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CO<sub>2</sub> role on the glycerol conversion over catalyst containing CaO-SiO<sub>2</sub> doped with Ag and Pt

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Graphical abstract







Highlights

- CaO-SiO<sub>2</sub> based catalysts produce useful chemicals from glycerol in the gas phase reaction.
- Ca(OH)<sub>2</sub> sites play an important role for the acetic acid formation.
- CO<sub>2</sub> has effect over the catalytic performance by forming CaCO<sub>3</sub>.
- Pt addition improve the hydrogen transfer modifying the selectivity.

#### Abstract

Solids with strong base sites of calcium-silica mixed oxides (CaO-SiO<sub>2</sub>), and zirconia (ZrO<sub>2</sub>), both doped with platinum (Pt) or argentum (Ag), were synthesized and catalytically evaluated in the dehydration of glycerol for valuable chemical intermediates production. The samples were characterized by X-ray diffraction (XRD), Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy (SEM-EDS), Basicity measurements by CO<sub>2</sub> temperature programmed desorption (CO<sub>2</sub>-TPD), thermal analyses (TG/DTA) and N<sub>2</sub> adsorption–desorption isotherms. The effect of two different carrier gas, inert (N<sub>2</sub>) or a soft oxidant (CO<sub>2</sub>) over the activity and selectivity were evaluated in glycerol dehydration for all the samples. The high affinity between Ca and glycerol has effect over the product selectivity, which shows CO<sub>2</sub> effect. The promotion with Ag or Pt (0.2wt%) increase the glycerol conversion and change the product selectivity. The data points out to the hydrogen transfer improving due to the Pt presence. Both, Pt or Ag doping or CO<sub>2</sub> addition as the carrier gas may inhibit the acetic acid production, over calcium containing catalyst. The promotion of ZrO<sub>2</sub> with Ag or Pt play a less marked effect over the glycerol conversion, under CO<sub>2</sub> or N<sub>2</sub>.

Keywords: glycerol, CaO, CO<sub>2</sub>, dehydration.

#### 1. Introduction

The change of the world energy matrix toward renewable sources, which is being implemented, is necessary and very important to improve the quality of life of the world population [1,2]. The research in this sense is motived by the expectation of a decline in oil reserves [3,4], and the need to minimizing the environmental impacts inherent to the transfer and use of energy processes [5,6]. The biomass using, or the biomass derived materials, to produce chemicals or fuels is an excellent alternative to oil reserve [7,8], since it is considered a neutral carbon dioxide source. Worldwide, the biodiesel play a crucial role in this context [9,10]. However, despite the actual development stage of the biodiesel using, it is not economically feasible [11,12]. Research toward the use of the by-product (glycerol), to synthesize chemicals with high added value can change the perspective of the biodiesel economy [13–15]. Actually, the glycerol is applied in various industrial process [2,16,17]; however, due to its chemical structure it is considered an excellent raw material for a wide range of chemicals with high added-value [18,19].

The glycerol, similarly to ethanol, may be used for hydrogen production, which is interesting from energetic and environmental point of view [12,20–24]. It is known that a high hydrogen to carbon (H/C) ratio make the feedstock more attractive for the H<sub>2</sub> production. The glycerol has a lower H/C ratio, if compared with ethanol and methane, which are 8/3, 3 and 4, respectively. Consequently, the CO<sub>2</sub> amount produced for the glycerol steam reforming is high [25]. However, it have been shown that a high-purity H<sub>2</sub> generation by steam reforming is achieved by using a catalyst with simultaneous CO<sub>2</sub> removal [20,21,24,26]. Therefore, despite the low H/C ratio, the glycerol may play an important role on the H<sub>2</sub> market.

The synthesis of liquid chemical products from glycerol generally is carried out under heterogeneous catalytic process, such as dehydration and/or dehydrogenation reaction, which

make use of solids with acidic properties [19,27,28]. Catalysts such as Al<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, WO<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub> and zeolites, are active to produce acrolein by glycerol dehydration [29]. Recent studies have shown that the use of a catalyst comprising of bifunctional metals, i.e., containing acid/base and redox sites have high activity and selectivity compared to other monometallic systems for glycerol conversion to fuels and chemicals products [13,30,31].

On the other hand, copper based catalysts, such Cu/SiO<sub>2</sub> or Cu/Al<sub>2</sub>O<sub>3</sub> and Cu/Cr<sub>2</sub>O<sub>3</sub> [13,19,32] present a high selectivity to acetol, a product of glycerol dehydration or dehydrogenation process. The acetol, is an interesting compound, since it present various application in industrial processes [33]. Due to its high reactivity, acetol plays a key role as an intermediate substance in organic synthesis and also as a starting material in some chemical reactions, including dehydration, dehydrogenation, hydrogenation, oxidation and polymerization [34–37].

As previously mentioned, the glycerol structure ( $C_3H_8O_3$ ), a C3 molecule with 3 O-H group, make it a high reactivity raw material. Therefore, the catalytic mechanism for the glycerol transformation may be more complex than the suggested until now. The proposed reaction mechanism for the dehydration process suggest the acrolein as the main product for the Brönsted acid sites [1,38]. However, the Lewis acid/base pair can produce mainly acetol [14,19]. Additionally, the action of redox catalytic sites is also suggested to favour the acetol production [13,39].

A base catalytic sites can play an important role in the process, since the mechanism proposed consider the action of the Lewis acid/base pair [39–42]. On the other hand, few works make use of solids with basic properties for the glycerol conversion. Using solid catalytic with various composition such, hydrocalcite containing sodium aluminate, calcium oxide or magnesium hydroxide, researches have been carried out the glycerol conversion in a liquid medium, aiming the synthesis of glycerol carbonate, 1,2 propanediol, glyceric acid or lactic acid

[43–47]. The solid base catalyst play an important role in the glycerol oxidation, since it can replace the sodium hydroxide, making the process more practical for industrial application. Despite the rapidly adsorption of  $H_2O$  and  $CO_2$  from the air at CaO surface [48], the high affinity between CaO and glycerol observed by various researchers [47,49,50], may be explored for the glycerol conversion process. However, in order to decrease the residence time and consequently decreasing the selectivity for condensation products, it is interesting to carry out the process in the gas phase.

Therefore, considering the previous reports, in this work we present the investigation of the catalytic reactivity and selectivity of the calcium-silica mixed oxide and zirconia, both doped with Pt or Ag, on the glycerol dehydrogenation/oxidation reaction. The process was carried out in the gas phase under inert (N<sub>2</sub>) or a soft oxidant (CO<sub>2</sub>) flow gas, to evaluate the effect over the products selectivity. These data may help in the elucidation of the mechanism process of the glycerol transformation over the base sites on catalyst containing calcium oxide. In addition, results from the amphoteric solid (ZrO<sub>2</sub>) performance are shown, in order to evidence the CO<sub>2</sub> effect over the catalytic process. Then, under the light of the results presented by various researchers previously and the data presented in this paper, it is proposing a reaction pathway for the glycerol transformation with participation of solid base catalyst.

#### 2. Experimental

#### 2.1. Catalyst preparation

The syntheses of the supports of calcium-silica (CaO-SiO<sub>2</sub>) mixed oxides and zirconia was performed based on the polymeric precursor method previously described [51,52]. The method consists on the chelation of cations (metals) by citric acid (CA) in a water solution with subsequent polyesterification reaction of the remaining carboxylic acid groups with ethylene glycol (EG).

Calcium carbonate, tetraethylorthosilicate (TEOS, Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>), zirconium acetate, citric acid monohydrate (CA) {C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>.H<sub>2</sub>O} and ethylene glycol (EG) {C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>} were used as starting chemicals.

The CaO-SiO<sub>2</sub> sample was prepared as follows: CA (0.369 mol) was dissolved in 100 ml of water. Separately, the calcium carbonate (0.738 mol) was dissolved in 50 ml of HNO<sub>3</sub> aqueous solution. Always under stirring, the calcium solution and TEOS (0.369 mol) were added in the CA solution and kept for 15 min at 50 °C. EG (1.476 mol) was subsequently added to the solution. After polymerisation at 100 °C under stirring, the viscous resin was heat-treated at 350 °C for 3 h in a muffle furnace. The resulting precursor compound was ground and heat-treated at 700 °C for 2 h under airflow. Similar synthesis conditions were used to prepare the ZrO<sub>2</sub> sample, but using a EG/CA/metal molar ratio of 1:1:1.

The Pt or Ag incorporation over CaO-SiO<sub>2</sub> mixed oxide and ZrO<sub>2</sub>, was carried out by wet impregnation method. An aqueous solutions of potassium hexachloroplatinate, ( $K_2$  [Pt(Cl)<sub>6</sub>]) and silver nitrate (AgNO<sub>3</sub>) containing appropriate amount of the precursors salts to obtain 0.2 wt.% of Pt or Ag was added for supports impregnation. The mixture, support oxide and the metal solution (Pt or Ag), was placed in a rotary evaporator and, under constant vacuum at 70 °C the water was extracted. After the sample drying at 100 °C for 8 h, the calcination was carried out in a muffle furnace at 700 °C for 2 h under airflow. The samples were prepared to achieve a composition of 0.2 wt.% (percentage by mass of Pt or Ag) loaded on the CaO-SiO<sub>2</sub> or ZrO<sub>2</sub> oxides and, Ca/Si molar ratio of 2.

#### 2.2. Catalyst characterization

The crystalline structure of the solids was characterized by X-ray diffraction (XRD) using XPert – Panalytical diffractometer operated at 40 kV and 40 mA employing Cu-K $\alpha$  radiation source ( $\lambda = 1.5406$  Å). The experiments were performed at high diffraction angles (from 10 to

90°). Using the software X-Pert HighScore Plus® (PANalytical), the crystalline phases were identified, and the crystallographic data for all phases were determined using the Inorganic Crystal Structure Database (ICSD).

Textural properties of the catalysts were determined by adsorption/desorption isotherms at -196 °C on a Quantachrome instrument, Autosorb-1B model. The samples were degassed at 200 °C prior to the measurement. The specific surface area of the samples was determined using the BET method. The pore size distribution was derived from the adsorption branches of the isotherms using the Barrett–Joyner–Halenda (BJH) method. Scanning electron micrographs (SEM) were recorded using a TESCAN VEGA XMU electron microscope equipped with an EDS Bruker QUANTAX system coupled to the SEM microscope. The acceleration voltage of 20 kV was used. Prior the analysis, the powder samples were dispersed on conductive carbon strip placed on an aluminium sample holder and sputtered with gold.

The presence of base sites were determined by temperature-programmed desorption of CO<sub>2</sub> (TPD - CO<sub>2</sub>) experiments. Prior to TPD, the samples were heat treated under He flow (20 mL min<sup>-1</sup>) at 700 °C for 30 min and cooled under the same gas flow to 25 °C. CO<sub>2</sub> adsorption was carried out by using a flow of pure CO<sub>2</sub> through the reactor for 30 min at 25 °C. After baseline stabilization under He flow (20 mL min<sup>-1</sup>) at room temperature, the CO<sub>2</sub>-TPD run was carried out with a heating rate of 10 °C min<sup>-1</sup> from room temperature up to 700 °C. The CO<sub>2</sub> desorption was monitored using a thermal conductivity detector (TCD).

The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the spent catalyst samples were performed in a Shimadzu DTA-60H equipment to examine the amounts of carbon deposits. The measurements were made under airflow (40 ml/min) from room temperature to 800 °C, with a heating rate of 10 °C/min.

#### 2.3. Catalytic activity

Catalytic tests were carried out in a fixed bed flow reactor at atmospheric pressure using 0.100 g of catalyst. Previously, the samples were activated at 700 °C under H<sub>2</sub> flow of 20 mL/min. The catalytic reaction was carried out at 280 °C under different carrier gas, inert (N<sub>2</sub>) or a soft oxidant (CO<sub>2</sub>), for all the samples. The aqueous solution of 5wt% glycerol was fed to the reactor by means of an injection pump at a flow rate of  $3.6 \text{ cm}^3 \text{ h}^{-1}$ . This experimental condition was used since the CaO in H<sub>2</sub>O presence form Ca(OH)<sub>2</sub>, while the Ca(OH)<sub>2</sub> with CO<sub>2</sub> presence form CaCO<sub>3</sub>. Possibly the Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> phases should present different properties, which may have effect over the catalytic performance.

The reaction mixture was condensed in a cold trap maintained in a bath containing an icewater-salt trap (-15 °C). The main products were identified by GC–MS in a QP 2010 Plus, Shimadzu model, and the quantification was performed using a Simple Chrom GC gas chromatograph equipped with flame ionization detector and DB-5 column (20m x 0.18mm x  $0.4\mu$ m), by using 1,4-butanediol as standard. The glycerol conversion and the main products selectivity were calculated as follow:

$$Conversion(\%) = \frac{c_0 - c_t}{c_0} x 100 \tag{1}$$

Products Selectivity (%) = 
$$\frac{c_{CS}}{c_0 - c_t} x 100$$
 (2)

Where,  $C_0$  and  $C_t$  are the initial and the final amount of glycerol in the reaction mixture, respectively. The  $C_{CS}$  is the amount of chemical substance formed.

#### 3. Results and discussion

#### 3.1. Structural features of the solids by X-ray diffraction (XRD)

The Fig. 1a shows the XRD patterns of the samples containing calcium (Ca<sup>2+</sup>). The calcination temperature of 700 °C is enough to decompose the Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> phases and produce CaO [53]. However, unlike the other samples, the peaks with highest intensity for the sample CaO-SiO<sub>2</sub> correspond to Ca(OH)<sub>2</sub> phase. It is known that the formation of calcium hydroxide from CaO and H<sub>2</sub>O vapour (Eq. 3), is thermodynamically possible up to 400 °C [53].

$$CaO(s) + H_2O(g) \to Ca(OH)_2(s)$$
  $\Delta H^0_{298} = -109kJ/mol$  (3)

Therefore, possibly this high ratio of Ca(OH)<sub>2</sub> phase is due to the higher storage time and the exposition to the atmospheric air humidity [48], before the XRD measurement. In the experimental procedure, the sample was heat treated at 700 °C and cooled to room temperature under atmospheric air. Therefore, despite the high calcination temperature (700 °C), as the formation of CaCO<sub>3</sub> from CaO and CO<sub>2</sub> or Ca(OH)<sub>2</sub> from CaO and H<sub>2</sub>O at atmospheric pressure and ambient temperature are thermodynamically possible [48,54,55], the diffraction peaks are consistent with the experimental conditions used.

On the other hand, the diffractogram of the samples Pt/CaO-SiO<sub>2</sub> and Ag/CaO-SiO<sub>2</sub> shows a low intensity for the peaks corresponding to the Ca(OH)<sub>2</sub> phase, which suggest the formation of CaCO<sub>3</sub> from Ca(OH)<sub>2</sub> after the Ag or Pt impregnation and the new calcination. None of the samples (Pt/CaO-SiO<sub>2</sub>, Ag/CaO-SiO<sub>2</sub>, Pt/ZrO<sub>2</sub> and Ag/ZrO<sub>2</sub>), showed characteristic diffraction peaks of Ag or Pt oxide phases (Fig. 1a and b), suggesting the high dispersion; however, the low weight amount of Pt or Ag in the samples may be the main reason.

Fig. 1b shows the XRD patterns of pure  $ZrO_2$  support and the samples doped with Pt or Ag. Diffraction peaks ascribed to the tetragonal and monoclinic crystalline phases of zirconia are observed in all the samples, which are consistent with the calcination temperature of 700 °C [56].

As cited previously, the absence of Pt or Ag diffraction peaks is due to low content of Pt and Ag in the sample composition (0.2 wt.%).



**Fig. 1.** XRD patterns of the samples calcined at 700 °C on different supports. (a) CaO-SiO<sub>2</sub> mixed oxides and, (b) ZrO<sub>2</sub>.

#### 3.2. Textural properties and SEM-EDS analysis

The  $N_2$  adsorption-desorption isotherms and the corresponding pore size distribution of fresh catalysts are shown in Fig. 2 and 3. The isotherms profile point out to the predominance of macroporous or a non-porous characteristic of the solids [57]. The samples containing calcium oxide displayed isotherms of type III, according to the IUPAC classification (Fig. 2a), which results in a pore size distribution with high volume of  $N_2$  adsorption for pores with larger diameter. The isotherm profile of the sample CaO-SiO<sub>2</sub> present the H3 hysteresis loop, which may be due to the formation of non-rigid particle aggregates, giving rise to slit-shaped pores [57,58].



Fig. 2. N<sub>2</sub> adsorption/desorption isotherms. (a) CaO-SiO<sub>2</sub> mixed oxides and, (b) ZrO<sub>2</sub>, supports.

The silver or platinum addition (Ag/CaO-SiO<sub>2</sub>, Pt/CaO-SiO<sub>2</sub>) lowered the inexpressive hysteresis loop of the CaO-SiO<sub>2</sub> sample (Fig. 2a), which not means the absence of pores. These features of isotherms are typical from macroporous material (type III according to the IUPAC classification).

The synthesis methodology affect directly on the morphological properties of the material. Generally, the using of the sol-gel methods leads to the formation of mesoporous zirconia [59]. However, the N<sub>2</sub> adsorption/desorption isotherms analysis for the zirconia containing samples indicates a process of stacking crystalline plates, giving rise to narrow mesoporous in the form of slits, as indicated by type V isotherms with H4 hysteresis loop obtained for ZrO<sub>2</sub>, Ag/ZrO<sub>2</sub> and Pt/ZrO<sub>2</sub> (Fig. 2b).

Noticeably, the BJH pore size distribution for all the catalysts, reveals a relatively wide pore size distribution, with a significant fraction of pore diameter in the range of 100–300Å, confirming the existence of large mesopores, resulting in a broad pore size distribution (Fig. 3). The addition of Pt or Ag over ZrO<sub>2</sub> support resulted in a decrease of the pore volume, which is perceptible in the pore diameter range of 100–300Å, pointing to the partial filling or obstruction of zirconia pores (Fig. 3b).



**Fig. 3.** Pore size distribution of the samples determined by the BJH model. (a) CaO-SiO<sub>2</sub> and, (b) ZrO<sub>2</sub>, supports.

The specific surface area and the pore volume of the catalysts are summarize in Table 1, and it shows that all the samples present a not meaningful surface area. However, the calcination of the pure CaO-SiO<sub>2</sub> support at 700 °C shows a surface area higher than the value observed normally [60]. This surface area value observed may be due to the SiO<sub>2</sub> effect, which contributed positively for the morphology property of the sample.

Samples	BET surface area	*Pore volume
	$(m^2g^{-1})$	$(cm^3g^{-1})$
CaO-SiO <sub>2</sub>	41	0.47
Ag/CaO-SiO <sub>2</sub>	48	0.51
Pt/CaO-SiO <sub>2</sub>	50	0.43
$ZrO_2$	14	0.13
Ag/ZrO <sub>2</sub>	9	0.07
Pt/ZrO <sub>2</sub>	8	0.09

**Table 1**. Textural properties of the supports and prepared catalysts.

\* Pore volume at  $P/P_0 = 0.99$ .

The samples containing  $ZrO_2$ , despite of the low fraction of mesoporous presence suggested by the low hysteresis loop (Fig. 2), shows a lower surface area and pore volume (Table 1), than the values usually observed [61].

The silver or platinum addition in the sample composition has little effect over the textural properties (Fig. 2, Fig. 3 and Table 1). However, the data suggest that the deposition of Ag or Pt on the CaO-SiO<sub>2</sub> reduces the sintering process of the support, which is emphasized by a small increase of the surface area.

On the other hand, as pointed out by the XRD (Fig. 1a), the samples  $Ag/CaO-SiO_2$  and  $Pt/CaO-SiO_2$  present a low relative intensity for the peaks from the  $Ca(OH)_2$  phase, if compared with CaO-SiO\_2 sample. Therefore, the higher surface area for the samples  $Ag/CaO-SiO_2$  and  $Pt/CaO-SiO_2$  may be due to the lower  $Ca(OH)_2$  presence, which may have effect over the porous availability, since the Ca(OH)\_2 phase present a lower density than CaCO\_3 phase.

The opposing effect is observed for the samples containing  $ZrO_2$ . Although, the real role of silver and platinum over the samples morphologic properties is not clear, all the catalysts

containing  $ZrO_2$  present a hysteresis suppression due to the Ag or Pt addition. Such behaviour has been ascribed to the porous blocking by the Ag or Pt particles [62]. However, the Ag or Pt presence in the composition may also have effect over the crystal grow or particle sintering, which results in a textural property change.

The Fig. 4 shows the SEM micrographs. The samples containing calcium oxide shows a spongy like feature, which is characteristic for the materials synthesized by the Pechini method [63].



Fig. 4. Scanning electron micrographs of the samples after calcination at 700 °C.

This feature may suggests a sample with high surface area. Of course, the porous observed with the SEM magnification of 8000x is far above the diameter of the pores detected by  $N_2$  adsorption isotherms. Therefore, the porous observed in Fig. 4 do not have effect over the hysteresis loop of  $N_2$  adsorption/desorption isotherms.

Silver or platinum addition over the solid sample containing CaO, despite the low magnification does not produce a significant change in the morphologic appearance of the sample, which is consistent with the data presented in Table 1. Having as reference the samples that contain CaO, the SEM micrography of the samples containing ZrO<sub>2</sub> present a material feature with high density, characteristic of the ZrO<sub>2</sub> phase; which suggests a solid with low surface area, being consistent with the Table 1 values and pore diameter distribution (Fig. 3). The low amount of citric acid used in the synthesis procedure (CA:Zr of 1:1), contributes to this feature of the samples containing ZrO<sub>2</sub>, since the organic precursor decomposition is the main process which promotes the porous structure formation [63].

Figs. 5 and 6 shows EDS mapping imagens and spectrum to evaluate the distribution of metals over both supports studied. The EDS mapping imagens of the pure CaO-SiO<sub>2</sub> support and doped with Pt or Ag (Fig. 5), shows a non-homogeneous distribution of the Ca and Si elements on surface. Elemental mapping (EDS) of the materials can provide clear imagens of element distributions, to further clarity the presence of Pt or Ag particles well dispersed. In contrast, the signal is much weaker, which show that the metallic Pt or Ag species are at doping level on surface of the particles. Additionally, during the Pt or Ag impregnation process the Ca(OH)<sub>2</sub> and a fraction of the CaCO<sub>3</sub> may be dissolved, which with the solvent extraction precipitate again. This process should promote a new dispersion of the calcium, which may also partially cover the Pt or Ag particles. However, the EDS spectrum analysis also suggest a decrease of the Ca/Si ratio on the surface samples due to the Pt or Ag impregnation process. Therefore, considering the XRD and

the MEV-EDS, the results point out that a ratio of the calcium is leached out during the impregnation process, which have effect over textural properties, and is consistent with the data presented in Table 1.



**Fig. 5**. EDS mapping images and respective spectrum of the pure CaO-SiO<sub>2</sub> support and doped catalysts with Pt or Ag.

The EDS mapping images and spectrum of the samples ZrO<sub>2</sub> and Ag/ZrO<sub>2</sub> (Fig. 6), similarly to Fig. 4, reveal the formation of large aggregates of zirconium oxide particles. The chemical element Hf present in both samples is due to the contamination of the zirconium acetate solution used as precursor. Although, Zr and Au signals overlapped, and silver can be detected on the Ag/ZrO2 catalyst the majority component is Zr. Unlike the samples containing calcium and siliceous mixed oxide, the EDS image of the sample Ag/ZrO2 suggest a lower dispersion of the

silver over the zirconia surface, since it is possible to visualize small agglomerations, which are highlighted with an arrow.



Fig. 6. EDS mapping images and respective spectrum for ZrO<sub>2</sub> and Ag/ZrO<sub>2</sub> catalysts, respectively.

#### 3.4. Basic properties by CO<sub>2</sub>-TPD measurements

The base properties of CaO-SiO<sub>2</sub> and ZrO<sub>2</sub> samples were investigated by CO<sub>2</sub>-TPD, a commonly used experiment for measure the strength of base sites. It is well known, the affinity of CaO or Ca(OH)<sub>2</sub> to interact with CO<sub>2</sub> [64,65]. Therefore, it is not surprising that CO<sub>2</sub> addition to the reaction mixture results in a catalytic effect under low temperature reaction. The chemisorption of CO<sub>2</sub> also occurs over ZrO<sub>2</sub> [66], therefore the CO<sub>2</sub> presence also may have effect over ZrO<sub>2</sub> catalytic performance. The CO<sub>2</sub>-TPD profiles (Fig. 7), point out to the different base site strength distribution in the CaO-SiO<sub>2</sub> sample with evident two desorption peaks of CO<sub>2</sub> at around 100 and 650 °C, implying the presence of weak and strong base sites [67]. This CO<sub>2</sub> desorption may result from the SiO<sub>2</sub> contribution or effect.

On the other hand, the CO<sub>2</sub>-TPD profile for the sample  $ZrO_2$  shows only a weak CO<sub>2</sub> desorption peak, and at low temperature, which mean a low CO<sub>2</sub> adsorption ability and weak interaction. This CO<sub>2</sub> profile observed for  $ZrO_2$  sample, possibly is a consequence of the high calcination temperature (700 °C), which can decrease drastically the surface area (Table 1) and modify the surface acid-base properties of the  $ZrO_2$  [66]. Therefore, the results from CO<sub>2</sub>-TPD can better to elucidate the catalytic effect produced by CO<sub>2</sub> addition in the reaction mixture, which results are presented below.



**Fig. 7**. Carbon dioxide temperature-programmed desorption (CO<sub>2</sub>-TPD) profiles of the samples. The curves were divided for weak, medium and strong base sites, according to temperature range.

3.5. Catalytic activity

#### 3.5.1. Effect of atmosphere reaction on glycerol conversion

The catalytic activity of all samples was evaluated for the gas phase glycerol conversion at  $N_2$  or CO<sub>2</sub> gas flow (Fig. 8 and 9). The Fig. 8 (a and b) shows a superior initial catalytic conversion

for the samples containing CaO in both reaction atmosphere, which is the result of the interaction of glycerol with the weak and strong basic sites on surface of calcium-silica support. The pronounced deactivation may be ascribed to the Ca(OH)<sub>2</sub> formation, since the reaction of CaO with H<sub>2</sub>O occurs promptly at 280 °C [43]. However, the compounds formation between Ca and glycerol [49] also may contribute to deactivation process, due to a strong interaction.



Fig. 8. Catalytic conversion of glycerol for the samples containing CaO-SiO<sub>2</sub>, at different reaction atmosphere. (a) Reaction carried out under  $N_2$  and (b) CO<sub>2</sub> flow.

It has been reported that acid sites are responsible for the glycerol dehydration activity, while the dehydrogenation reaction of alcohol requires both, strong base sites and weak acid sites [14,19,38,39]. Therefore, the glycerol conversion observed for the sample CaO-SiO<sub>2</sub> under N<sub>2</sub> flow suggests that base solid can catalyse both, dehydration and/or dehydrogenation reactions of glycerol. Additionally, the initial deactivation suggest that the CaO is more active than Ca(OH)<sub>2</sub>. The addition of Ag and Pt on the CaO-SiO<sub>2</sub> catalyst improved the glycerol conversion for the first

hour of time on stream, under  $N_2$  flow. This behaviour is consistent with the superior surface area (Table 1) and redox properties of the catalysts doped with Ag or Pt. Therefore, there is an improvement of the catalytic conversion due to the Pt or Ag addition; but it have no effect over the catalytic stability.

On the other hand, the reaction carried out under  $CO_2$  flow shows a low initial catalytic conversion for all the samples containing calcium oxide (Fig. 8b). It is known that in the experimental condition used here, such as high vapour pressure and  $CO_2$  flow, the CaO undergoes to the CaCO<sub>3</sub> phase. Therefore, the CaCO<sub>3</sub> phase formation is prejudicial to the catalytic activity, and considering the similarity of the deactivation rate of the samples, the CaCO<sub>3</sub> formation, likewise to the Ca(OH)<sub>2</sub>, should result in a partial covering process of the Ag or Pt metals.

The profiles of Fig. 8b, shows that the Ag or Pt addition in the CaO-SiO<sub>2</sub> sample do not produced a meaningful change for the glycerol conversion along the time on stream. These results indicate that, under the experimental conditions used, the Pt or Ag metallic sites are not the main active sites for the glycerol conversion, therefore it is the basicity of the catalysts the key parameter to perform the reaction. By using CO<sub>2</sub> flow, the data points out that the change from CaO to Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> should be the main responsible by the catalytic deactivation observed. However, despite the lower glycerol conversion on time on stream for all the samples, the data points to the Ca(OH)<sub>2</sub> activity for the glycerol dehydration process.

On the other hand, there are also two factors to be considered for the observed improving of the catalytic activity for the samples containing Pt and Ag sites, under N<sub>2</sub> flow. One is the possible electronic effect from Ca to Pt or Ag. This behaviour is suggested due to the low Ag or Pt amount (nominal value of 0.2 wt.%) and good dispersion of particles as evidenced by EDS analysis (Fig. 5). A second effect is the superior surface area of the samples Pt/CaO-SiO<sub>2</sub> and

Ag/CaO-SiO<sub>2</sub> (Tale 1), which suggest to be the result from the lower  $Ca(OH)_2$  phase ratio in these samples composition (Fig. 1).

Textural and chemical properties as well as the loading or dispersion of the active metals have been reported to play an important role in the catalytic performance [68–70]. However, the Fig. 9 points out no effect over the glycerol conversion due to the Ag or Pt addition on the amphoteric ZrO<sub>2</sub> oxide. The samples containing ZrO<sub>2</sub>, for the reaction condition applied, in addition to the low glycerol conversion also shows deactivation process (Fig. 9). Despite the lower initial conversion, compared to the samples containing calcium, the Fig. 9a suggests that under N<sub>2</sub> flow the deactivation process is less pronounced. Therefore, although less expressive, the Fig. 9b shows that the CO<sub>2</sub> also has effect over the catalytic performance of the samples containing ZrO<sub>2</sub>, despite the initial glycerol conversion remain near 10% (under N<sub>2</sub>) or under CO<sub>2</sub>, differently from the samples containing CaO.

The data presented in Fig. 8 and 9, therefore, clearly points out to a strong CO<sub>2</sub> effect over the glycerol conversion only for the samples containing CaO. On the other hand, it is important to emphasize that the impregnation process and a high temperature of the heat treatment under H<sub>2</sub> flow has a considerable effect of the  $ZrO_2$  over the Pt active sites [71–73]. Therefore, the low effect observed due to the Pt or Ag addition for the  $ZrO_2$  samples, over the catalytic performance, may be a consequence of the metal-support interaction effect, which may results in the Pt or Ag partial covering by the zirconium oxide. This process is possible considering the high temperature of activation used (700 °C under H<sub>2</sub> flow).



**Fig. 9**. Catalytic conversion of glycerol for the samples containing  $ZrO_2$ , at different reaction atmosphere. (a) Reaction carried out under N<sub>2</sub> and (b) CO<sub>2</sub> flow.

#### 3.5.2. Effect of atmosphere reaction on the products selectivity

The product selectivity analysis may provide interesting information about the solid property change and  $CO_2$  effects over the catalytic process. The Fig. 10 shows the selectivity to the main products identified for the catalysts studied, based on the different supports.

The catalysts of CaO-SiO<sub>2</sub> support presented acetol, methanol, acetic acid and ethylene glycol as the main product. However, the acetic acid production is affected by the Pt or Ag addition and by reaction conditions under  $CO_2$  atmosphere. Nevertheless, under N<sub>2</sub> flow, the Ag addition improved significantly the methanol selectivity, while Pt presence improve mainly the acetol selectivity.



**Fig. 10**. Catalytic selectivity for the samples. Reaction carried out under (a)  $N_2$ , (b) CO<sub>2</sub> flow. (c) Selectivity to acetol at different gas flow for samples containing  $ZrO_2$ .

It is well accept that the glycerol dehydration produce acetol, and such reaction is an acid catalysed process [13,74]. Therefore, the data suggest a modified reaction pathway, in which the –OH group play a role, despite the lower basicity of the Ca(OH)<sub>2</sub> relatively to CaO. It is known that CaO reacts with glycerol forming calcium glycerides [49,50], additionally it is reported that Ca(OH)<sub>2</sub> solubility in glycerol/water mixture is higher than in water only [75], possibly due to the formation of calcium glycerides. Lu Chen et all [47], by using CaO as solid base catalyst in glycerol conversion to lactic acid, showed that the water content on reaction mixture has effect over the lactic acid yields from glycerol; however, the decrease of the glycerol conversion is not significantly affected. Therefore, the water presence produce Ca(OH)<sub>2</sub>, which should change the reaction pathway, modifying the product selectivity.

The Scheme 1 present a proposed reaction pathway for acetol formation from glycerol with Ca(OH)<sub>2</sub> catalysed process. Due to the high water content in the reaction mixture (95 wt.%), it is reasonable to propose the water action in the process. Considering the high affinity between glycerol and CaO or Ca(OH)<sub>2</sub> reported early [49,50,75], firstly is proposed an alkoxy formation under CaO or Ca(OH)<sub>2</sub> action. Following, with water participation (as OH group from Ca(OH)<sub>2</sub>), the acidic hydrogen from C2 is abstracted, which may make easer the C-O bond rupture with

Ca(OH)<sub>2</sub> and enol formation. The acetol is formed from the keto-enol tautomerization (Scheme 1) [13,47]. The acetol may be desorbed or undergoes to posterior reactions.



**Scheme 1.** Reaction pathway proposed for acetol formation from glycerol over basic sites with terminal OH abstraction.

It is accepted that the allyl alcohol may be produced from acetol by the hydrogen transfer process [13], likewise it is reasonable to accept that the adsorbed species like the enol is subjected to the hydrogen transfer. Therefore, the hydrogen transfer may occurs from enol to enol or from an alkoxy to enol, producing allyl alcohol and pyruvaldehyde (Scheme 2a), or glyceraldehyde and 1,2-propanediol (Scheme 2 b). The glyceraldehyde may undergoes to a new dehydration under a base action to form 2-hydroxypropenal [47], which by the keto-enol tautomerization produce pyruvaldehyde.



**Scheme 2.** Reaction pathway proposed for the formations of (a) allyl alcohol and pyruvaldehyde and, (b) glyceraldehyde and 1,2-propanediol.

The pyruvaldehyde, which present two carbon atom with low electron density, in water or Ca(OH)<sub>2</sub> presence may undergoes to nucleophilic addition reaction producing formaldehyde and acetic acid or, formic acid and acetaldehyde (Scheme 3a). Subsequently, the formaldehyde and/or the acetaldehyde are transformed to methanol and ethanol (Scheme 3b), by hydrogen transfer, which may be from the glycerol adsorbed. The glyceraldehyde in the base presence (Ca(OH)<sub>2</sub>), also may undergoes, by the retro-aldol process, to the production of 2-hydroxyacetaldehyde and formaldehyde, which by hydrogen transfer will produce ethylene glycol and methanol [76].

Unfortunately, the pyruvaldehyde may undergoes to the condensation process with various alkoxy structure present in the catalyst surface [47], which may neutralise the active sites.



**Scheme 3.** Reaction pathway proposed for the formations of (a and b) acetic acid and methanol from pyruvaldehyde and hydrogen transfer, (c) methanol and ethylene glycol from glyceraldehyde, with the metal site participation, adapted from [76].

Despite the low catalytic conversion (Fig. 8 and 9), the catalysts presented a relatively large distributions of products. The Fig. 10 display the main products only; however other products identified were: acetaldehyde, acetone, isopropanol, allyl alcohol, 1,3-propanediol.

The data presented, suggests that CO<sub>2</sub> has effect over the catalytic activity and selectivity, by forming calcium carbonate (CaCO<sub>3</sub>), which decreases the Ca or Ca(OH)<sub>2</sub> ratio available to interact with glycerol. The main change is observed for the acetic acid production, which is affected by Ag or Pt addition and by the CO<sub>2</sub> presence. The low effect over the glycerol conversion observed after the Pt or Ag addition is consistent with a low amount and with a partial Pt or Ag covering during the reaction process, by the in situ formed Ca(OH)<sub>2</sub> or CaCO<sub>3</sub> species, which neutralise the metals catalytic activity. In addition, the partial covering of Pt or Ag particles may occurs also during the impregnation procedure, since it was carried out using water solution of Pt or Ag salts. However, the Pt presence clearly has effect over the product selectivity, by suppressing the acetic acid production and improving the acetol, methanol and glyceraldehyde. Therefore, Pt may act mainly on the hydrogen transfer process, favouring the acetol desorption, which have effect over the production of acetic acid, since the pyruvaldehyde production may be affected by the acetol desorption, according to Scheme 3a.

On the other hand, the product selectivity is significantly changed by altering the catalytic system from CaO-SiO<sub>2</sub> to  $ZrO_2$ , an amphoteric support [66], which must have a superior stability in the vapour presence. The selectivity observed for the samples containing  $ZrO_2$  (Fig. 10c), shows acetol as the main product. However, it is observed the CO<sub>2</sub> effect, despite the CO<sub>2</sub>-TPD profile (Fig. 7) do not show CO<sub>2</sub> desorption at the reaction temperature.

The samples  $Pt/CaO-SiO_2$  and  $Pt/ZrO_2$  were tested for the benzene hydrogenation reaction, in order to detect the Pt particle or atom on the catalyst surface. The test was carried out with 0.100

g of sample with activation at 450 °C under  $H_2$  flow. The benzene vapour pressure in the reactional mixture ( $H_2$  and benzene), was maintained at 35 mmHg, the total flow used was 15 cc/min at reaction temperature of 60 °C. Both samples showed a very low hydrogenation product, lower than 1% of benzene conversion. The low conversion points out to the Pt partial covering by the support. It may explain the low effect over the glycerol conversion.

3.6. Characterization of spent catalysts by thermogravimetric and differential thermal analysis (TGA/DTA)

Many catalytic process are affected by coke or carbonaceous material deposition [77–79], which results in catalyst deactivation or selectivity change. The thermal analysis (TG-DTA) results of the used catalysts are presented in Fig. 11.



**Fig. 11**. Thermal analysis (TGA-DTA) of the spent catalysts after 5 h of reaction at 280 °C. (a, b, c) Catalysts CaO-SiO<sub>2</sub> based, from reaction carried out under N<sub>2</sub> flow, (d, e) ZrO<sub>2</sub> catalysts at different reaction atmosphere and, (f) Pt/CaO-SiO<sub>2</sub> catalyst under CO<sub>2</sub> flow.

The catalysts containing CaO-SiO<sub>2</sub> shows an interesting profile of weight loss (Fig. 11a, b and c). The samples subjected to the catalytic test carried out under N<sub>2</sub> flow, clearly shows two exothermic peaks in the range of 250 to 450 °C. These events are not perceptible for the sample after the catalytic test under CO<sub>2</sub> flow. This occurrence can be attributed to the combustion of complex organic species of Ca with glycerol products deposited at the surface of the catalyst [47,75,80]. This weight loss is of about 4.9, 3.1 and 16.3% for the pure calcium-silica and Ag or Pt doped catalysts, respectively. The high amount of deposited organic products over Pt/CaO-SiO<sub>2</sub> catalyst, which corresponds to a weight loss of 16.3% is resulted of higher glycerol conversion with formation of stable carbon species. The TG data point out that CO<sub>2</sub> act in a competitive way with glycerol, producing CaCO<sub>3</sub>, which is no active in the glycerol conversion. Therefore, the weight loss observed above at 600°C in all calcium-silica based samples is associated to the endothermic CaCO<sub>3</sub> decomposition [65].

The sample  $ZrO_2$  shows a low mass elimination, near 1wt%, in a large temperature range, independently of the carrier gas applied (Fig. 11d and e). This profile suggest a partial rehydration of the  $ZrO_2$  during the catalytic test, which is gradually eliminated. The carbonaceous material presence can not be ruled out, however.

The Fig. 11f also shows that the events of weight loss between 250 and 450 °C are not perceptible for the Pt/CaO-SiO<sub>2</sub> sample after the catalytic test under CO<sub>2</sub> flow. The glycerol conversion over CaO based catalyst containing a large amount of water in the reaction mixture, should produce the reactive Ca(OH)<sub>2</sub>. However, for the reaction carried out under CO<sub>2</sub>, the water produce a low amount of Ca(OH)<sub>2</sub>, which can react with glycerol. Therefore, the TG curve analysis show no accumulation of the Ca-glycerol complex products on the Pt/CaO-SiO<sub>2</sub> surface (Fig. 11f). The endothermic event in the range of 600 to 700 °C is characteristic of the CaCO<sub>3</sub> decomposition, consequently, the mass elimination due to the CaCO<sub>3</sub> decomposition is less intense for the samples

produced after the reaction under N<sub>2</sub> flow. Additionally, it should be considered that a ratio of the CaCO<sub>3</sub> decomposition observed for the samples produced after the reaction under N<sub>2</sub> flow, may be formed during the decomposition event at lower temperature (400 °C) of the TG analysis. From the thermal analysis, it can be inferred that CO<sub>2</sub> excess act in a competitive way with glycerol and thus a high fraction of Ca(OH)<sub>2</sub> should be converted to CaCO<sub>3</sub> as precipitant on catalyst surface, which is no active in the glycerol conversion.

#### 4. Conclusions

A comparative investigation of the catalytic performance of platinum or silver catalysts supported on CaO-SiO<sub>2</sub> and ZrO<sub>2</sub> to synthesize products with higher added value, through the gas phase glycerol dehydration reaction was performed. It was found that using the base CaO-SiO<sub>2</sub> support led to better dispersion of platinum or silver species and increasing the surface area when compared to the amphoteric zirconia catalyst. Both, CaO-SiO<sub>2</sub> and ZrO<sub>2</sub>, presents catalytic activity for the glycerol conversion, but catalysts containing CaO doped with Ag or Pt shows better catalytic performances producing mainly acetol, methanol, ethylene glycol and 1,2 propanediol. The reactions pathway proposing consider the main base sites species present on catalyst surface, calcium hydroxide, for the formation of the different products. It is also clear that the presence of metallic platinum has effect over the reaction, increasing the glycerol conversion to acetol and inhibin the formation of acetic acid. However, Ag addition to CaO-SiO<sub>2</sub> increase the selectivity to methanol. The data points out to a Ca(OH)<sub>2</sub> phase as the main active site able to produce oxidation products, but the presence of metallic redox sites produce mainly methanol and acetol. On the other hand, the CO<sub>2</sub> presence decrease the catalytic conversion, mainly for the CaO-SiO<sub>2</sub> based samples, since CO<sub>2</sub> react with the active Ca(OH)<sub>2</sub> species on catalyst surface. For the samples containing ZrO<sub>2</sub> acetol was the main product observed and, the CO<sub>2</sub> addition do not produce a meaningful effect, which is due to the lower ability for CO<sub>2</sub> adsorption.

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