HYDROGENOLYSIS OF GLYCEROL WITH EXTERNAL H_2 SUPPLY AS VALUE-ADDED LIQUID CHEMICALS SOURCE

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ABSTRACT: The hydrogenolysis process of glycerol with external H_2 supply has been studied using Ni-exchanged zeolites (FAU, LTA, ZSM-5). The reaction temperature and the oxidation state of the active phase were investigated in this work. Ni/zeolite catalysts were tested for 3 hours in a batch reactor, at different temperatures between 200 and 250 ºC and at 33 bar of initial H_2 pressure. A water solution of 5 wt.% glycerol was used as a feedstock. The liquid products collected were analyzed afterwards by GC-MS and GC-FID. Several catalyst characterization techniques were performed: N_2 physisorption, XRD, AAS, NH_3-TPD and FTIR of adsorbed probe molecule (pyridine or NH_3). The relevance of the metallic function for the hydrogenation reaction was proved. In most cases, the increase of the reaction temperature between 200 and 250 ºC implies a steady increase in the glycerol conversion and in the carbon conversion to liquid products, both for the reduced and non-reduced catalysts. The temperature also influences the selectivity to liquid products. Moreover, some temperatures were proposed as optimal for the production of certain liquids under these conditions.
Keywords: biorefinery, glycerol, hydrogenolysis, Ni, zeolite.

1 INTRODUCTION

Currently the biodiesel production has been increased due to the environmental concerns and the restrictions for fuels commerce. The second-generation biodiesel is proposed as one of the substitutes of fossil fuels and according to EN 14214, some profiles and standards, which are not possible without additives, must be enforced. In addition, during the biodiesel production, approximately 1 kg of glycerol is obtained per 10 kg of biodiesel and this surplus of glycerol needs to be managed. Considering this, several processes have been investigated in order to valorize the glycerol towards different value-added chemicals and/or energy [1]. Among these valorization processes, the aqueous phase hydrogenolysis process (APH) is proposed in this work.

APH is a catalytic process performed at quite low temperatures (200 to 250 ºC) and moderate to high pressures (30 to 50 bar), allowing the production of several liquids from an organic feedstock. The catalysts used in this process are generally metals, such as Pt, Cu or Ni among others, supported on different oxides: Al_2O_3, ZrO_2, SiO_2 among others.

In this context, zeolites are of interest due to their different catalytic behavior related to their morphologies and physical-chemical properties. Several types of zeolites have been studied as catalysts for different catalytic processes in liquid phase, feeding biomass-based feedstock [2].

It can be also found in the literature several works about the APH of glycerol using zeolite-based catalysts. Generally, metal supported on zeolites allow producing mainly 1,2 propanediol (1,2-PDO) using in-situ H_2 produced from the aqueous phase reforming reaction or using an external supply of this gas to promote the hydrogenation reaction [3]. Other products such as acrolein, 1-propanol, 2-propanol, propanal, among others, can be also produced.

This work has been considered as a preliminary study to determine the viability of different Ni supported catalysts, using zeolite type FAU (zeoltite X), type LTA and Type MFI (ZSM-5) as support, on the APH process of glycerol. The role of the oxidation state of the active phase, so as the influence of the operating temperature, on the liquid products distribution have been investigated, as well as the physical-chemical properties of the catalysts.

2 EXPERIMENTAL

2.1 Catalyst preparation and characterization

All the catalysts were prepared by the ion-exchanged method. Each bare zeolite was exposed to 0.1 M $Ni(NO_3)_2$ 6 H_2O aqueous solution, considering a ratio of 20 g solution/g zeolite. The suspension was kept under stirring during 24 h at 80 ºC. Subsequently, it was filtered and washed with ultra-pure water. The cake was dried overnight at 100 ºC and then calcined at 500 ºC for 8 h. Finally, the catalysts were pressed and sieved to a particle size of 500-700 µm. Some of the catalysts were reduced at 550 ºC for 1 h, using 100 cm^3 STP/min of pure H_2.

The non-reduced catalysts will be called as NiO/zeolite and the reduced ones, as Ni/zeolite, being "zeolite" the corresponding X, LTA or ZSM-5 zeolite.

The catalysts were characterized by several techniques. The specific surface area and pore distribution of the catalysts and the supports are determined by N_2 physisorption. Crystalline phases of the catalysts were determined by XRD (X-Ray diffraction). The chemical composition of the fresh catalysts was measured by atomic absorption spectroscopy (AAS). The total acidity was measured by NH_3-TPD. The Lewis and Brønsted acid sites distribution was determined by FTIR of adsorbed probe molecules (pyridine for X and ZSM-5-supported catalysts and NH_3 for the LTA-supported catalyst).

2.2 Experimental system

The experiments were performed in a 500 mL stainless steel batch reactor (Series 4560 Mini Reactors, 100-600 mL Parr Instrument Company), equipped with a temperature and stir controller (4848 Reactor Controller, Parr Instrument).

100 mL of a 5 wt.% glycerol aqueous solution and 0.65 g of catalyst were placed into the reactor, which was closed and pressurized until 33 initial bar of H_2, after successive H_2 purges, in order to avoid residual air inside the reactor. After setting the pressure, the temperature was increased until the reaction conditions (200, 227 or 250 ºC), under mild stirring to get an homogeneous temperature inside the reactor. When the temperature set point was achieved, the stirring was increased and then, the reaction was hold for 3 h.

After the experiment, the reactor was cooled down and the reactor was open. The liquid samples were filtered and, subsequently, analyzed by GC-MS (Agilent Technologies Inc. 7890A) and quantified by GC-FID (Agilent Technologies Inc. 7820A). In addition, total organic carbon was also measured (Shimadzu TOC-L).

3 RESULTS AND DISCUSSION

3.1 Catalyst characterization

The textural properties of the fresh catalysts are summarized in Table I.

Table I: Textural properties of calcined catalysts

	Sg (m^2/g)	Vp (cm^3/g)
NiO/X	410	0.11
NiO/LTA*	18	-
NiO/ZSM-5	323	0.16

* Inaccurate measurement

It was not possible to determine correctly the textural properties of the NiO/LTA catalyst using N_2 physisorption. According to these results and previous published works, liquid N_2 is not able to access into the LTA zeolite structure due to is framework.

NiO/X presents higher values of specific surface area and smaller pore volume than the NiO/ZSM-5 catalyst. These results are in line with previous literature and clearly influenced by zeolite type.

The chemical composition of the catalyst has been determined by Atomic Absorption Spectroscopy (AAS). From this technique the Si/Al atomic ratio and the molar percentage of the Ni in the zeolite framework, introduced after the ion exchanged process (Ni int), considering all the species available for the ion exchange. These results are shown in Table II.

Table II: Chemical composition of the calcined catalysts

	NiO/X	NiO/LTA	NiO/ZSM-5
Al (wt.%)	16.6	19.0	3.5
Si (wt.%)	19.2	20.5	41.2
Na (wt.%)	4.1	11.9	2.0
Ni (wt.%)	9.6	6.7	1.2
Ca (wt.%)	-	0.1	-
Si/Al	1.11	1.03	11.44
*Ni_{int} (mol%)	65	31	32

* $Ni_{int} = (2 \cdot n_{Ni})/(2\ n_{Ni} + 2\ n_{Ca} + n_{Na}) \cdot 100$

NiO/X and NiO/LTA catalysts show similar values of Si/Al ratio, which are much smaller than that of the NiO/ZSM-5 catalyst. The amount of exchanged Ni is different between catalysts and it depends directly on zeolite type, despite of using the same Ni solution for the ion exchange process, being much higher the amount of Ni exchanged of the NiO/X catalysts.

XRD patterns of the calcined catalysts are shown in Fig. 1. The catalysts show peaks at 37, 43 and 63 º, typical of the bunsenite type NiO (JCPDS 47-1159) and their low peak intensity could be related to the high dispersion of the NiO nanoparticles in the zeolite structure.

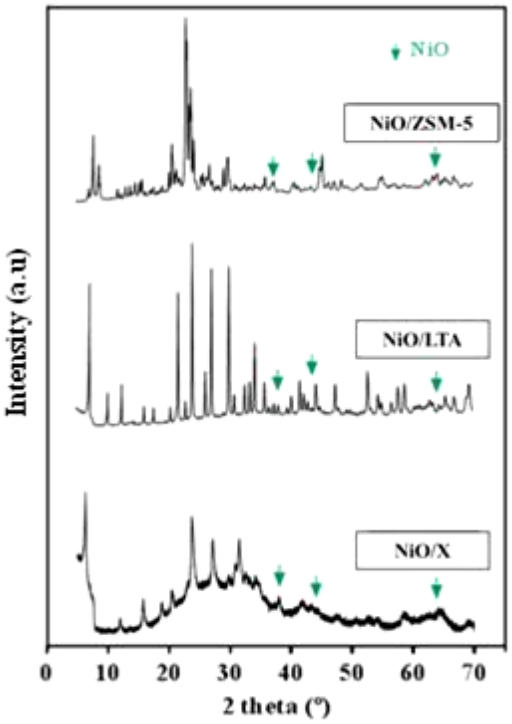

Figure 1: XRD diffractograms of the calcined catalysts

Despite the differences between the proper zeolite structures, it is clear that the catalysts NiO/LTA and NiO/ZSM-5 present much crystalline structures than the NiO/X. It is also observed the low stability of the zeolite X in the aqueous media, which could imply the partial breakdown of the zeolite crystalline structure, even during the ion-exchange synthesis process.

The acidity of the catalysts is shown in Table III. All the catalysts present a high acidity value, typical of the alumino-silicates structures. However, the catalyst NiO/X shows a lower acidity than the other two catalysts, which show no significant differences.

Table III: Total acidity values of calcined catalysts

	Acidity (μmol NH_3/g)
NiO/X	375
NiO/ZSM-5	739
NiO/LTA	772

Fig. 2 shows the NH_3-TPD deconvoluted profiles. The peak between 185-200 ºC is related to the low strength acid sites, which is present in all the catalysts. Those acid sites between 226-252 ºC would indicate the presence of medium-low strength acid sites, only observed in the catalysts NiO/X and NiO/ZSM-5.

Meanwhile, more acid sites are located between 283-293 ºC would be related to medium acid sites, only shown in the NiO/LTA and NiO/ZSM-5 catalysts.

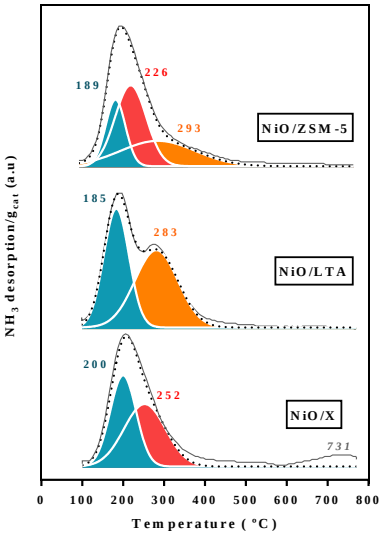

Figure 2: NH_3-TPD profiles of the calcined catalysts

NiO/X catalyst shows a peak at temperatures around 731 ºC which could be related to higher strength acid sites. However, this catalyst was calcined at 500 ºC and reduced at 550 ºC, so the stability of this catalyst at greater temperatures cannot be assured.

Fig. 3 shows the different FTIR spectra of the calcined catalysts in the range 1700 – 1300 cm^{-1}.

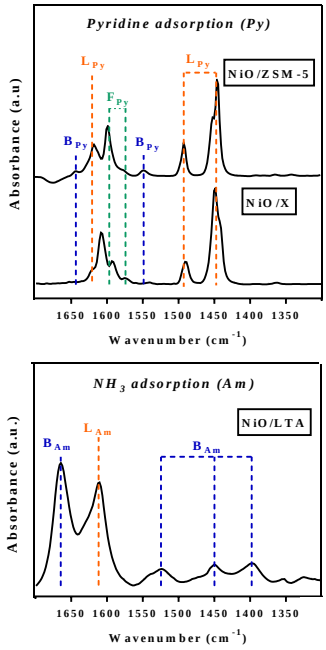

Figure 3: FTIR spectra of adsorbed probe molecules (L: Lewis acid sites, B: Brønsted acid sites, F: physisorbed pyridine).

The analysis of the catalyst NiO/LTA was performed using NH_3 as probe molecule, because the LTA zeolite structure does not allow a correct adsorption of the pyridine into its cavities.

According to the spectra of NiO/X and NiO/ZSM-5 and the values of acid sites concentration (Table IV), the Lewis acidity is predominant in these catalysts.

Table IV: Lewis and Brønsted acid sites quantification

	C_{Lewis} (µmol/g)	$C_{Brønsted}$ (µmol/g)	Total (µmol/g)	Ratio B/L
NiO/X	653	10	663	0.02
NiO/ZSM-5	1262	110	1372	0.09
NiO/LTA	573	97	670	0.17

3.2 Experimental results

The liquids products were a mix of ketones, mono and poly-alcohols, aldehydes, acids, water and unreacted glycerol. The main products detected in the analysis were acetone, ethanol, acetol, acrolein, propionic acid and 1,2-PDO.

The reaction mechanism followed by these catalysts is shown in Fig. 4.

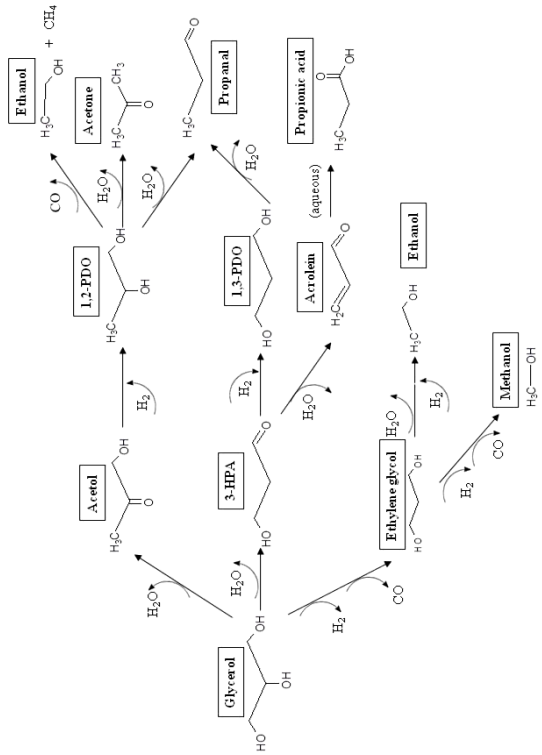

Figure 4: Reaction mechanism followed by zeolite supported catalysts [4]

It is generally considered that the dehydration of glycerol to acetol takes place in the Lewis acid sites, whereas the dehydration to 3-HPA occurs in the Brønsted acid sites, which could further produce acrolein and propionic acid [4].

The catalytic activity has been studied through the global results of the glycerol conversion, carbon conversion to liquid (CCliq) and carbon conversion to gas (CCgas), so as the carbon selectivity to liquid

products. Because the CCgas is very low, the glycerol is mainly converted to liquids.

Fig. 5 shows the influence of the reaction temperature (200 – 250 ºC) on the results of CCliq for each catalyst. In most cases, the increase of the reaction temperature has a positive effect on the catalytic activity, for both the non-reduced and the reduced catalysts. This effect is more remarkable for the catalysts supported on zeolite X, which show a gradual increase of activity when increasing the reaction temperature.

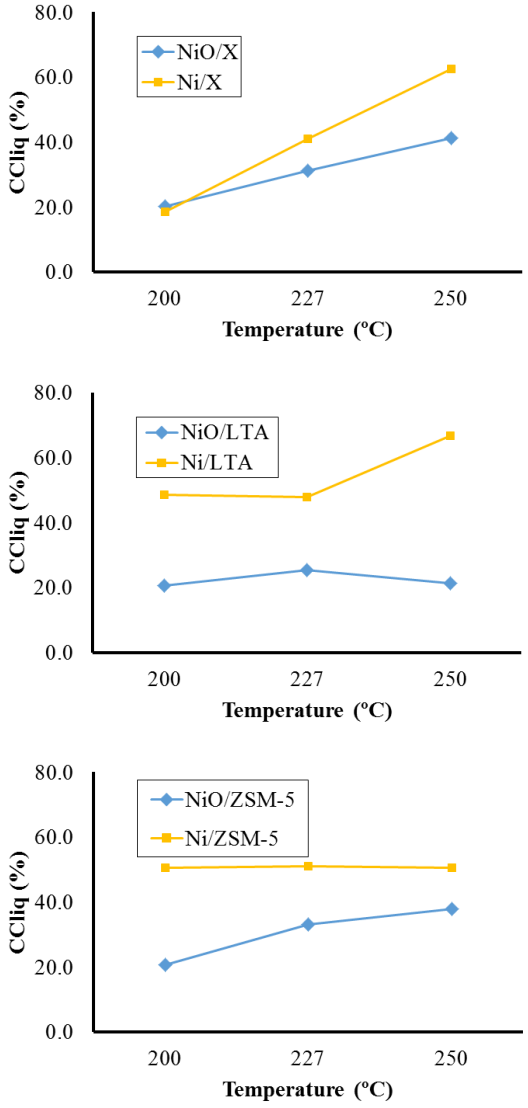

Figure 5: Influence of temperature on CCliq for the catalysts supported on X, LTA and ZSM-5 zeolites.

The changes in the reaction temperature and the oxidation state of the active phase have also a great effect on the reaction mechanism followed by the catalysts. Fig. 6 to 8 show the selectivity to the majoritarian liquid products generated by each catalyst. Only selectivity values higher than 5% have been considered.

In the case of the catalysts supported on X zeolite (Fig. 6), at 200 ºC the non-reduced catalyst (NiO/X) only dehydrates the glycerol to form mainly acetone. At 227 ºC the reaction mechanism varies, hindering the selectivity to acetone and promoting the formation of propionic acid from acrolein. At 250 ºC, the selectivity to acetone increases, while the selectivity to propionic acid decreases slightly.

When the Ni/X catalyst is used, acetol and propionic acid are mainly produced at 200 ºC. The selectivity to 1,2-PDO shows lower but also significant values. At 227 ºC, the selectivity to 1,2-PDO is maximized at the expense of dehydration products (acetol and propionic acid), promoting the hydrogenation reaction. In contrast to the NiO/X catalyst, the selectivity to ethanol increases notably. When the temperature is increased up to 250 ºC, the selectivity to 1,2-PDO decreases, for the benefit of acetol and propionic acid, while the ethanol selectivity keeps on raising.

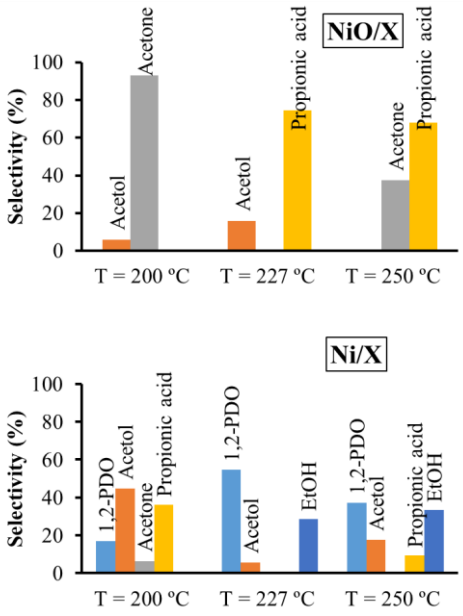

Figure 6: Influence of temperature on carbon selectivity to liquid products for the catalysts supported on X zeolite.

For the NiO/LTA catalyst, (Fig. 7) the main products are glycerol dehydration-derived products, such as propionic acid and acetol. The increase of temperature from 200 to 250 ºC increases acetol selectivity, while propionic acid decreases.

Ni/LTA catalyst presents as majoritarian products ethanol and acetol at 200 ºC, followed by propionic acid and small amounts of methanol. The liquid products distribution changes when increases the temperature up to 227 ºC, being the 1,2PDO the main product, followed by the ethanol and acetol. A new increase in the temperature up to 250 ºC promotes the production of acetol and ethanol, as expense of the 1,2-PDO.

As for the NiO/ZSM-5 catalyst (Fig. 8), at 200 ºC the main products are again those derived from glycerol dehydration (acetol and propionc acid). An increase up to 227 ºC implies an increase of the acetol selectivity, as expense of propionic acid. In addition, small amounts of 1,2-PDO have been also produced. At 250 ºC the acetol selectivity keeps increasing, being this reaction route clearly favored with regard to propionic acid route. The 1,2-PDO selectivity does not show significant changes, whereas acetone selectivity increases its value.

Finally, for the Ni/ZSM-5 catalyst, the main product is acetone at 200 ºC. There is no significant formation of

acetol or 1,2-PDO, nor propionic acid or acrolein, at that temperature. At 227 ºC the production of acetone remarkably decreases for the benefit of acetol and 1,2-PDO production and also of propionic acid and acrolein production. An increase up to 250 ºC promotes the production of acetone again, being mainly the only product of reaction.

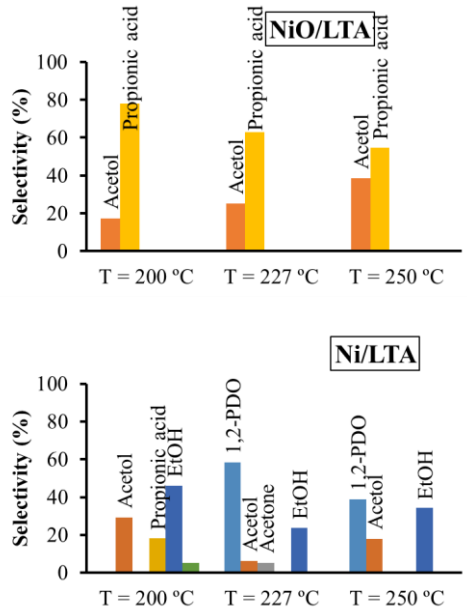

Figure 7: Influence of temperature on carbon selectivity to liquid products for the catalysts supported on LTA zeolite.

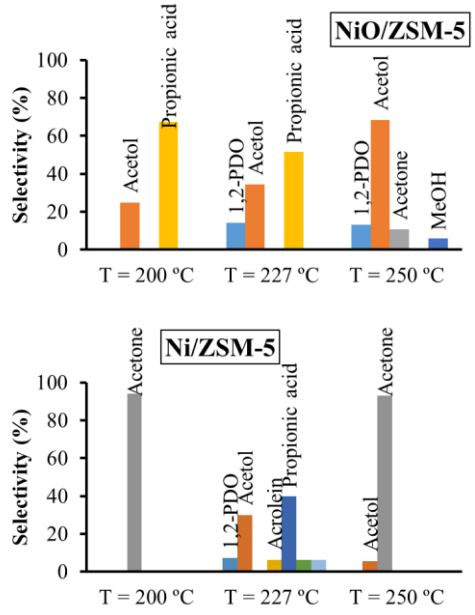

Figure 8: Influence of temperature on carbon selectivity to liquid products for the catalysts supported on ZSM-5 zeolite.

According to the previous results, the reaction temperature influences significantly on liquid products selectivity. This could be related to the kinetics and thermodynamics of chemical reaction involved, which would require a deeper study in order to stablish clear activity tendencies.

However, considering these catalysts and these results, a proposal of operating temperatures for certain liquid products is shown in Table V

Table V: A proposal of operating temperatures for liquid products

	Temperature (ºC)	Product (selectivity, %)
NiO/X	200	Acetone (93.10)
NiO/X	227	1,2-PDO (54.53)
NiO/LTA	200	Propionic acid (77.83)
Ni/LTA	227	1,2-PDO (58.26)
NiO/ZSM-5	250	Acetol (68.39)
Ni/ZSM-5	200	Acetone (94.04)

4 CONCLUSIONS

The possibility of Ni catalysts supported on X, LTA and ZSM-5 zeolites for the glycerol hydrogenolysis under H_2 atmosphere has been studied in this work. The influence of the oxidation state of the active phase has been set, as well as the influence of the reaction temperature.

In most cases, only the reduced catalysts allow the production of hydrogenation products, such as 1,2-PDO. This would indicate the relevance of the reduced active phase, Ni^0, to carry out the hydrogenation. On the contrary, in the case of non-reduced catalysts, mainly dehydration reaction routes take place, both in Lewis acid sites (to produce acetol and acetone) Brønsted acid sites (to produce 3-HPA, acrolein and propionic acid).

The selectivity values to liquid products (acetol, 1,2-PDO, propionic acid, acetone or ethanol) varied notably depending on the reaction temperature, between 200 and 250 ºC. This first preliminary study allowed setting which temperature range promotes the selectivity to certain products. However, this would require a more detailed and specific studies for each catalyst to determine clear activity trends.

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7 LOGO SPACE