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# Study of hydrotalcite-supported transition metals as catalysts for crude glycerol hydrogenolysis



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ARTICLE INFO	A B S T R A C T
<i>Keywords:</i> Hydrotalcite Crude glycerol Hydrogenolysis Transition metals	Hydrotalcites containing Fe, Ni-, Zn- and Cu were synthesized by the coprecipitation method. These catalysts were characterized and employed for the hydrogenolysis of pure glycerol. The catalyst with the best performance (HDT-Cu) was used to carry out the hydrogenolysis of crude glycerol. The best yield (74.1%) for the real, low purity (62%) glycerol was obtained at 3.4 MPa of H <sub>2</sub> and 200 °C for 24 h of reaction. The regeneration capacity of the catalysts was also studied in order to develop an economically feasible process for industrial application.

# 1. Introduction

In recent years, the interest in the use of biodiesel as an alternative to fossil fuels has increased due to the problems stemming from the energy crisis and the environmental deterioration being faced by the world population. With the use of biodiesel, it is possible to reduce the emissions of carbon monoxide, sulfur, aromatic hydrocarbons, among other solid particles, which are mainly attributed to environmental deterioration [1]. As the production of biodiesel is more expensive than that of fossil diesel, the governments of many countries subsidize it to stimulate this fuel production branch [2].

In biodiesel production via transesterification of the triglycerides present in animal or vegetable origin oils, about 10% of crude glycerol is obtained as a by-product [3,4]. The increase in the biodiesel production has generated a glycerol surplus, causing a decrease in its price due to the production-demand effect. As a result, research aimed at transforming glycerol into other chemicals with higher added value has considerably increased, which contributes significantly to the profitability of the biodiesel production process [5].

Currently, there are several routes for the generation of higheradded-value products from glycerol such as oxidation [6], dehydration [7], pyrolysis [8], esterification [9], and etherification [10], among others [11–14].

One of the glycerol valorization strategies that has received more attention is a hydrogenolysis reaction that produces mainly 1,2- and 1,3-propanediols (1,2-PDO and 1,3-PDO), which are low-toxicity and high-added-value chemicals [15–24].

1,2-PDO is used not only in the synthesis of unsaturated polyester resins and antifreezes, but also in the pharmaceutical, food, cosmetic, detergent, flavoring, personal care, paint and animal food industries [25,26]. On the other hand, the main application of 1,3-PDO is the manufacture of polyester fibers with high commercial interest [27].

In recent years, glycerol hydrogenolysis has received significant attention, and most research works on this topic have been developed by using high purity commercial glycerol and very expensive catalysts with high loads of noble metals (i.e. Pd and Pt); unfortunately, the possibility of regenerating and reusing these catalysts in order to develop a process that is economically feasible for industrial application has not been explored. Since glycerol purification is a highly demanding energy process that greatly increases the cost of this raw material from about \$1000 for 200–400/metric ton [28], the development of processes for the hydrogenolysis of crude glycerol as it is obtained from biodiesel production with technical and economically feasible reaction conditions is needed [29].

Different noble and transition metals (e.g. Pt, Pd, Rh, Ir, Ni, and Cu) [15–24] and different supports (e.g.  $SiO_2$ , ZnO,  $Cr_2O_3$ , MgO,  $Al_2O_3$ ,  $TiO_2$ , zeolites and hydrotalcites) [30–37] have been used in glycerol hydrogenolysis, but in most cases, this reaction has been carried out using highly pure glycerol and the possibility of regenerating and reusing these catalysts in order to develop a process that is economically feasible for industrial application has not been explored.

In the present work, hydrotalcites containing Fe, Ni-, Zn- and Cu were synthesized by the coprecipitation method. These catalysts were characterized by  $N_2$ -adsorption, X-ray diffraction, scanning electron

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microscopy, Fourier transform infrared spectroscopy and  $CO_2$  temperature programmed desorption, and evaluated in the hydrogenolysis of pure glycerol. The best performance catalyst (Cu-HDT) was used to study the reaction conditions of the hydrogenolysis of crude glycerol. Finally, the regeneration and reusability capacities of the catalysts were studied in order to develop a feasible process for the industrial production of glycerol-added-value products from the environmental and economic viability standpoints.

# 2. Experimental section

#### 2.1. Crude glycerol characterization

Crude glycerol was supplied by the Biodiesel Pilot Plant of Sinaloa University, Mexico. The following analyses, in triplicate, were carried out on the crude glycerol by using the following standard test methods: heavy metal and sodium (D-5856), ashes (D-482-07), moisture content (D-203-08), pH (E-70-90), and specific gravity (D-1298-12b). Glycerol contents were determined by the iodometric-periodic acid method conducted according to the AOCS Official Method Ca14-56. Mono-, diand triesters were identified by gas chromatography (GC) analysis (D6584-10a).

# 2.2. Preparation of catalysts

All Nitrate salts (Sigma-Aldrich) were used as metal sources: magnesium nitrate (Mg (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 98%), zinc nitrate (Zn (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 98%), copper nitrate (Cu (NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O, 98%), nickel nitrate (Ni (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 98.5%), iron nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, 98%) and aluminum nitrate (Al (NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, 98%).

The materials were synthesized by coprecipitation at constant pH, which consisted in the preparation of 3 M metal solutions from the corresponding nitrate salts and a second KOH solution used as precipitating agent; both solutions were added dropwise into a glass reactor to keep pH 10. In all the samples, the content of the divalent cation was 15 wt. % with  $M^{2+}/M^{3+}$  molar ratio of 3. The mixture was aged for 24 h under vigorous stirring. The synthesized materials were washed and centrifuged to eliminate the presence of salts, then dried and calcined at 600 °C for 5 h.

#### 2.3. Characterization of catalysts

The chemical compositions of Al, Mg, Cu and K were determined by the EPA 6010C method using a Perkin-Elmer Plasma 400 piece of equipment. Each sample was disintegrated in HNO<sub>3</sub> at 10% before carrying out the analysis. For the quantification of carbon, nitrogen and hydrogen, a Carlo Erba EA1108 elemental analyzer was used.

The gas adsorption/desorption isotherms are the most used for the characterization of textural properties of porous materials, such as surface area, pore volume and pore size distribution. Nitrogen adsorption was measured at its normal boiling point (- 196 °C) using an ASAP 2405 analyzer (Micromeritics) after pretreating samples at 250 °C for 4 h in vacuum. The BET surface area and pore structure were calculated from the adsorption branches.

XRD patterns were collected on an X SIEMENS D5005 diffractometer with  $CuK_{\alpha}1$  signal 2 = 1.5416 Å with angular interval of 4-70° in 20.

SEM images were obtained by means of a field emission piece of equipment JEOL JSM-6700 F, working at an acceleration voltage of 5 kV, and a JEOL JSM6400 piece of equipment in the 30–35 kV range. In some cases, the SEM technique was combined with energy dispersive X-ray analysis (SEM-EDX). The samples were metallized with gold or palladium to create the necessary contrast.

Fourier-transform infrared spectroscopy (FTIR) was used to analyze the synthesized material HDT-Cu-15; the infrared spectra were obtained by employing a Thermo-NICOLET spectrometer model MAGNA 560 with spectral resolution of 4 cm<sup>-1</sup>, 50 scans and equipped with a DTGS detector. The samples were analyzed in the form of self-supporting tablets in absorbance-transmittance to analyze the adsorption-desorption of CO<sub>2</sub> during the thermal treatment from room temperature (25 °C) to 600 °C.

Temperature Programmed Desorption (TPD) of CO<sub>2</sub> was carried out in an Autosorb-1 of Quantachrome. Prior to CO<sub>2</sub> adsorption, all catalysts (-100 mg) were heated up to 500 °C under helium as carrier gas (flow rate 25 cm<sup>3</sup> h<sup>-1</sup>). The CO<sub>2</sub> temperature adsorption occurred at 50 °C for 30 min and the corresponding desorption patterns of desorption were obtained by heating (10 °C min<sup>-1</sup>) up to a final temperature of 500 °C. The gas mixture was analyzed by means of a Mass Spectrometer equipment by Pfeiffer Prisma.

# 2.4. Hydrogenolysis reactions

The glycerol reaction was carried out in a custom-designed, stainless steel, 100-mL Parr reactor, model 4598, equipped with a thermoelectric couple and magnetically stirred. An aqueous solution of glycerol (10.0 mL at 60 wt. % of pure glycerol, or crude glycerol without dilution) was mixed with the corresponding catalyst in a 1:12 ratio (w/w). The reactor was purged with H<sub>2</sub> at 3.4 MPa and placed in oil bath preheated at 200 °C and kept at that temperature (180 or 200 °C, specified in each case) for a maximal time of 24 h with vigorous stirring (250 rpm) at a pressure range of 0–3.4 MPa (monitored by an electronic transducer).

Each evaluated catalyst was calcined in air atmosphere at the corresponding temperature, conditioned in N<sub>2</sub> flow (70 mL/min) at 120 °C for 1 h in order to eliminate humidity and finally activated by reduction at 350 °C with H<sub>2</sub> flow (70 mL/min) for 3 h.

The reactant solution was cooled to room temperature after reaction and analyzed by GC on an HP-6890 chromatograph with an Innowax column (30 m  $\times$  320 µm  $\times$  0.5 µm), using a flame ionization detector (FID); 1-butanol was used as the internal standard in the samples prepared with 100 µL of the reaction product diluted with 900 µL of methanol. The areas under the curve of the chromatograms were transformed into weight percentages by means of calibration curves for each of the likely reaction products as 1,2- and 1,3-propanodiols (1,2-PDO and 1,3-PDO), ethyleneglycol (EG), propionic acid (PA), and glyceraldehyde (GA).

The conversion of glycerol and selectivity of products were calculated by using the following expressions:

$$Conversion(\%) = \frac{moles of glycerol_{(in)} - moles of glycerol_{(out)}}{moles of glycerol_{(in)}} \times 100$$

Selectivity(%) =  $\frac{\text{moles of product}}{\text{moles of all product}} \times 100$ 

# 3. Results and discussion

We decided to synthesize catalysts by using transition metals such as Fe, Ni, Cu and Zn supported on hydrotalcites (HDTs) in order to produce scalable, stable, highly active and low cost catalysts to be used for more than one reaction cycle because it is well known that Cu-based catalysts can show low stability and suffer from severe deactivation in this kind of reaction [31].

HDT-supported catalysts have attracted much attention in the last year because these materials have shown many potential applications as effective catalysts for transforming biomass-derived molecules with environmental protection [38–40].

#### 3.1. Characterization of catalysts

XRD patterns of the synthesized catalysts containing 7% of the added metal are presented in Fig. 1, where the presence of the



Fig. 1. XRD patterns of the synthesized catalysts.

characteristic plane signals of the HDT-type materials is shown: (003), (006), (009), (015), (0012), (110) and (1013). It is observed that all the samples present only the hydrotalcite phase, since they display characteristic peaks of a natural hydrotalcite with the exception of HDT-Zn-7, which presents other non-characteristic peaks of the hydrotalcite phase, attributed to unidentified impurities.

The sharp and symmetrical peaks at 11.7, 23.0, 60.6 and 61.8° are designated to the planes of the laminar structure (003), (006), (110) and (113). By comparing these peaks, it is observed that the intensity of the characteristic peak (003) increases with the replacement of the metals iron, nickel, copper and zinc, respectively, in the environment with laminar octahedral brucite coordination, indicating an increase in the structural integrity by assuming that the stacking of the layers is trilaminar rhombohedral.

#### 3.2. Nitrogen adsorption-desorption

The adsorption-desorption isotherms of the catalysts are presented in Fig. 2. By analyzing the characterization results of the surface properties of the different HDT-type catalytic materials, an area decrease can be observed (Table 1) with respect to the increase in the cation ionic radius (ionic radius, Fe < Ni < Cu < Zn). However, an exception is shown for HDT-Ni, since it displays an area value that is smaller than those obtained with materials containing Cu and Zn. It was expected that the catalyst containing Ni could have a greater surface



Fig. 2. N<sub>2</sub> adsorption-desorption isotherms of the catalysts.

Table 1
Textural properties of the calcined catalysts (600 °C).

Sample	Ratio <sup>a</sup> M <sup>2+</sup> /M <sup>3+</sup>	Surface area <sup>b</sup> m <sup>2</sup> /g	Pore volume <sup>b</sup> cm <sup>3</sup> /g	Pore diameter <sup>b</sup> Å
HDT-Fe	2.5	286.4	0.91	127.0
HDT-Ni	2.5	248.9	0.51	82.61
HDT-Cu	3.1	204.1	0.37	73.15
HDT-Zn	2.5	234.4	0.79	134.3

<sup>a</sup> Determined by atomic absorption.

<sup>b</sup> Based on the isotherm desorption branch.

area because this element has a lower ionic radius than Cu and Zn. This fact could be probably attributed to the synthesis or maturation of the material.

In Table 1, the main results of the characterization of the family of basic catalysts are shown. It is observed that the value of the surface area is greater than  $200 \text{ m}^2/\text{g}$ ; the metal molar ratio  $M^{2+}/M^{3+}$  determined by atomic absorption is in the range from 2.5 to 3, thereby confirming the presence of the divalent cation ( $M^{2+} + Mg^{2+}$ ) in the final catalyst.

HDT-Cu presents the smallest volume and pore diameter, so presumably these parameters play a key role in the activity of the catalyst.

The  $N_2$  adsorption-desorption isotherms of the HDT-Ni, HDT-Cu, HDT-Fe and HDT-Zn materials are shown in Fig. 3, where they are all type IV isotherms according to the IUPAC classification, which indicates that these are materials with relatively large pores. In addition, hysteresis loops formed by the capillary condensation produced in the mesopores and by the limits of adsorbed quantity at high relative pressure are characteristic in this type of isotherms.

The hysteresis loops that these materials present in the multilayer zone are type H3. Loops or H3-type hysteresis loops are associated with plate-shaped materials, giving rise to pores in the form of a slit. The closure points of the hysteresis loops were produced at a relative pressure of 0.5 in HDT-Fe, 0.6 in HDT-Ni, 0.4 in HDT-Cu and 0.8 in HDT-Zn; based on this, it was found that there was an increase in the relative pressure as the ionic radius of the metals increased, with the exception of HDT-Cu. Then, as the relative pressure of the closure point increased, the pore diameter also increased.

#### 3.3. Fourier transform infrared spectroscopy (FTIR)

Within the FTIR spectra of the HDL-type materials, three general types of vibration zones were found: area of vibrations of molecular elongation of the hydroxyl groups, zone of the vibrations of the octahedral sheets and vibrations of the interlaminar anions. Fig. 3 shows the FTIR spectra of the HDT-Ni, HDT-Cu, HDT-Fe and HDT-Zn materials.

The HDT-Zn spectrum presents the typical broad band at around  $3612 \text{ cm}^{-1}$ , which is attributed to the tension vibration mode of hydrogen carbonates that are formed in the presence of basic hydroxyl group [41]. The shoulder observed at  $3000 \text{ cm}^{-1}$  is assigned to the hydrogen bridge between water and carbonates in the interlaminar space while the low intensity band at  $1643 \text{ cm}^{-1}$  shows the water deformation mode ( $\delta$ HOH). Due to the thermal treatment, the carbonate bands underwent a reorganization in the interlaminar space of symmetry  $D_{3h}$  to  $C_{3v}$  or  $C_{2v}$ , so that the band that appears at  $1367 \text{ cm}^{-1}$  decreases in intensity, which can be assigned to interlaminar carbonates (united both in the form of a chelate or as a bidentate); two peaks are observed at around 1510 and  $1400 \text{ cm}^{-1}$  due to  $CO_2^{3-}$  and  $Mg^{2+}$  interactions [42].

As it can be seen, the HDT-Ni and HDT-Fe materials show very similar spectra, presenting a barely visible band at around  $3700 \text{ cm}^{-1}$ , which is attributed to the tension mode of hydrogen carbonates that are formed in the presence of basic hydroxyls [41]. Very intense broad bands are seen at around  $3530 \text{ cm}^{-1}$ , which are attributed to the vibrations of physisorbed water, elongation vibration bands of OH-



Fig. 3. FTIR spectroscopy (300 °C) of the catalysts studied in the 4000–2500 cm<sup>-1</sup> (A) and 1750-1000 cm<sup>-1</sup> regions (B).

structural groups and M–OH vibrations in hydroxycarbonates. The shoulder observed at around  $3000 \text{ cm}^{-1}$  is assigned to the hydrogen bridge between water and carbonates in the interlaminar space, which occurs because the calcination treatment is of low intensity. On the other hand, there is a band at around  $1575 \text{ cm}^{-1}$ , characteristic of an asymmetric vibration band (O–C–O in a monodentate adsorbed species of CO<sub>2</sub> on an O<sub>2</sub>-basic site). Bands at around 1510, 1400 and  $1360 \text{ cm}^{-1}$  are also observed, which have already been explained above.

In the case of the HDT-Cu material, it only shows wide bands of very low intensity at around  $3448 \text{ cm}^{-1}$  and a shoulder at around  $3000 \text{ cm}^{-1}$ , which were already discussed above. The bands with very low intensity are also observed at wave numbers around 1510, 1400 and  $1360 \text{ cm}^{-1}$ .

 $CO_2$ -TPD for the calcined samples in the range 30–500 °C is shown in Fig. 4. The amount of  $CO_2$  desorbed throughout in the temperature range was calculated from the TPD curves.

In Table 2, the basic site density and amount of desorbed  $CO_2$  by TPD are presented.

The relationship between glycerol conversion and  $CO_2$  basic site density can be seen in Table 2. A remarkable correlation between the catalyst basicity and glycerol conversion in the hydrogenolysis reaction can be observed (Fig. 5).

# 3.4. Pure glycerol hydrogenolysis with HDT type catalysts

The activity of the HDT-Metal catalysts in the hydrogenolysis of



Fig. 4. CO<sub>2</sub> TPD curves of the HDT-Me catalysts.

# Table 2

Basic site density and amount of desorbed CO<sub>2</sub> by TPD.

Sample	$\mu$ mol CO <sub>2</sub> /g cat.	$\mu mol \ CO_2/m^2$
HDT-Fe HDT-Ni	57 101	0.20 0.40
HDT-Cu	128	0.63
HDT-Zn	43	0.18



**Fig. 5.** Correlation between the basicity of the HDT-Me catalysts and glycerol conversion in the hydrogenolysis reaction.

aqueous glycerol was tested at 200 °C for 24 h, 250 rpm of stirring and a glycerol/catalyst ratio of 12:1 w/w after screening several temperature,  $\rm H_2$  pressure, reaction time and glycerol/catalyst ratio conditions.

The results concerning the conversion and selectivity of the glycerol hydrogenolysis as a function of the reaction time are shown in Figs. 6a and b, which were evaluated at a hydrogen pressure of 3.4 MPa and different reaction temperatures.

As shown in Fig. 6a, the reaction rate increases when temperature also increases. In the first two hours of reaction at 180 °C, only a conversion of 24% was achieved, instead of a conversion of 67% at 200 °C. Thus, after 24 h of reaction, glycerol conversions of 78 and 97% were reached at 180 and 200 °C, respectively. In addition, it can be said that the conversion of glycerol increased rapidly in the first 6 h, for both temperatures; after this time, the conversion rate decreased, which can be attributed to the glycerol concentration diminishing in the reaction mixture. This fact is in good agreement with S. Xia et al., who stated that in addition to catalyst basicity, glycerol conversion also depends strongly on the concentration present in the reaction mixture [43].



Fig. 6. Evaluation of the temperature effect on the hydrogenolysis reaction of crude glycerol. Conversion of crude glycerol (a) and selectivity towards 1,2-PDO (b).

 Table 3

 Quantification of liquid products obtained in the pure glycerol hydrogenolysis using HDT catalysts containing Fe, Ni, Cu and Zn.

Catalyst	Conversion (%)	Selectivity	Selectivity			
		1,2-PDO	1,3-PDO	EG	Acetol	(%)
Fe-HDT	50.6	0	0	0	100	0
Ni-HDT	47.8	100	0	0	0	47.8
Cu-HDT	66.0	95.7	0	4.3	0	63.1
Zn-HDT	0	0	0	0	0	0

<sup>a</sup> Experimental conditions: 200 °C, 24 h, Pr = 3.4 MPa, 250 rpm of stirring, glycerol/catalyst ratio of 12:1 w/w.

In Table 3, the results of the pure glycerol hydrogenolysis using HDT catalysts containing Fe, Ni, Cu and Zn are summarized.

In this family of catalysts, it can be seen that iron is a cation that preferentially tends to perform deep oxidation reactions by breaking C–C bonds, and despite having conversions greater than 50%, it does not have the desired selectivity. On the other hand, Zn did not present any catalytic activity under these evaluation conditions; Ni-HDT showed a total selectivity to 1,2-PDO with moderated yield and Cu-HDT was the catalyst with higher reaction yield. In the case of Fe-HDT, the conversion of glycerol was totally directed to the formation acetol.

Fig. 7 shows the results obtained when evaluating the Cu content effect on the hydrotalcite type material. When the metal content increases from 7 to 15 wt. %, the conversion of glycerol is improved by 12.1%, maintaining the selectivity towards 1,2-PDO. These results can

be attributed to the fact that when the metal load is increased, also the number of active sites is raised for the dehydrogenation to happen, which is the initial step in the mechanism by the basic route.

Thus, HDT-Cu-15 was selected as the catalyst for studying the crude glycerol hydrogenolysis.

# 3.5. Characterization of HDT-Cu-15

# 3.5.1. N2 adsorption-desorption isotherm of HDT-Cu-15

A study of the textural properties of this catalyst shows a surface area of 166.34  $m^2/g,$  pore volume of 0.479  $\rm cm^3/g$  and pore size of 115.25 Å.

For HDT-Cu-15, the surface area decreased with respect to HDT-Cu-7 (Table 3) as a function of the  $Cu^{2+}$  ion increase in the  $Cu^{2+}/Mg^{2+}$  ratio, attributed to the fact that the order of the crystals decreases with the increase in copper content.

The  $N_2$  adsorption-desorption isotherm of HDT-Cu-15 is shown in Fig. 8, which is also type IV according to the IUPAC classification, indicating that it is a material with relatively large pores. In this type of isotherms, hysteresis loops are characteristic, which are formed by the capillary condensation produced in the mesopores. The hysteresis loop is presented from the relative pressure of 0.7, giving the hysteresis the H3 type form that is associated with plate-shaped materials.

By comparing the isotherms of the HDT-Cu-7 (Fig. 2) and HDT-Cu-15 (Fig. 8) materials, it is observed that the hysteresis loops of the calcined materials, which also have a higher  $Cu^{2+}/Mg^{2+}$  ratio, occur at higher relative pressures; these results indicate that there is a large



Fig. 7. Conversion of glycerol (XGLY), selectivity to 1,2-PDO (S1,2-PDO) and yield of 1,2-PDO (Y1,2-PDO) of the glycerol hydrogenolysis catalyzed by HDT-Cu.



Fig. 8. N<sub>2</sub> adsorption-desorption isotherm of HDT-Cu-15.



Fig. 9. Pore diameter distribution of HDT-Cu-15.

number of pore channels with slot opening, formed due to the aggregation of plate-like layers (Fig. 9).

# 3.5.2. Scanning Electron Microscopy (SEM)

SEM images were obtained to investigate the morphology of the calcined HDT-Cu-15 catalyst, which are shown in Fig. 10 at different magnifications. The micrographs show that the mixed oxide materials calcined at 600 °C kept the laminar structure with similar morphology to that of a fresh hydrotalcite material.

# 3.5.3. Energy dispersive X-ray (EDX)

The HDT-Cu-15 material was analyzed by EDX. The results are shown in Fig. 11, where as expected, in the calcined material, only Mg, Al, Cu and O are present.

### 3.5.4. Transmission Electron Microscopy (TEM)

Another analysis that was carried out to obtain more information about the morphological characterization was Transmission Electron Microscopy (TEM), which is presented in Fig. 12.

It can be confirmed in Fig. 12 that the calcined HDT-Cu-15 material still presents part of the laminar structure. Fig. 12a shows the cross-section of the layered platelet from which the gallery structure can be found, which can be observed with higher magnification in Fig. 12b.

#### 3.5.5. Temperature programed reduction (H2-TPR)

Fig. 13 illustrates the H<sub>2</sub>-TPR profile of the calcined HDT-Cu-15.

The profile only shows a single peak between 180 and 230 °C, which indicates the consumption of hydrogen used in the reduction of  $Cu^{2+}$  ions located in the laminar structure of the material and the peak observed at 510 °C can be considered as impurity due to its minimal intensity.

#### 3.5.6. FTIR

The FTIR spectrum of the HDT-Cu-15 calcined material, synthesized by the coprecipitation method, is shown in Fig. 12. As it can be seen, the spectrum shows the typical broadband at  $3448 \text{ cm}^{-1}$  with low intensity, because it decreases due to dehydroxylation caused by the calcination treatment. The shoulder observed at around  $3000 \text{ cm}^{-1}$  is assigned to the hydrogen bridge between water and carbonates in the interlaminar space, which due to the calcination treatment is of low intensity. On the other hand, as it is known, with the thermal decomposition of the material, water is lost physisorbed in the sheets, which is demonstrated with the disappearance of the bands at  $1643 \text{ cm}^{-1}$ (corresponding to the water deformation vibration), at  $1739 \text{ cm}^{-1}$ (water deformation vibration restricted in the interlaminar space) and at  $3050 \text{ cm}^{-1}$  (H<sub>2</sub>O - CO<sub>2</sub><sup>3-</sup> interaction in the interlaminar space).

Due to the thermal treatment, the carbonate bands underwent a reorganization in the interlaminar space of symmetry  $D_{3h}$  to  $C_{3v}$  or  $C_{2v}$  so that the band that appears at  $1374 \, \mathrm{cm}^{-1}$  decreases in intensity, which can be assigned to interlaminar carbonates (united both in the form of a chelate or a bidentate), and two peaks are observed at around 1513 and 1406 cm<sup>-1</sup> due to the  $CO_2^{3-}$  and  $Mg^{2+}$  interactions [40].

The presence of a low intensity band at around  $1458 \,\mathrm{cm}^{-1}$  is also observed, which is attributed to carbonates adsorbed after thermal decomposition. Therefore, it can be said that the applied calcination temperature of 600 °C is not sufficient to completely eliminate hydroxyl and carbonates, even if the hydrotalcite phase is destroyed. This fact is in agreement with the results of the TGA analyses, which indicate the presence of a first stage of carbonate loss in the form of CO<sub>2</sub> (accompanied by water vapor in minimal form) that is carried out before 600 °C. The IR studies indicate that above this temperature there are still highly refractory carbonates that can still be observed at up to 1000 °C, since CO<sub>2</sub> is still being released at this temperature.

The intensity of the carbonate losses due to the formation of  $CO_2$  was quantified from the TGA studies in the 50–600 °C range. From this analysis, a total loss of 13.91% of the mass (2.7 mg) is observed at 600 °C. The released gases were analyzed by FTIR and  $CO_2$  bands are observed in the spectra, which helped calculate the amount of carbonates, obtaining a result of 2.19 mg, which agrees with the TGA result.

The FTIR analysis (Fig. 14) shows the bands assigned to metal carbonates that evaporate before 600 °C, leaving residual carbonates. After the heat treatment, the sample was allowed to return to room temperature in a  $CO_2$  atmosphere to observe the regeneration of the band (1700–1200 cm<sup>-1</sup>) forming carbonates of the same species (the shape of the bands is the same) as the degraded ones. The analysis of the areas of this signal indicates the loss of 13.91% of the initial mass. The recovered area is 187.51 m<sup>2</sup> after exposure to  $CO_2$ . Using the area ratio data, the sample recovered 47.21 wt. % due to the readsorption of  $CO_2$  in the form of carbonates.

# 3.6. Crude glycerol hydrogenolysis

The composition of crude glycerol utilized in this study is shown in Table 4.

As it can be seen in Table 4, the raw sample used in this study had low glycerol content and was accompanied by water, methanol and mono, di and triglycerides as main impurities, as well as high content of sodium due to the catalyst (NaOH) employed in biodiesel production.

According to the results with pure glycerol, HDT-Cu-15 was selected as the catalyst to study the hydrogenolysis of crude glycerol. The process was evaluated at various pressures (0–3.4 Mpa) and temperatures (180 and 200  $^{\circ}$ C). The results are summarized in Table 5.



Fig. 10. SEM of HDT-Cu-15 at a) 10,000X, b) 20,000X, a) 50,000X and b) 100,000X.





(a)

Fig. 12. TEM of HDT-Cu-15.



Fig. 13. H<sub>2</sub>-TPR profile of the calcined HDT-Cu-15.



Characterization of crude glycerol utilized in this study.

Parameter	Unit	Content
Glycerol content	%w/w	62.10
Monoester content	%w/w	3.60
Diester content	%w/w	0.09
Triester content	%w/w	1.08
Moisture content	%w/w	4.92
Ash Content (550 °C)	%w/w	2.99
pH at 25 °C(10% water)	-	10.6
Specific gravity (25 °C)	-	0.989
Heavy metals	ppm	11.54
Sodium content	ppm	888.12

The obtained results according to Table 5 indicate that the best yields were produced at 3.4 Mpa of  $\rm H_2$  pressure at 200  $^\circ \rm C$  for 24 h. The maximum yield obtained for real loads was 72% of 1,2-PDO with a glycerol conversion of 74.1%, contrast with the results obtained with pure glycerol (89.7% of 1,2-PDO and 92% of conversion, Table 4). The results with crude glycerol are significantly high if we consider the



Fig. 14. FTIR of HDT-Cu-15.

#### Table 5

Results of the catalytic evaluation of HDT-Cu-15 in crude glycerol hydrogenolysis.

Temperature	H <sub>2</sub> Pressure	Conversion	Selectivity			Yield <sup>b</sup>	
( ( )	(мра)	(%)	1,2-PDO	EG	N.I <sup>a</sup>	(70)	
200	0	89.6	28.6	5.5	65.9	25.6	
200	0.7	92.9	57.0	7.8	35.3	52.9	
200	2.0	90.6	59.3	6.8	33.9	53.8	
200	3.4	97.2	74.1	3.7	22.3	72.0	
180	2.0	72.9	50.4	5.0	44.6	36.7	
180	3.4	81.6	55.5	3.3	41.2	45.3	

<sup>a</sup> Unidentified products including acetol, ethanol and others.

<sup>b</sup> Experimental conditions: 24 h, 250 rpm of stirring, glycerol/catalyst ratio of 12:1 w/w.

#### Table 6

Composition of the gas phase in the hydrogenolysis reaction (24 h) of crude glycerol using the HDT-Cu-15 catalyst.

Pressure $H_2$ (Mpa) Temperature (°C) Compound	3.4 200 weight %	2.0 200	0.7 200	0 200	3.4 180	2.0 180
Methane	0.04	0.03	0.03	0.07	0.04	0.02
Ethane		0.02	0.02	0.03	0.11	0.02
Propane	0.08	0.03	0.02	0.00	0.10	0.01
Iso-Butane	0.03	0.06			1.69	0.02
<i>n</i> -Butane	0.10	0.02	0.02	0.02	0.18	0.02
2,2-Dimethylpropane	0.07	0.01	0.01	0.01		0.01
Iso-Pentane		0.13	0.12			0.06
n –Pentane		0.01	0.08	0.01	0.14	0.01
n –Hexane					0.06	
2-Methylpentane		0.04				
1-Hexene			0.01			
Carbon dioxide	94.26	96.93	97.74	94.31	97.68	97.83
Non-identified	5.42	2.72	1.95	5.55	0	2.00

large amount of impurities present in the crude glycerol used in this study.

Interestingly, the hydrogenolysis of crude glycerol showed a marked selectivity to the formation of 1,2-PDO even in the absence of initial pressure of hydrogen, which indicates that the hydrogen necessary to hydrogenate the intermediates to propanediols is taken from the glycerol molecule; in addition to crude glycerol, there is a remnant of methanol used in the production process of biodiesel that can participate as a hydrogen donor molecule [43].

# 3.7. Analysis of the gas phase in the hydrogenolysis reaction

The composition of the compounds present in the gas phase in the hydrogenolysis reaction of crude glycerol is presented in Table 6.

As it can be seen, the compound with the highest presence in all the reactions is carbon dioxide, which is attributed to the fact that as it is crude glycerol and when it reaches reaction temperatures, cracking of compounds present in the reaction mixture begins. In addition, a minimal presence of hydrocarbons, mostly paraffins, can be seen.

The performance of the HDT-Cu-15 catalyst is comparable with that reported in recently published articles about glycerol hydrogenolisys (Table 7). In previous studies, higher selectivity to 1,2-propanediol with lower glycerol conversion or vice versa has been reported using pure glycerol and higher temperature and/or pressure. The work of Zhu et al. [47] being an exception, in that work, the addition of suitable  $B_2O_3$  to Cu/SiO<sub>2</sub> catalyst pronouncedly enhanced the catalyst activity and stability for glycerol hydrogenolysis. The catalyst 3CuB/SiO<sub>2</sub> afforded up to complete conversion with 98.0% of 2-PDO selectivity.

#### 3.8. Regeneration of the catalyst

The reuse of the HDT-Cu15 catalyst was evaluated in the hydrogenolysis reaction of crude glycerol at 200 °C and 3.4 MPa. After several studies, it was found that the catalyst could be efficiently recovered by a vacuum filtering process and then washed with *n*-hexane and finally conditioned by calcination and reduction. Once recovered and conditioned, the catalytic material was put in reaction with a fresh load of crude glycerol.

Fig. 15 shows the catalytic activity of the catalyst after 24 h of reaction for various numbers of catalyst regeneration cycles. As it can be observed, Cycle 2 shows catalytic activity that is similar to the one in Cycle 1; on the other hand, Cycles 3 and 4 show glycerol conversion drops of 61.75 and 67.78%, respectively while the selectivity towards 1,2-PDO remained practically constant for 4 regeneration cycles.

Although it has been well described that this type of copper catalyst is easily deactivated [29], in our case, the catalyst showed good stability only for the first and second reaction cycles, after third cycle, the activity fell remarkably. According to the results shown in Fig. 13, the process developed for the catalyst regeneration could be used for at least two reaction cycles without considerable 1,2-PDO yield loss and at least for four cycles of reuse without losing considerable selectivity in the case of the crude glycerol used in the present study which had fairly low purity.

According to our studies, the metal content in the catalyst did not change during the recycling processes and the catalyst performance

Table 7

Comparison of the results obtained in this work with recent sources about glycerol hydrogenolysis using Cu-based catalyst.

Catalyst	Reaction temp. (°C)	Reaction pressure (Mpa)	Glycerol type	Conversion (%)	Selectivity to 1,2-PDO (mol.%)	Reference
Cu/Ni/TiO <sub>2</sub>	230	3.5	pure	100	82.2	[37] <sup>a</sup>
Cu-HDT	180	3.0	pure	80.0	98.2	[39] <sup>b</sup>
Cu-HDT	210	3.0	pure	95.1	92.2	[43] <sup>c</sup>
Cu/Zn/Al	230	7.0	pure	96.1	81.4	[44] <sup>b</sup>
Cu-HDT	220	1.5	pure	74.3	78.8	[45] <sup>b</sup>
CuO/ZnO	225	5.0	pure	83.0	79.0	[46] <sup>b</sup>
3CuB/SiO2	200	5.0	pure	100	98.0	[47] <sup>d</sup>
Cu-SBA-15	180	0.1	pure	90.0	84.0	[48] <sup>e</sup>
Cu/Al <sub>2</sub> O <sub>3</sub>	220	5.0	pure	61.0	93.3	[49] <sup>b</sup>
Cu-HDT	200	3.4	pure	89.7	92.0	This work <sup>b</sup>
Cu-HDT	200	3.4	crude	97.2	74.1	This work <sup>b</sup>

<sup>a</sup> Fixed-bed flow reactor, using 2-propanol as hydrogen source, 10 wt% glycerol in 2-propanol, nitrogen flow rate, 50 mL·min<sup>-1</sup>.

<sup>b</sup> Reactions in batch using H2.

 $^{\rm c}$  using ethanol as hydrogen source, 0.087 mol ethanol and 0.022 mol glycerol, 0.25 g catalyst, 3.0 MPa N<sub>2</sub>, 10 h.

<sup>d</sup> Fixed-bed flow reactor,  $H_2$  flow rate 150 mL min<sup>-1</sup>, WHSV = 0.075 h<sup>-1</sup>.

<sup>e</sup> Fixed-bed flow reactor,  $H_2$  flow rate 30 mL min<sup>-1</sup>, WHSV = 1.03 h<sup>-1</sup>.



Fig. 15. Behavior of glycerol conversion (x), 1,2-PDO selectivity (S) and 1,2-PDO yield (Y) during four regeneration cycles and catalyst reuses.

decrease seems to be related to the contamination of the catalyst active sites.

#### 4. Conclusions

In summary, in the present work, hydrotalcite-like catalysts containing Fe, Zn, Ni and Cu were synthesized, characterized and evaluated in glycerol hydrogenolysis. The copper catalyst exhibited the highest activity and was very selective to 1,2-PDO even when crude glycerol (62% purity) was employed. The pore volume distribution and basicity of Cu-HDT played most probably a decisive part in the glycerol hydrogenolysis reaction. The catalyst could be regenerated and reused for at least two reaction cycles using low purity crude glycerol without considerable loss of 1,2-PDO yield and for at least for four reuse cycles without considerable selectivity loss for the crude glycerol case; then, the HDT-Cu15 catalyst could be considered for the industrial valorization of crude glycerol.

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