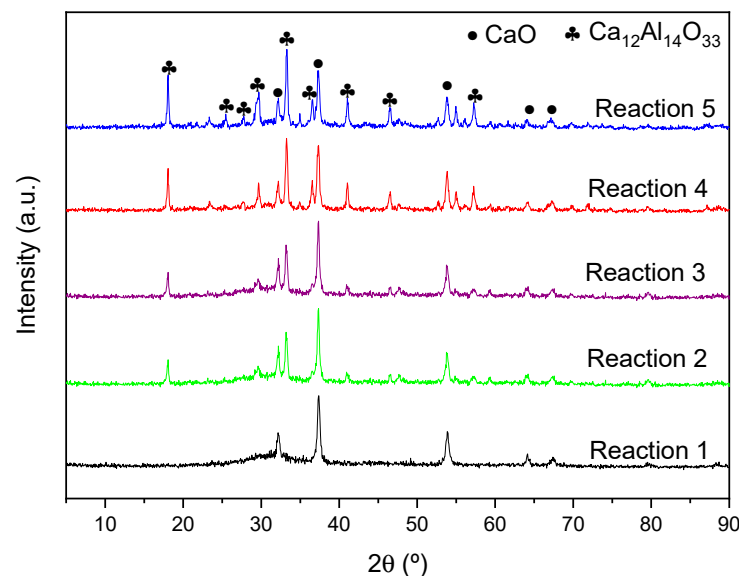


Figure 13. XRD patterns of the 60CaO/ γ -Al₂O₃ catalyst evaluated in recycle tests.

Figure 13 presents the XRD patterns of the catalysts subjected to recycling tests. A significant observation is the formation of the mayenite phase during the recycling tests. The emergence of these peaks indicates that some degree of phase transformation occurs during the recycling process. This transformation could be attributed to the interaction between CaO and γ -Al₂O₃ during the calcination process to recover the catalyst. Despite the formation of mayenite, it is noteworthy that the crystallite size of CaO remained unchanged throughout the recycling tests (233 ± 14 Å before the first reaction and 244 ± 20 Å after reaction 5, using the peak at 37.4°). This constancy in crystallite size sug-

gests that the core structural integrity of the CaO component is maintained, even though new phases like mayenite form. To extend the catalyst's life, it is important to implement a more thorough regeneration process. This may involve milder calcination conditions or targeted chemical treatments to effectively remove organic residues and restore the active sites, thus preserving the catalyst activity. Additionally, surface modification, such as coating the catalyst with a thin layer of stable material, presents a promising strategy to mitigate leaching.

4. Conclusions

In this study, a series of heterogenous catalysts were assessed for the production of glycerol carbonate from glycerol and DEC. Catalysts based on oxides of different alkaline earth metals were tested, with CaO and SrO showing the highest yields of glycerol carbonate, since they presented superior overall basicity and higher concentrations of strong basic sites than MgO.

CaO was chosen to be supported on different materials (ZSM-5, K-10, MCM-41, SiO₂, and γ -Al₂O₃). Concerning the influence of support porosity, mesoporous materials presented better catalytic performance when compared to microporous materials, indicating that textural properties, especially pore volume, play an important role in glycerol transesterification to glycerol carbonate. The production of glycerol carbonate is directly related to catalyst basicity: the higher and stronger the basicity, the higher the glycerol conversion.

When CaO is supported on γ -Al₂O₃, glycerol conversion and GlyC selectivity increase with the CaO content due to the increase in total basicity. Among the supported catalysts, the 60CaO/ γ -Al₂O₃ catalyst displayed remarkable performance, achieving high conversion (86%) and selectivity to GlyC (91%). 60CaO/ γ -Al₂O₃ fitted well as a catalyst for the production of GlyC using DEC, especially due to its relatively low cost and straightforward synthesis method. Furthermore, it exhibited good stability during the initial three recycling reactions. Given the outstanding performance of the 60CaO/ γ -Al₂O₃ catalyst, further evaluation under varying reaction conditions, such as temperature, glycerol/DEC ratio, and catalyst loading, should be conducted to optimize its application.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/pr12102256/s1>, Table S1: Total amount and distribution of basic sites, calculated from NH₃-TPD profiles, Figure S1: N₂ adsorption–desorption isotherms of (A) ZSM-5 and (B) 20CaO/ZSM-5, Figure S2: N₂ adsorption–desorption isotherms of (A) MCM-41 and (B) 20CaO/MCM-41, Figure S3: N₂ adsorption–desorption isotherms of (A) K-10 and (B) 20CaO/K-10, Figure S4: N₂ adsorption–desorption isotherms of (A) SiO₂ and (B) 20CaO/SiO₂, Figure S5: N₂ adsorption–desorption isotherms of (A) γ -Al₂O₃, (B) 5CaO/ γ -Al₂O₃, (C) 10CaO/ γ -Al₂O₃, (D) 20CaO/ γ -Al₂O₃, (E) 40CaO/ γ -Al₂O₃, and (F) 60CaO/ γ -Al₂O₃, Figure S6: SEM images of the catalysts (A) K-10, (B) MCM-41, (C) ZSM-5, (D) SiO₂, (E) 20CaO/K-10, (F) 20CaO/MCM-41, (G) 20CaO/ZSM-5, and (H) 20CaO/SiO₂, Figure S7: SEM images of Al₂O₃ catalysts. (A) Al₂O₃, (B) 5CaO/Al₂O₃, (C) 10CaO/Al₂O₃, (D) 20CaO/Al₂O₃, (E) 40CaO/Al₂O₃, and (F) 60CaO/Al₂O₃, Figure S8: SEM/EDS images of 20CaO/K-10 catalyst, Figure S9: SEM/EDS images of 20CaO/MCM-41 catalyst, Figure S10: SEM/EDS images of catalyst 20CaO/SiO₂ catalyst, Figure S11: SEM/EDS images of 20CaO/ZSM-5 catalyst, Figure S12: SEM/EDS images of 5CaO/ γ -Al₂O₃ catalyst, Figure S13: SEM/EDS images of 10CaO/ γ -Al₂O₃ catalyst, Figure S14: SEM/EDS images of 20CaO/ γ -Al₂O₃ catalyst, Figure S15: SEM/EDS images of 40CaO/ γ -Al₂O₃ catalyst, Figure S16: SEM/EDS images of 60CaO/ γ -Al₂O₃ catalyst, Figure S17: Pore size distribution of (A) ZSM-5 and (B) 20CaO/ZSM-5, Figure S18: Pore size distribution of (A) MCM-41 and (B) 20CaO/MCM-41, Figure S19: Pore size distribution of (A) K-10 and (B) 20CaO/K-10, Figure S20: Pore size distribution of (A) SiO₂ and (B) 20CaO/SiO₂, Figure S21: Pore size distribution of (A) γ -Al₂O₃, (B) 5CaO/ γ -Al₂O₃, (C) 10CaO/ γ -Al₂O₃, (D) 20CaO/ γ -Al₂O₃, (E) 40CaO/ γ -Al₂O₃, and (F) 60CaO/ γ -Al₂O₃.

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