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# Hydrogenolysis through catalytic transfer hydrogenation: Glycerol conversion to 1,2-propanediol

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# ABSTRACT

Important biorefinery processes imply hydrogenolysis reactions where high hydrogen pressures are required. As most of the nowadays available hydrogen gas is produced from fossil fuels there are great incentives to develop alternative technologies able to both substitute non-renewable reactants and operate at lower severity conditions. The use of hydrogen donor molecules from renewable origin can be a promising alternative to tackle simultaneously with both objectives. In the present study the use of methanol, 2-propanol and formic acid in the glycerol hydrogenolysis process to obtain 1,2-propanediol was investigated using a Ni–Cu/Al<sub>2</sub>O<sub>3</sub> catalyst, prepared by sol–gel method, and under N<sub>2</sub> atmosphere. A semi-continuous set-up was designed in which the donor solution was continuously fed into the autoclave reactor containing the glycerol aqueous phase. The best results in terms of glycerol conversion and 1,2-propanediol selectivity were obtained with formic acid.

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#### 1. Introduction

Biodisel production from vegetable oils through transesterification processes cogenerates glycerol at an approximate rate of 1 kg for every 10 kg of biodiesel. The rapid growing production of biodiesel has generated an oversupply of glycerol in the market, leading to a significant decrease in the price of glycerol [1]. Excess glycerol disposal is an expensive and environmentally problematic alternative. Effective valorization of glycerol will therefore contribute to (i) improve the cost-competitiveness of biodiesel processes and (ii) gradually replace fossil fuels by biomass as the source of organic carbon [2-4]. One promising and valuable compound that can be obtained from glycerol is 1,2-propanediol (1,2-PDO). 1,2-PDO is widely used as an anti-freeze agent, as a monomer for polyester resins and in paints, cosmetic, food, etc. [5]. Currently, 1,2-PDO is commercially produced from propylene oxide. The conversion of glycerol into 1,2-PDO is a promising process that might help in the gradual replacement of petroleum-derived liquid fuels and plastics by biomass derived products [6].

Glycerol hydrogenolysis process to obtain 1,2-PDO involves C—O bond dissociation and simultaneous addition of hydrogen [7]. Since hydrogenolysis uses hydrogen as a reactant, most of the published studies related to glycerol hydrogenolysis have been performed under hydrogen pressure, both in gas [8–11] or liquid phase [12–25]. Nevertheless, the use of molecular hydrogen presents some drawbacks. First, because nowadays molecular hydrogen is still derived from fossil fuels through energy intensive processes. Second, because hydrogen has high diffusivity is easily ignited and presents considerable hazards on a large scale [26]. Finally, because the low solubility of hydrogen in aqueous solutions requires to operate at elevated pressures. In situ generation of the hydrogen required obviates most of these difficulties [27].

Hydrogenolysis of glycerol combined with in situ production of hydrogen by the simultaneous reforming of glycerol has already been studied [19,28,29]. It was recently reported that catalytic transfer hydrogenation (CTH) using 2-propanol (2-PO) as a hydrogen donor molecule gives higher yields to 1,2-PDO as compared to aqueous reforming of glycerol on Ni–Cu/Al<sub>2</sub>O<sub>3</sub> based catalysts [30]. It was also observed that 2-PO was not able to hydrogenate acetol, and that therefore when 2-PO was used as hydrogen donor molecule glycerol hydrogenolysis to 1,2-PDO did not occur through the widely accepted dehydration–hydrogenation mechanism (glycerol  $\rightarrow$  acetol  $\rightarrow$  1,2-PDO). Based on characterization results and reactivity trends, a reaction mechanism through intermediate alkoxide formation was proposed (see Scheme 1).

In this previous work it was also observed that the amount of hydrogen donor affects both glycerol conversion and selectivities to main reaction products, as there is a competition between the OH groups of glycerol and of 2-PO for the active sites of the catalyst to



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Scheme 1. Proposed reaction mechanism for direct glycerol hydrogenolysis to 1,2-PDO using 2-PO as a hydrogen donor molecule [30].

form the intermediate alkoxides. High initial 2-PO concentrations reduced glycerol reaction rate while increasing 1,2-PDO selectivity. For low initial 2-PO concentrations, there was not enough hydrogen available to convert all the glycerol. Based on these findings, the use of a semi-continuous batch system seems to be interesting as the hydrogen donor could be continuously pumped into the glycerol water solution, lowering active site competition and, at the same time, avoiding hydrogen supply problems.

In this article, the use of methanol, 2-PO and formic acid as hydrogen donor molecules in glycerol hydrogenolysis process over  $Ni-Cu/Al_2O_3$  catalyst is investigated in a semi-continuous batch system. The effect of the type of hydrogen donor and donor feed rate on glycerol conversion and selectivity to 1,2-PDO is discussed.

# 2. Experimental

# 2.1. Catalyst

Ni-Cu/Al<sub>2</sub>O<sub>3</sub> was prepared by the sol-gel method. Aluminum isopropoxide (99.99%; Sigma Aldrich) was dissolved in deionized water (9 mL of H<sub>2</sub>O per gram of aluminum isopropoxide) by vigorous stirring of the solution at 313 K. The pH was measured and kept between 3.8 and 4.2 adding the required amounts of HNO<sub>3</sub> (0.5 M). Simultaneously, nickel (II) nitrate hexahydrate (99.999%; Sigma Aldrich) and copper (II) nitrate hemi pentahydrate (98.0%; Alfa Aesar) were dissolved in ethanol. The precursor solution was slowly added to the aluminum isopropoxide solution. The mixture was stirred for 30 min at 313 K and then introduced into an ultrasonic apparatus for another 30 min. The mixture was then rested for 24 h at 313 K and subsequently for another 12 h at 375 K. The product obtained was crushed and calcined from room temperature to 723 K at a heating rate of 2 K/min. This temperature was maintained for 4 h. Catalyst samples for activity tests were used in powdered form with a granule size between 320 and 500  $\mu$ m.

# 2.2. Activity test

The hydrogenolysis of glycerol was carried out in a 50 mL stainless steel autoclave with a magnetic stirrer. The catalyst powder (0.5 g) was introduced into the autoclave and the reactor was then purged with N<sub>2</sub>. After purging, the catalyst was pre-treated during 4 h under a 300 mL/min flow of 50 vol%  $H_2/N_2$  at 1 bar and 723 K. The pre-treatment of the catalysts was done in situ in the autoclave in order to avoid the contact of reduced samples with air when the catalyst is transferred to the reactor. After the pre-treatment, the reactor was purged with N<sub>2</sub> or H<sub>2</sub>, the temperature was set to 493 K, and the pressure was increased to 45 bar. 20 mL of the aqueous solution having 20 wt% of glycerol (99.0%; Sigma Aldrich) was placed in a feed cylinder, heated to the reaction temperature and pressurized to 50 bar. Next, the stirring speed was set constant at 550 rpm. The reaction starting time was established when the line connecting the feed cylinder and the reactor was opened. N<sub>2</sub> or H<sub>2</sub> was directed through the feed cylinder for 3 min to stabilize the pressure of the reactor and to guarantee that all the feed went into the reactor. During the 10h reaction time, hydrogen donor aqueous solution, 2-PO (99.9%; Sigma Aldrich), formic acid (98.0%; Fluka) or methanol (99.9%; Alfa Aesar), was pumped at a constant rate of 0.02 mL/min. In order to investigate the effect of the amount of hydrogen donor added on glycerol hydrogenolysis process, the concentration of hydrogen donor in the aqueous solution pumped was different in each test.

Four liquid samples (1.2–1.5 mL) were taken throughout the reaction time in order to obtain the evolution of reactant and product concentrations. These samples were analyzed using a gas chromatograph (Agilent Technologies, 7890 A) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). A Meta-Wax capillary column (diameter 0.53 mm, length 30 m) was used for product separation. For formic acid detection all the liquid samples were also analyzed by a GC–MS (Agilent Technologies, 5973). After reaction, the gas phase was collected in a gas bag and analyzed with another GC–TCD–FID (Agilent Technologies, 7890 A) equipped with a molecular sieve column (HP-MOLESIEVE, diameter 0.535 mm, length 30 m) and a capillary column (HP-PLOT/Q, diameter 0.320 mm, length 30 m).

From the GC–FID analysis of the liquid samples, the concentration (mol L<sup>-1</sup>) of each reactant and product was obtained. In order to estimate the moles of each reactant and product in the reactor, it was necessary to know the volume inside the reactor at the time the sample was taken. 1 mL of the withdrawn sample (taken with an automatic pipette) was weighted to know the density of the liquid phase. Next, the grams of the liquid solution in the reactor at the given time ( $g_t$ ) were calculated using the mass balance equation below. By multiplying the grams inside the reactor in the time the sample was taken by the density of the liquid phase, the volume of the liquid phase inside the reactor was obtained.

$$g_t = g_i + g_{pt} - g_{st} - g_{gt}$$

where  $g_i$  are the total grams of the glycerol aqueous solution in the reactor at the beginning of the test;  $g_{pt}$  are the grams pumped at a given time t;  $g_{st}$  are the grams of the reaction mixture withdrawn during liquid sampling at a given time t;  $g_{gt}$  are the total grams that has gone to the gas phase at a given time t.

The gas phase was only analyzed at the end of the activity tests. To calculate  $g_{gt}$ , it was assumed that gas products were formed homogenously during the reacting time. Moreover, for simplification it was considered that there were not liquid products saturating the gas phase of the reactor. Therefore:

$$g_{gt} = g_{gt=600} \frac{t}{600}$$

where  $g_{gt=600}$  is the amount of grams converted to gas products at the end of the activity test (after 600 min) and *t* is any given time in minutes.

The conversion and selectivity values were calculated on carbon bases:

Conv. of glyc.% = 
$$\frac{\sum \text{C-based mol prod. } t = t}{\sum \text{C-based mol glyc. } t = 0} \times 100$$

Select. of prod.% =  $\frac{\sum \text{C-based mol of prod.}_i \quad t = t}{\sum \text{C-based mol of all prod.} \quad t = t} \times 100$ 

For mechanistic interpretation, acetol (90.0%; Sigma Aldrich) was also utilized as reactant in some activity tests.

#### 2.3. Catalyst characterization

Ni–Cu/Al<sub>2</sub>O<sub>3</sub> fresh catalyst was characterized by ICP-AES, N<sub>2</sub>-physisorption, H<sub>2</sub>-chemisorption, TPD of NH<sub>3</sub>, TPR and XPS. Characterization methods and results are reported elsewhere [30]. A summary of the main characteristics of Ni–Cu/Al<sub>2</sub>O<sub>3</sub> catalyst is presented in Table 1.

Temperature-programmed oxidation analyses of fresh and used reduced catalysts were carried out using a thermo-gravimetric analyzer (Mettler Toledo TGA/SDTA 851e). The standard protocol involved the pre-treatment of the sample (45-50 mg) in 125 mL/min of N<sub>2</sub> flow from 297 K to 673 K at a heating rate of 10 K/min. The sample was then cooled to 323 K and the weight change of the sample was continuously monitored during its heating in 75 mL/min of 10 vol% O<sub>2</sub> in He as reactive gas from 323 to 1173 K at a heating rate of 5 K/min.

For TEM characterization, a Phillips CM200 microscope equipped with a LaB6 filament and a super win lent operating at 200 kV was used. Bright field images were acquired using a CCD camera (TVIPS GmbH). Powders of the catalysts samples were dispersed in ethanol with ultrasound and drops were deposited on copper grids coated with amorphous carbon films.

# 3. Results and discussion

# 3.1. Hydrogen donor selection

Three different hydrogen donor molecules were used in the activity tests: 2-PO, methanol and formic acid. 2-PO has already been reported to be active in glycerol hydrogenolysis process to 1,2-PDO [30,31]. The main reactions taking place with the selected hydrogen donors are represented in Scheme 2. Under the experimental conditions, 2-PO can be dehydrogenated to acetone or dehydrated to propene. Propene can be further hydrogenated to propane using the hydrogen available from 2-PO dehydrogenation. It was observed that, under the experimental conditions used, acetone is also dehydrated to propene [30]. Formic acid together with levulinic acid and furfural are formed from non-food biomass feedstock by acid catalyzed hydrolysis [32]. Formic acid can also be used as efficient storage material for H<sub>2</sub> [33,34], as it can release hydrogen at low temperatures using iron catalysts [35,36]. Other potential uses of formic acid are currently being investigated and catalytic transfer hydrogenation with formic acid as hydrogen source could be an important application. Formic acid can be catalytically decomposed to give hydrogen and CO<sub>2</sub>. A parallel reaction gives water and CO, which can be further converted to CO<sub>2</sub> and hydrogen through water gas shift reaction [37]. Methanol is a widely used molecule in the catalytic hydrogenation of unsaturated compounds [38,39]. CTH using methanol is promoted in water solutions as formaldehyde readily reacts with water to form formic acid, which further reacts to yield H<sub>2</sub> and CO<sub>2</sub> [35]. Therefore, from each molecule of methanol, three hydrogen molecules can be formed.

An additional advantage is gained when the products of the decomposing donor have large negative Gibbs energy of formation. Thus, hydrogen donor molecules that produce gaseous products after their dehydrogenation, like formic acid giving CO<sub>2</sub>, have added driving force to their reactivity. In Scheme 2 the standard Gibbs energy of the dehydrogenation reactions of the three hydrogen donors are represented. These values were calculated from the following equation:

$$\Delta G_R^0 = \sum n \Delta G_{f(\text{products})}^0 - \sum m \Delta G_{f(\text{reactants})}^0$$

Being *n* and *m* the stoichiometric coefficients, of reactants and products, respectively, and  $\Delta G_f^0$  the Gibbs energy of formation at 298 K, 1 bar and assuming that all reactants and products behave as an ideal gas ( $\Delta G_f^0$  values were obtained from the *Chemical Engineers' Handbook* [40]). Even though the activity tests were carried out at higher temperatures and pressures, the calculated  $\Delta G_R^0$  values allow a qualitative discussion about the dehydrogenation reaction of each selected donor being or not thermodynamically favored. As observed in Scheme 2, methanol conversion to formaldehyde and H<sub>2</sub> is the thermodynamically most disfavored reaction, as it has the higher positive value for  $\Delta G_R^0$  while formic acid dehydrogenation is a thermodynamically favored reaction due to the negative value of the  $\Delta G_R^0$ .

# 3.2. Glycerol hydrogenolysis under N<sub>2</sub> atmosphere

2-Propanol, methanol and formic acid were studied as hydrogen donor molecules for the hydrogenolysis of glycerol to 1,2-PDO. The hydrogen donor water solution was continuously pumped, at a constant rate of 0.02 mL/min, to the 20 mL glycerol aqueous solution initially placed in the reactor. In order to investigate the effect of the hydrogen donor pumping rate on glycerol conversion and selectivity to main reaction products, the concentration of the donor in the pumping solution was kept constant in each test but modified from test to test. In the activity tests without hydrogen donor addition, distilled water was not pumped to the system.

# 3.2.1. $N_2 + 2$ -propanol

As it can be observed in Table 2, glycerol conversion and selectivity to 1,2-PDO values were higher in all tests where 2-PO was added as compared to the test without donor addition. This indicates that glycerol hydrogenolysis to 1,2-PDO by transfer hydrogenation using 2-PO is more effective than glycerol hydrogenolysis using the hydrogen produced by simultaneous reforming of glycerol. At the same time, the positive effect of hydrogen donor addition was much more significant than the possible negative effect of glycerol dilution with the pumped water. Indeed, the low reaction order on glycerol concentration has already been reported [41,42].

Regarding the effect of 2-PO pumping rate, it can be observed in Table 2 that both glycerol conversion and 1,2-PDO selectivity increased with increasing pumping rate of 2-PO, until a maximum was achieved at 7.2 mmol  $h^{-1}$  of 2-PO fed. For higher feeding rates of 2-PO (runs 4 and 5), similar glycerol conversions but lower selectivities to 1,2-PDO were observed. Therefore, there is an optimum 2-PO feeding rate that maximizes 1,2-PDO formation. At low feeding rates, increasing 2-PO feeding rate increased 1,2-PDO selectivity and glycerol conversion, because more 2-PO molecules reacted providing a higher number of active hydrogen atoms. Nevertheless, above 7.2 mmol  $h^{-1}$ , further increments in 2-PO feeding rate did not increase glycerol conversion and had a negative effect on 1,2-PDO selectivity. It seems that there are negative factors associated to high 2-PO availability in the system that affect glycerol hydrogenolysis to 1,2-PDO.

Focusing on hydrogen donor behavior, it can be noticed in Table 2 that the pumping rate of 2-PO did not have significant influence in the conversion of 2-PO, but affected the selectivity to dehydrogenation and dehydration products. For low 2-PO feeding rates (runs 2 and 3), low selectivities to acetone were detected, indicating a further dehydration of the formed acetone to propene. In all the tests propane was detected in the gas phase, indicating that part of the formed propene was hydrogenated to propane.

In the light of these results, the reason why above 7.2 mmol  $h^{-1}$  further increments in 2-PO pumping rate did not increment glycerol conversion and had a negative effect on 1,2-PDO selectivity seems to be a combination of various factors. It was previously

Characteristics of the catalyst.

Sample	Ni (wt%) <sup>a</sup>	Cu (wt%) <sup>a</sup>	$S_{\text{BET}}$ (m <sup>2</sup> /g Al <sub>2</sub> O <sub>3</sub> )	Dispersion (%)	$MSA^b\left(m^2/g\right)$	Particle size (nm) <sup>c</sup>	Des. $NH_3\times 10^4~(molg^{-1})^d$
Ni-Cu/Al <sub>2</sub> O <sub>3</sub>	7.7	28.0	208	1.6	3.7	65.6	3.4

<sup>a</sup> Chemical composition determined with ICP.

<sup>b</sup> Metal surface area.

<sup>c</sup> Determined from H<sub>2</sub> chemisorption analysis.

<sup>d</sup> Acidity of the fresh samples from temperature-programmed desorption of ammonia.



Scheme 2. Main reactions taking place with the selected hydrogen donors.

#### Table 2

Glycerol conversion and selectivity to 1,2-PDO and acetol, and 2-PO conversion and selectivity to acetone, propene and propane as a function of 2-PO feed rate. 45 bar N<sub>2</sub> pressure, 10 h, 493 K, 20 mL (20 wt%) glycerol aqueous solution, 166 mg catalyst/g glycerol, 0.02 mL/min donor solution feed rate.

Run	2-PO conc. pumped solution (wt%)	2-PO feed-rate (mmol h <sup>-1</sup> )	Glyc. conv. (%)	Selectivity (%) <sup>a</sup> (from glycerol)		C-balance	2-PO conv. (%)	Selectivity	r (%) (from 2-	PO)
				1,2-PDO	Acetol			Acetone	Propene	Propane
1 <sup>b</sup>	-	-	15.8	49.3	38.8	97.2	-	-	-	-
2	20.0	3.6	17.8	53.1	44.5	103.4	51.8	1.2	90.6	8.2
3	40.0	7.2	28.2	77.4	15.4	97.5	46.4	7.7	58.8	33.4
4	60.0	9.8	27.8	53.0	42.3	93.6	50.4	18.0	60.4	21.5
5	80.0	12.5	27.6	56.3	40.7	94.1	49.7	19.7	60.5	19.8

<sup>a</sup> The other products detected coming from glycerol were ethylene glycol, ethanol, 1-propanol and methane.

<sup>b</sup> No solution was pumped to the reactor.

reported that glycerol and 2-PO compete for the same active sites for the formation of alkoxides [30]. In fact, the donor and the acceptor need to be adsorbed on contiguous active sites in order to make possible the transfer hydrogenation [27]. If the active hydrogen atoms formed from 2-PO are not adsorbed near a glycerol molecule, they combine to yield molecular hydrogen, while if glycerol is not adsorbed near an active hydrogen atom it does not react to 1,2-PDO. Hence, it seems that there should be an optimum proportion between adsorbed donor and acceptor molecules that maximizes the production of 1,2-PDO. For 2-PO, this optimum was obtained for a feeding rate near 7.2 mmol h<sup>-1</sup>. Another factor that needs to be considered is that propene, formed from 2-PO and acetone dehydration, hydrogenates to propane competing with glycerol for the active hydrogen atoms. At high 2-PO feeding rates, there is higher propene formation and therefore higher competition.

Carbon dioxide was only detected in run 1, indicating that aqueous phase reforming of glycerol did only take place when no hydrogen donor was introduced in the system. It has already been observed that glycerol APR did not take place when external hydrogen is introduced in the system [19], due to a decrease in the surface concentrations of reactive intermediates formed from glycerol dehydrogenation reactions [43].

Glycerol conversion and selectivity to 1,2-PDO and acetol, and formic acid conversion and selectivity to CO and CO<sub>2</sub> as a function of formic acid feed rate. 45 bar N<sub>2</sub> pressure, 10 h, 493 K, 20 mL (20 wt%) glycerol aqueous solution, 0.5 g of catalyst, 0.02 mL/min donor solution feed rate.

Run	Formic acid conc. pumped solution (wt%)	Formic acid feed-rate (mmol h <sup>-1</sup> )	Glyc. conv. (%)	Selectivity (%) <sup>a</sup> (from glycerol)		C-balance	Formic acid conv. (%)	Select (from	tivity (%) formic acid)
				1,2-PDO	Acetol			со	CO <sub>2</sub>
1 <sup>b</sup>	0	0	15.8	49.3	38.8	97.2	-	-	_
2	3.5	0.9	22.4	63.5	28.0	94.3	100	0	100
3	7.0	1.8	33.5	85.9	6.7	96.8	100	0	100
4	14.0	3.6	28.0	78.7	11.5	95.1	100	0	100
5	28.0	7.2	20.2	77.6	12.3	93.9	100	0	100
6	42.0	10.8	4.5	73.0	17.9	101.7	100	0	100
7 <sup>c</sup>	7.0	1.8	1.2	0.0	35.5	104.5	164.5	0	100
8 <sup>d</sup>	-	-	16.2	55.8	32.4	98.5	100	0	100

<sup>a</sup> The other products detected coming from glycerol were ethylene glycol, ethanol, 1-propanol and methane.

<sup>b</sup> No solution was pumped to the reactor.

<sup>c</sup> This test was carried out without catalyst

<sup>d</sup> 18 mmol of formic acid were placed from the beginning of the reaction in the reactor and no solution was pumped to the reactor.

#### 3.2.2. $N_2$ + formic acid

As observed in Table 3, glycerol conversion and selectivity to 1,2-PDO increased with formic acid feeding rate until a maximum was obtained in the test with 1.8 mmol  $h^{-1}$  feeding rate. With this optimized hydrogen donor supply, a selectivity value to 1,2-PDO of 86% was achieved, which is a considerable high value and comparable to the best values previously reported in processes under H<sub>2</sub> pressure [8,10,23]. For higher pumping rates, both glycerol conversion and the selectivity to 1,2-PDO decreased.

Regarding formic acid behavior, the most interesting aspect is that in all the activity tests, and therefore for all the range of pumping rates studied, there was 100% conversion of formic acid. No formic acid was detected in any of the tests and in any of the five liquid samples taken during each test, which means that formic acid readily reacts under the experimental conditions. As it was pointed out before, the formation of gaseous  $CO_2$ , with a large negative Gibbs energy of formic acid. Negligible CO amounts were detected in the analysis of the gas phase, indicating that the possible CO formed through formic acid decomposition was readily converted to  $CO_2$  by water gas shift reaction The mol of  $CO_2$  detected in the gas phase quite precisely coincided with the mol of formic acid fed, which indicates that glycerol reforming did not significantly take place when formic acid was fed.

In order to ensure that formic acid decomposition occurred in the active sites of the catalyst, a further activity test was performed (run 7 of Table 3) without the addition of the catalyst. As it can be observed, without catalyst, formic acid conversion after 10 h was only 14.5%. This proves that under the operating conditions used, formic acid dehydrogenation mainly took place in the active sites of the Ni–Cu/Al<sub>2</sub>O<sub>3</sub> catalyst. It is likely that formic acid adsorbs dissociatively to give a formate species and an adsorbed hydrogen atom, and that the formate species then dissociate to give gaseous  $CO_2$  and another adsorbed hydrogen atom [37].

As it was previously stated, when formic acid pumping rate increased above  $1.8 \text{ mmol }h^{-1}$ , glycerol conversion significantly decreased. In fact, high formic acid pumping rates affected in greater extent glycerol conversion than high 2-PO pumping rates. It seems that glycerol and formic acid compete for the active sites of the catalyst, and that formic acid has higher affinity for adsorption sites than glycerol and 2-PO. The high activity of formic acid under the operating conditions used supports this idea. For the pumping rate interval between 0.0 and 1.8 mmol  $h^{-1}$ , increments in formic acid feeding rate increased both glycerol conversion and selectivity to 1,2-PDO, as higher number of active hydrogen atoms were available in the system. However, above 1.8 mmol  $h^{-1}$  the positive effect of higher hydrogen atoms availability with increasing formic acid pumping rate was offset by the increase in active site competition. Indeed, the occupation of active sites by formic acid was so significant that in the test with the higher pumping rate (run 6 of Table 3) the achieved glycerol conversion was even lower than the one obtained under N<sub>2</sub> pressure (run 1 of Table 3) without donor addition.

Finally, a further test was carried out in order to compare the semi-batch system, in which the donor is continuously pumped into the reactor, with the batch system in which the donor is placed directly in the feed cylinder with glycerol at the beginning of the test. In this test, run 8 Table 3, the mmol of formic acid (18) placed in the feed cylinder at the beginning of the test were the same as the mmol of formic acid pumped into the reactor during run 3. As it can be observed, even though the total mmol of formic acid that reacted, and therefore the total active hydrogen atoms formed, were the same in both tests, glycerol conversion was doubled in the test performed with the semi-batch system. It needs to be considered that in the first liquid sample of run 8, after 2 h, no formic acid was detected. This means that the 18 mmol of formic acid initially placed in the batch reactor readily reacted at the beginning of the test, without transferring most of the active hydrogen atoms to glycerol or intermediates, but forming molecular hydrogen that was released to the gas phase. This result demonstrates the superiority of the semi-batch reactor, as it reduces the competition between formic acid and glycerol for active sites, ensuring a continuous supply of active hydrogen atoms at an appropriate rate.

# 3.2.3. $N_2$ + methanol

The results of the activity tests carried out under nitrogen atmosphere and methanol as hydrogen donor molecule are shown in Table 4. Again, glycerol conversion presented a maximum as a function of methanol pumping rate. Nevertheless, the effect of methanol pumping rate on glycerol conversion was not so marked as compared to formic acid pumping rate, indicating a lower affinity for active sites of methanol than of formic acid.

It can be observed in Table 4 that methanol conversion decreased with increasing pumped methanol. As compared to 2-PO and formic acid conversions (see Tables 2 and 3), methanol conversions were considerably lower. Moreover, neither formaldehyde nor formic acid was detected in any of the liquid samples analyzed during the experiments. This means that the controlling step is the thermodynamically disfavored methanol dehydrogenation to formaldehyde, while the further reaction of formaldehyde with water to yield formic acid and the subsequent formic acid decomposition to hydrogen and  $CO_2$  occurred almost instantaneously. This behavior has already been observed for heterogeneous transfer

Glycerol conversion and selectivity to 1,2-PDO and acetol, and methanol conversion and selectivity to formaldehyde, formic acid and CO<sub>2</sub> as a function of methanol feed rate. 45 bar N<sub>2</sub> pressure, 10 h, 493 K, 20 mL (20 wt%) glycerol aqueous solution, 0.5 g of catalyst, 0.02 mL/min donor solution feed rate.

Run	Methanol conc. pumped solution (wt%)	Methanol feed-rate (mmol h <sup>-1</sup> )	Glyc. conv. (%)	Selectivity (%) <sup>a</sup> (from glycerol)		Selectivity (%) <sup>a</sup> (from glycerol)		C-balance	Methanol conv. (%)	Selectivity (from meth	(%) Ianol)	
				1,2-PDO	Acetol			Formald.	Form. ac.	CO <sub>2</sub>		
1 <sup>b</sup>	-	-	15.8	49.3	38.8	97.2	-	-	-	-		
2	3.5	1.2	21.0	47.0	49.7	92.9	43.0	0	0	100		
3	7.0	2.4	24.4	49.0	48.1	100.8	40.8	0	0	100		
4	10.0	4.0	26.2	51.2	44.3	95.3	39.1	0	0	100		
5	21.0	7.2	21.5	49.7	46.8	96.7	38.2	0	0	100		
6	30.0	9.8	21.3	50.7	45.9	96.5	27.6	0	0	100		

<sup>a</sup> The other products detected coming from glycerol were ethylene glycol, ethanol, 1-propanol and methane.

<sup>b</sup> No solution was pumped to the reactor.

hydrogenation using methanol as hydrogen donor over Pd-based catalysts [38].

#### 3.2.4. Comparison between hydrogen donors

In order to get a better understanding of the different performance of the three hydrogen donors tested, it seems interesting to relate the total moles of hydrogen atoms formed from each donor to the total moles of 1,2-PDO obtained (see Fig. 1A). For each donor, the test with higher 1,2-PDO yield was selected. It has to be considered that for every molecule of 2-PO or formic acid that reacted, two hydrogen atoms were obtained, while for every molecule of methanol that reacted, 6 hydrogen atoms were obtained. Taking into account that two hydrogen atoms are needed to convert glycerol to 1,2-PDO, the efficiency of each donor was calculated by dividing the moles of 1,2-PDO obtained by the half of the moles of hydrogen atoms formed (see Fig. 1B).

As it can be observed in Fig. 1A, the greater number of moles of 1,2-PDO was obtained when formic acid was used as a hydrogen donor molecule, while the smallest with methanol. Even though, much more hydrogen atoms were formed from methanol. The efficiency of each donor can be better compared in Fig. 1B. For formic acid, around 72% of the hydrogen atoms formed were transferred to 1,2-PDO, being the efficiency in the case of 2-PO and methanol much lower (30 and 13%, respectively). As it was addressed before, in the case of 2-PO one reason for the lower efficiency is that part of the propene coming from acetone dehydration was hydrogenated to propane, consuming hydrogen atoms. In the case of methanol, it is not clear why so low efficiency was obtained. Maybe the fact that hydrogen is formed in three consecutive steps is not appropriate for the glycerol hydrogenolysis reaction. In fact, it was observed that under the operating conditions used the first dehydrogenation to formaldehyde was the rate controlling step, while the other two dehydrogenations occur readily. Therefore, an adsorbed glycerol molecule might interact with two active hydrogen atoms, coming from methanol dehydrogenation to formaldehyde, and yield 1,2-PDO. Nevertheless, the subsequent 1,2-PDO desorption and occupation of the active site by another glycerol molecule might not be as fast as formaldehyde reaction with water and consecutive formic acid dehydrogenation. As a consequence of this, the four additional hydrogen atoms formed might not find a near adsorbed glycerol molecule, and hence, are combined to form two hydrogen molecules that are released to the gas phase. Indeed, the highest H<sub>2</sub> concentration in the gas phase was detected for the activity tests performed with methanol.

In the light of these results it is clear that formic acid is the best hydrogen donor molecule for the glycerol hydrogenolysis process under the studied conditions, as the highest yield to 1,2-PDO was obtained with the smallest amount of donor used. If we compare the obtained results with other reference works in liquid phase glycerol hydrogenolysis with in situ generated hydrogen, DĭHont et al. using Pt–NaY [28] and Roy et al. using a mixture of Ru/Al<sub>2</sub>O<sub>3</sub> and Pt/Al<sub>2</sub>O<sub>3</sub> [29] obtained higher glycerol conversions. Nevertheless, reported selectivities were significantly lower (64.0%) and (47.2%) respectively. The lower C–C bond cleavage activity of Ni–Cu metal sites as compared to Pt sites, and the fact that the addition of formic acid suppresses glycerol reforming might be the main factors behind the higher measured selectivities.

# 3.3. Glycerol hydrogenolysis under H<sub>2</sub> pressure

It is well known that there are differences between heterogeneous catalytic hydrogenation using molecular hydrogen as the hydrogen source, and heterogeneous catalytic hydrogenation using hydrogen donor molecules as the source of hydrogen [27]. Indeed, for glycerol hydrogenolysis process, different mechanisms are involved as a function of the hydrogen source [30]. Consequently, it was decided not only to compare, the activity and selectivity regarding the hydrogen source, but also to perform activity tests under H<sub>2</sub> pressure and adding a hydrogen donor. The aim was to determine if there is a useful synergy for glycerol hydrogenolysis through the simultaneous use of both types of hydrogen sources.

As formic acid was the most appropriate hydrogen donor molecule under the experimental conditions used, activity tests under  $H_2$  pressure and with the addition of formic acid were carried out. Again, in order to study the effect of the amount of formic acid added on glycerol conversion and selectivity to main reaction products, the concentration of formic acid in the pumping solution was kept constant in each run but modified from run to run. In the test without donor addition (run 1 of Table 5), no water solution was pumped to the system.

In Table 5 the main results achieved in the activity tests under  $H_2$  pressure are displayed. It is interesting to recognize that formic acid was not detected in any of the samples of the different activity tests, which proves that formic acid readily reacts also in the presence of dissolved molecular hydrogen. Again, CO<sub>2</sub> mol detected in the gas phase quite well coincided with the mol of formic acid fed; suggesting that also under hydrogen pressure formic acid was completely converted to CO<sub>2</sub> and two hydrogen atoms.

Formic acid feeding rate significantly affected glycerol conversion, with little effect on the selectivity to 1,2-PDO. For low pumping rates, the addition of formic acid had a positive effect. Indeed, in the test with a formic acid pumping rate of 1.8 mmol h<sup>-1</sup> (run 3 of Table 5) glycerol conversion and yield to 1,2-PDO were 26% higher than the one obtained under H<sub>2</sub> pressure without donor addition (run 1 of Table 5). It might appear that the amount of hydrogen supplied by formic acid is negligible as compared to all the hydrogen that is in the system. Nonetheless, two important aspects should be taken into account. First, the activity tests were carried out in liquid phase, and the solubility of hydrogen in water solutions is very low. Hence, even though the gas



**Fig. 1.** (A) Total mmol of 1,2-PDO obtained as a function of the mmol of hydrogen atoms formed from each donor (2-PO, formic acid or methanol) in the tests with the higher yield to 1,2-PDO. (B) Efficiency of each hydrogen donor in the test with higher yield to 1,2-PDO: hydrogen donor efficiency (%) =  $100 \times (mol 1,2-PDO formed/(1/2 \times mol H atoms formed))$ .

Glycerol conversion and selectivity to 1,2-PDO and acetol, and formic acid conversion and selectivity to CO and CO<sub>2</sub> as a function of formic acid feed rate. 45 bar H<sub>2</sub> pressure, 10 h, 493 K, 20 mL (20 wt%) glycerol aqueous solution, 0.5 g of catalyst, 0.02 mL/min donor solution feed rate.

Run	Formic acid conc. pump solution (wt%)	Formic acid feed-rate (mmol h <sup>-1</sup> )	Glyc. conv. (%)	Selectivity (%) <sup>a</sup> (from glycerol)		Selectivity (%) <sup>a</sup> (from glycerol)		Selectivity (%) <sup>a</sup> (from glycerol)		Selectivity (%) <sup>a</sup> (from glycerol)		C-balance	Formic acid conv. (%)	Select (from	ivity (%) formic acid)
				1,2-PDO	Acetol			со	CO <sub>2</sub>						
1 <sup>b</sup>	-	-	34.8	90.9	1.6	96.3	-	-	-						
2	3.5	0.9	35.4	89.8	1.2	97.7	100	0	100						
3	7.0	1.8	43.9	89.4	1.8	95.2	100	0	100						
4	14.0	3.6	27.4	89.5	3.0	104.4	100	0	100						
5	28.0	7.2	24.0	89.5	2.8	103.5	100	0	100						

<sup>a</sup> The other products detected coming from glycerol were ethylene glycol, ethanol, 1-propanol and methane.

<sup>b</sup> No solution was pumped to the reactor.

phase is mainly formed by H<sub>2</sub>, in the liquid phase the amount of dissolved hydrogen molecules is much lower. For a 20 wt% glycerol water solution, 45 bar of hydrogen pressure and 493 K, the concentration of H<sub>2</sub> in the liquid phase was calculated to be around 0.029 mol kg<sup>-1</sup> [19], which means that in our liquid phase there were around  $6 \times 10^{-4}$  mol of H<sub>2</sub> dissolved. The  $3.6 \times 10^{-2}$  mol of hydrogen atoms supplied by formic acid are not therefore negligible. Second, the hydrogen molecules dissolved in the liquid phase have to dissociate in the active sites of the catalysts before interacting with adsorbed glycerol molecules. In the case of formic acid, it provides those active hydrogen atoms directly in the active sites of

the catalyst. In other words, formic acid does not provide molecular hydrogen; it provides adsorbed hydrogen atoms ready to interact with a glycerol molecule adsorbed in a contiguous site.

However, for high pumping rates, the effect of adding formic acid is negative as lower glycerol conversions were obtained (runs 4 and 5 of Table 5) as compared to the test without formic acid addition (run 1 of Table 5). It seems that when the supply of formic acid is too high, and due to its high affinity for active sites, it reduces the active sites available for glycerol and as a result also glycerol activity. It should be noticed that the formic acid feeding rate that maximizes glycerol conversion was the same  $(1.8 \text{ mmol } h^{-1})$  regardless the test was conducted under H<sub>2</sub> or N<sub>2</sub> pressure.



**Fig. 2.** Time evolution of acetol conversion and selectivity to 1,2-PDO under  $H_2$  pressure and under  $N_2$  pressure with the continuous pumping of 1.8 mmol  $h^{-1}$  of formic acid. 45 bar  $H_2$  or  $N_2$  pressure, 493 K, 20 mL (20 wt%) acetol aqueous solution, 0.5 g of catalyst.



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Fig. 3. Relative weight change profile corresponding to the TGA-TPO of the reduced fresh Ni-Cu/Al<sub>2</sub>O<sub>3</sub> and Ni-Cu/Al<sub>2</sub>O<sub>3</sub> samples used under H<sub>2</sub> or N<sub>2</sub> pressure, with or without the addition of donor.



Fig. 4. TEM images of reduced fresh and used Ni-Cu/Al<sub>2</sub>O<sub>3</sub> samples: (a) reduced fresh, (b) used under N<sub>2</sub> pressure, (c) used under H<sub>2</sub> pressure + formic acid.



Number of Particles

Number of Particles



Fig. 5. Particle size distribution of reduced fresh and spent Ni-Cu/Al<sub>2</sub>O<sub>3</sub> samples used with different sources of hydrogen.

Concerning the selectivity to 1,2-PDO, there is not a significant influence of the amount of formic acid added. However, higher selectivities to 1,2-PDO were obtained under  $H_2$  pressure as compared to the same tests but under  $N_2$  atmosphere (see Tables 3 and 5). The main difference is the significant decrease in acetol selectivity in the tests under  $H_2$  pressure.

In order to check if formic acid is able to hydrogenate acetol to 1,2-PDO, another two tests were performed with acetol as reactant. In Fig. 2 the evolution of acetol conversion with reaction time for the test performed under H<sub>2</sub> pressure and for the test performed under N<sub>2</sub> pressure and with the addition of formic acid is displayed. Acetol quickly reacted in both activity tests. Nevertheless, in the test under H<sub>2</sub> pressure, most of the acetol was hydrogenated to 1,2-PDO, while under N<sub>2</sub> pressure and formic acid really low selectivity to 1,2-PDO was achieved. In the experiments under N<sub>2</sub> pressure, acetol reacted to many different products. Identification by GC-MS revealed the formation of a wide range of C5-C6 compounds, such as 3-hexanol-5-methyl, 3-hexanone, 3,5-hexadien-2-ol. Acetol could not be hydrogenated to 1,2-PDO when the hydrogen supply came from formic acid. This result (identical to the one obtained for 2-PO [26]) confirms that also for formic acid glycerol conversion to 1,2-PDO occurs through the direct hydrogenolysis of the intermediate alkoxide, 1,3-dihydroxy isopropoxide, and not through the dehydration to acetol and subsequent hydrogenation.

Both sources of hydrogen are therefore complementary. At low feeding rates, 1,2-PDO is formed not only from glycerol through intermediate alkoxide formation using the hydrogen species coming from formic acid, but also from acetol hydrogenation in the presence of dissolved molecular hydrogen. Consequently, for optimized amounts of the donor, the effect of adding formic acid was positive. However, at high donor feeding rates, the really active formic acid occupies a high proportion of active sites, reducing glycerol accessibility to catalytic sites and consequently also glycerol reaction rate.

# 3.4. Used catalyst characterization

Reduced fresh and spent Ni–Cu/Al<sub>2</sub>O<sub>3</sub> samples were characterized by TGA–TPO and also analyzed by TEM images in order to determine if changes occurred in the catalyst during the activity test, and if these changes were different as a function of the reacting atmosphere.

As the thermogravimetric equipment used was not coupled to mass spectrometry, it was not possible to quantify the exact amount of coke formed in the spent samples. Nevertheless, it was possible to carry out a qualitative discussion comparing the final weight loss between reduced fresh and spent samples after the TGA-TPO analysis. Fig. 3 illustrates the relative weight change profile for each reduced sample. In all the samples, increments in sample weight were measured, assigned to the oxidation of previously reduced Cu and Ni metal sites. The weight loss suffered by the fresh Ni–Cu/Al<sub>2</sub>O<sub>3</sub> sample at high temperature range (T > 700 K) might be related to the decomposition of the nitrates remaining in the catalyst after calcination at 723 K [44]. The relative differences in the final weights between the reduced fresh and the used samples can be ascribed to the formation of coke deposits during the activity tests. These relative weight variations as a function of the hydrogen source follow the order:  $H_2$  + formic (0.8%) <  $N_2$  $(3.5\%) \approx N_2$  + formic acid  $(3.8\%) < H_2$  (5.8%). As it can be observed, the presence of formic acid reduced coke formation under H<sub>2</sub> pressure, and had not significant effect under N<sub>2</sub> pressure. The relative differences are quite small, so it can be said that there were low coke formation rates during the tests under the operating conditions used. Nevertheless, long term activity tests and tests using recycled catalyst should be performed in order to check if the coke formation affects catalyst stability.

In Fig. 4 TEM images corresponding to reduced fresh and spent Ni-Cu/Al<sub>2</sub>O<sub>3</sub> samples are displayed, while the results from the size distribution analysis of the metallic particles in the alumina surface are presented in Fig. 5. For all the samples, the size intervals 30-40 and 40-50 nm were the ones with the highest amount of particles. In the case of the reduced fresh sample, the calculated average particle size was 42.2 nm, which is lower than the particle size obtained from the chemisorption analysis result (65.6 nm) presented in Table 1. In the case of the reduced fresh sample, particles with a size larger than 80 nm were not detected, however, for spent samples, some particles in the range of 80–110 nm were observed. Even though the proportion of these particles was small as compared to the ones in the range of 30-50, this result indicates that there is a small degree of sintering under the operating conditions used. Concerning coke formation, no coke deposits were observed in any of the images of the samples analyzed, which is consistent with the TGA-TPO results presented above.

#### 4. Conclusions

2-PO, formic acid and methanol were used as hydrogen donor molecules in the catalytic transfer hydrogenation process to convert glycerol into 1,2-PDO. As glycerol and the hydrogen donors compete for the same active sites, a semi-continuous process in which the donor was continuously pumped into the autoclave reactor containing the aqueous glycerol was developed. Activity test results showed that there must be a balance between the positive effect of the higher supply of active hydrogen and the negative effect of the higher competition for active sites when increasing the pumping rate of the hydrogen donor molecule. Therefore, for each hydrogen donor tested there was an optimum in the feeding rate that maximized the yield to 1,2-PDO. Formic acid proved to be the most effective hydrogen donor molecule, as higher glycerol conversions and selectivities to 1,2-PDO were obtained with the lowest amount of hydrogen donor used.

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