



Bio-hydrogen production using metallic catalysts

Producción de bio-hidrógeno con catalizadores metálicos

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Received: June 18, 2019; Accepted: December 15, 2019

Abstract

Many applications, including energy applications, require handling pressurized hydrogen gas. However, an alternative option is the use of a donor to generate hydrogen in situ (either by transfer and/or catalytic reforming), instead of using molecular hydrogen. Ethanol and formic acid, which are biorefinery streams, were used as donors. The effect of metallic catalysts of Pd and Pt, supported on C, γ -Al₂O₃ and zeolite USY was evaluated on the generation of hydrogen. Different ratios were used between the active phase and the donor, as well as different times and temperatures of reaction in a high pressure reactor (up to 1000 psi). The catalysts were characterized by XRD, SEM, FTIR and XRF, and High-Pressure Differential Scanning Calorimetry (HP DSC) was performed in the most promising systems with a ramp of 10 °C/min. Gas chromatography was used to analyze the production of hydrogen. Findings show that the system that generates more hydrogen, with 88%, is 5% Pd/C over 30% formic acid at 300 °C, 500 rpm and a ratio catalyst mass to donor from 1 to 10 (0.028 m).

Keywords: hydrogen, biodonor, catalytic transfer, ethanol, formic acid.

Resumen

Muchas aplicaciones, incluidas las energéticas, requieren el manejo de gas hidrógeno presurizado. Sin embargo, una opción alternativa es el uso de un donante que genere el hidrógeno in situ (ya sea por transferencia y/o reformado catalítico), en lugar de emplear el hidrógeno molecular. En este estudio, se usaron como donantes etanol y ácido fórmico, que son corrientes de biorrefinería. Se evaluó el efecto de catalizadores metálicos de Pd y Pt soportados en C, γ -Al₂O₃ y zeolita USY en la generación de hidrógeno. Se emplearon diferentes relaciones entre la fase activa y el donante y diferentes tiempos y temperaturas de reacción usando un reactor de alta presión (hasta 1000 psi). Los catalizadores fueron caracterizados por RXD, SEM, FTIR y XRF y se realizó una calorimetría diferencial de barrido a alta presión (DSC HP) en los sistemas más promisorios, con una rampa de 10°C/min. Para analizar la producción de hidrógeno, se empleó cromatografía de gases, donde se encontró que el sistema que más hidrógeno genera, con un 88%, es el de 5% Pd/C sobre ácido fórmico al 30%, a 300°C, 500 rpm y una relación másica de catalizador a donante de 1 a 10 (0.028 m).

Palabras clave: hidrógeno, biodonante, transferencia catalítica, etanol, ácido fórmico.

1 Introduction

One of the main aspects in some chemical processes (such as hydrogenations, hydroprocessing and power generation) is to provide enough hydrogen to carry out the chemical conversion. Molecular hydrogen is a very important raw material for both the chemical and petroleum industries, mainly due to its positive atomic economy (Toledano *et al.*, 2013). It is obtained from carbonaceous materials, mainly hydrocarbons and/or

water, by decomposition through the application of thermal (dissociation of natural gas), chemical (reformed hydrocarbons with steam) or electrical (electrolysis of water) energies. It is also produced by the partial oxidation of hydrocarbons and other methods such as the steam-iron process of water gas or lean gas, the separation of coke oven gas and refinery streams of synthetic gas (Austin, 1988).

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<https://doi.org/10.24275/rmiq/Cat652>

issn-e: 2395-8472

Currently, commercial hydrogen is being produced mainly from non-renewable raw materials, about 90% is obtained by reforming natural gas or fractions of naphtha, while the rest is obtained from coal gasification and water electrolysis (Martínez-Merino *et al.*, 2013).

All the above processes have disadvantages such as relying on fossil and non-renewable raw materials, being environmentally damaging or highly intensive in energy consumption. Then, considering the sustainability of the processes, an alternative route that has emerged recently is obtaining hydrogen from biomass, through biochemical processes such as fermentation and biodigestion (Gandía *et al.*, 2013; García-Amador *et al.*, 2019). Chemical processes for reforming vegetable oils and biomass have also been researched (L. He *et al.*, 2013; Lodeng *et al.*, 2013). In addition, photocatalytic processes have been developed for the production of hydrogen (Kondarides & Verykios, 2013).

Due to its high diffusivity, hydrogen has great accessibility to molecular structures, therefore, it is a highly flammable and dangerous gas and safe handling becomes a sensitive issue (Toledano *et al.*, 2013; Raikova *et al.*, 2016). The low solubility of gaseous hydrogen in both the aqueous and organic phases requires high pressures, which makes the process more intensive. In addition to high diffusivity, low density leads to higher storage and transport costs (Inaki *et al.*, 2013).

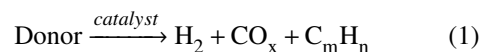
Considering the above, problems of accessibility and solubility could be avoided if the hydrogen required for hydrotreating is generated directly at the active sites of the catalyst, allowing a process with an inert atmosphere and a lower working pressure. The possibility of generating the hydrogen in situ, instead of feeding it to the hydrotreating reactor, is thus envisaged. Hydrogenation processes, in which hydrogen is transferred from a donor to an acceptor, are an interesting alternative for the hydrogenation of organic compounds. This can entail substantial advantages over processes that use molecular hydrogen (Gandarias *et al.*, 2011). After dehydrogenation and decomposition, hydrogen donor solvents readily transfer this molecule in situ. However, these dehydrogenation/decomposition processes usually lead to the production of undesirable byproducts, which in turn can lead to a significant increase in the system pressure if this decomposition is not controlled (Toledano *et al.*, 2013).

This in situ generation of hydrogen can be achieved by aqueous phase reforming (APR) or by

catalytic transfer of hydrogen (CTH). The first option requires the presence of water at intense conditions of temperature and pressure, while the second one requires a substance that donates hydrogen to an acceptor, that is, a donor, usually a solvent, that transfers hydrogen (Gandarias *et al.*, 2011). As an alternative to overcome these limitations, hydrogen generated from biomass, i.e. biohydrogen is not in the gas phase, but it is taken to the catalyst by a donor, capable of generating it on the surface of the catalyst, facilitating its handling and enhancing its effect.

In the CTH, the donor, which acts as a source of hydrogen, must be catalytically and/or thermally decomposed into molecular hydrogen and other gases. It is ideal that the donor is renewable, so biorefinery streams would be used, oxygenated hydrocarbons such as alcohols, aldehydes, ketones and carboxylic acids, (e.g. methanol, ethanol, formic acid and glycerol), including condensed aromatic compounds, or some alkanes and amines (Ramírez-Corredores, 2013). Some of these solvents, such as ethanol and formic acid, are relatively cheaper than molecular hydrogen for storage and transport (Jin, 2014).

Catalytic transfer reactions of the donor should not be confused with simple dehydrogenations. They are reactions for the generation of hydrogen and other more stable by-products, such as carbon oxides and light hydrocarbons (such as methane). In this sense, the generation of hydrogen from a donor (oxygenated hydrocarbons) is written as Eq. (1):



Recently, several research has been carried out to generate hydrogen from formic acid using a wide variety of metal catalysts, mainly transitional and especially the noble ones (Luo *et al.*, 2018), as well as using monometallic, bimetallic or polymetallic ones with different supports (Zhang *et al.*, 2018). In several cases, promoters are also used (Wang *et al.*, 2019). Some authors have focused on working at low temperatures (Wang *et al.*, 2018) or at low active phase loads (Huang *et al.*, 2017). Meanwhile, from ethanol or other alcohols, the number of jobs is less and is more focused on the reform than on the catalytic transfer (Kubacka, 2016), even with homogeneous catalysts (Onishi *et al.*, 2018). All these variations in catalytic transfer seek the improvement in hydrogen generation (Wang *et al.*, 2019).

In this work, the generation of hydrogen is evaluated with two biodonors, ethanol and formic acid, which are refinery streams: the first one is generated from carbohydrate fermentation and the second one from the acid hydrolysis of lignocellulosic biomass. The article proposes to study the use of biodonors capable of generating hydrogen in situ through CTH. At the same time, the metallic catalysts (such as Pd and Pt) tested have a high hydrogenating capacity, since in a process such as hydrotreatment, besides producing hydrogen, they must be able to use them for a later removal of unwanted elements in the substrate used, such as sulfur, oxygen, nitrogen, among others. Most research on the catalytic generation of hydrogen from donors has obviously focused on working at room temperature. However, in this study higher operating temperatures will be used, since they are typical of hydroprocessing (200-350 °C), which is the desired application.

2 Materials and methods

2.1 Materials

The reagents in analytical grade, formic acid (99.6%) and ethanol (99.9% v/v), were provided by ITW Reagents- PanReac AppliChem (Darmstadt, Germany). The gases of hydrogen and nitrogen grade 5.0 were delivered by LINDE (Bogotá, Colombia). The commercial catalysts purchased from Sigma-Aldrich were: 5% Pd/C (Reference 205680), 5% Pd/ γ -Al₂O₃ (Ref. 761176), 5% Pt/C (Ref. 80982) and 5% Pt/ γ -Al₂O₃ (Ref. 761176). The USY ultra-stabilized zeolites (Series CBV-712, 720 and 780) were provided by Zeolyst International. The catalysts of 1% Pt/USY

were prepared by wet impregnation from the tetraammine platinum (II) dichloride salt Pt(NH₃)₄Cl₂. The catalysts were activated at 200 °C for 2 hours in a reduced atmosphere of 30% H₂/N₂, with heating in a ramp of 3 °C/min.

2.2 Procedure

The project was developed in two systems: batch reactor and HP DSC.

2.2.1 Tests in batch reactor

The tests in the batch reactor of 300 mL had five stages as shown in Fig. 1. These stages were carried out in order to increase the concentration of hydrogen in the atmosphere and manipulating mainly the catalyst-donor ratio, time and temperature. In general terms, the stages were the following. First, different catalysts were evaluated in low ratio with respect to ethanol (according to the literature) as highly concentrated donor. Second, the catalyst had a higher ratio with respect to ethanol and formic acid, with different concentrations of aqueous solutions. Third, three major levels of catalyst-donor ratio were used (with the two best catalysts), with two levels of donor concentration (high and medium) for both, ethanol and formic acid. In addition, the reaction time was considerably increased. Fourth, considering the last result in the last step, the ratio catalyst-donor was fixed in an optimal value using two catalysts and both donors, but gaseous samples were taken each time to find the optimal time. Fifth, the best catalyst and donor were selected, the time was fixed in an optimal value, the temperature and agitation level were increased, but remained constant, and the only variable was the catalyst-donor ratio. Further details of each stage are presented below.

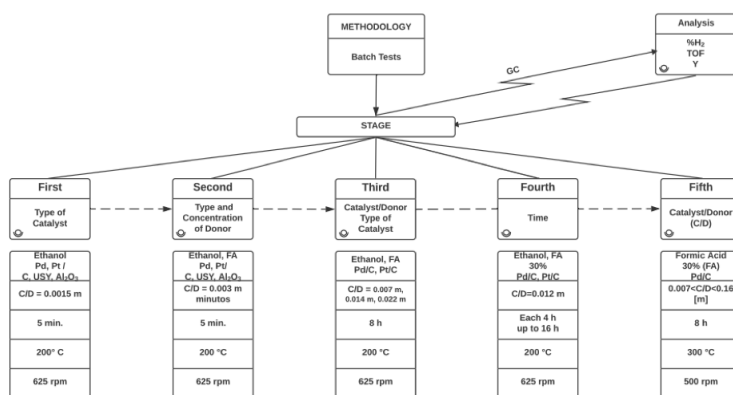


Fig. 1. Diagram flow of batch tests.

In the first stage, runs were made with 200 mL of ethanol 80% and 99.9% (v/v), using 1 mg/g of catalyst (approximately 0.15 g), with a heating ramp of 4 °C/min approx., 200 °C, 27-40 bar (pressures greater than 26.5 bar are required to keep the ethanol in liquid phase) and 625 rpm. The pressure increased in the set by the generation of autogenous pressure during heating. The catalysts used in this stage were 1% Pt/CBV 712, 1% Pt/CBV 720, 1% Pt/CBV 780, 5% Pd/C, 5% Pd/ γ -Al₂O₃ and 5% Pt/ γ -Al₂O₃. Once the operating temperature is reached, gaseous samples of 1 mL are taken.

In the second stage, the ratio of catalyst to donor was increased, that is, it went from 0.0015 molal of active phase to 0.003 molal (0.003 m = 0.003 mol of active phase per kg of donor). Concentrated formic acid was used (99.6% or 26.5 M), as well as ethanol at different concentrations (0.45, 1 and 2 M), while the rest of the conditions remained constant with the catalysts 1% Pt/CBV780, 5% Pd/C, 5% Pt/ γ -Al₂O₃.

In the third stage, higher ratio of catalyst to donor (0.022, 0.014 and 0.007 m), formic acid (30% and 99.6%) and ethanol (30% and 99.9% v) were used with catalysts of 5% Pt/C and 5% Pd/C, but the difference is that the gaseous samples were taken 8 h after the moment of reaction initiation. From this essay, the volume charged into reactor was 80 mL.

In the fourth stage, the catalyst that generated most hydrogen (in terms of %H₂) in the previous stages is used at a higher concentration of 0.012 m, at 200°C and 625 rpm using both donors, ethanol and formic acid. In order to observe a greater conversion of the donor, a 16 h reaction is made, taking samples of the gas phase every 4 h.

The fifth stage was developed at 300 °C and 500 rpm, with the best donor and varying the concentration of the best catalyst from 0.007 m to 0.165 m. The reaction time is that in which the highest concentration of hydrogen generated was obtained in the previous stage.

In these tests in the batch reactor, first the solvent must be adjusted by stripping the oxygen dissolved in the liquid by means of nitrogen bubbling, when formic acid and the Pd/C catalyst produce a highly spontaneous reaction. This reaction leads to a large generation of hydrogen that enters in contact with the oxygen of the air, which in turn enters in combustion. For this reason, in this case, the solvent enters frozen to the system. The reaction mixture is placed in the

borosilicate glass and introduced into the high pressure reactor, which has a heating jacket resistance with thermal insulation of glass wool, and a hydrogen and nitrogen supply system. The system is available in an inert atmosphere of minimum nitrogen of 10 bar when formic acid is used and minimum of 30 bar when ethanol is used. The system pressure increases to between 50 and 60 bar by the autogenous action of the system when it reaches the operating temperature (200 °C or 300°C), which remains stable through the action of the controller and the temperature sensor. The magnetic stirring of 625 rpm or 500 rpm given by the magnetic plate is activated when the system reaches 200 °C or 300 °C, respectively, and the reaction starts. From the second to the fifth stage, the initial volume of liquid inside the reactor was 80 mL.

2.2.2 Test in HP DSC

According to the previous results, the catalytic systems that had the best performance were selected for a run in the HP DSC1 Star System Mettler Toledo of the laboratory of polymers in the Chemical Engineering Laboratory of the Universidad Nacional de Colombia. In a crucible (40 μ L), the catalyst was placed together with the hydrogen donor (ethanol or formic acid) using a ratio of 7 mmol of active phase per kg of donor. The inert atmosphere is 50 bar N₂, and heating occurs with a ramp of 10 °C/min, from 25 °C to 220 °C in the case of ethanol or 280 °C in the case of acid formic. When discharging, the contents of the crucible are weighed and a gaseous sample is taken for gas analysis in a GC. The heat flow thermograms were analyzed.

2.3 Analysis

The gas samples were analyzed by GC using a Hewlett Packard 5890 chromatograph (series A). A molecular sieve packed column (Supelco 80/100 mole sieve 13X column 10' x 1/8" SS - Stainless Steel) was used for the identification and quantification of gaseous hydrogen (besides CO, CH₄, C₂H₄, N₂ and O₂). The drag is given with a flow of 12 ml He/min. at 20 psi. The temperature of the oven, injector and detector was 30 °C, 100 °C and 150 °C, respectively. In this case, 0.1 mL of gas sample was injected. The detector is by thermal conductivity - TCD. The program used for data acquisition was Clarity Lite.

The catalysts with the best behavior were characterized by XRD, XRF, FTIR and SEM.

3 Results and discussion

3.1 Tests in Batch Reactor

The results of hydrogen concentration as volume percentage %H₂ (or molar too) were calculated from the calibration curve made for each area value determined during the Gas Chromatography described above, according to Eq. (2):

$$\%H_2 = f_R \cdot A \quad (2)$$

where f_R is the response factor and A is the area, in $mV \cdot s$, of the hydrogen peak in the chromatogram.

For each assay, the Turnover Frequency of hydrogen, *TOF*, was calculated according to Eq. (3):

$$TOF = \frac{\text{mole of generated hydrogen}}{(\text{mole of active phase}) \cdot (\text{reaction time})} = \frac{n_{H_2}}{n_{APt} \cdot t} \quad (3)$$

Meanwhile, the hydrogen yield, *Y*, is defined under Eq. (4):

$$Y = \frac{\text{mole of generated hydrogen}}{\text{mole of charged donor}} = \frac{n_{H_2}}{n_{donor}} \quad (4)$$

3.1.1 First stage

In the tests of the first stage, the chromatograms indicated that the test that generated the highest amount of hydrogen after the first half hour of reaction was the use of 80% (v/v) ethanol with 1% Pt/CBV 780, as shown in Table 1. This catalyst also exhibits the best yield to hydrogen, then, it seems that ethanol catalytic transfer is favored by the acidity of the support. But among the three zeolites (as support of the catalyst) the least acidic was the one that had the best selectivity toward the generation of hydrogen, thus, it is expected that by increasing the acidity, a greater amount of collateral reactions can occur. In consequence, the acidity of zeolites USY in decreasing order is CBV

712 > CBV 720 > CBV 780. This matches to a certain extent with the results of production of hydrogen. With respect to the catalysts supported in alumina, a lower hydrogen production is observed, and there is no notable difference when the active phase is platinum or palladium. In the test with platinum, the ethanol was almost pure (99%) compared to the less concentrated ethanol of the palladium test.

However, the test with a higher hydrogen *TOF* is the one that uses 5% Pd/C. The palladium has a better activity than platinum for methanation reactions, which is what happens to ethanol when it is going to generate hydrogen (Bond, 1987). In these experiments, formic acid is not used as a donor because it does not show compatibility with the catalysts supported in zeolite and alumina. This occurs because these acidic solutions have a pH below 3.0 and the crystalline network of these supports is destroyed.

3.1.2 Second stage

Regarding the results of the second stage, a marked improvement is observed with respect to the previous stage, due to the increase of the catalyst load with respect to the donor, as seen in Table 2. This is clearly observed when increasing the concentration of the donor and the active phase. For formic acid, the best catalyst is 5% Pd/C, while for ethanol, it is 5% Pt/Al₂O₃, which is verified with the values of %H₂, *TOF* and *Y*. Once again it is confirmed that the acidity of the support favors the generation of hydrogen from ethanol.

In addition to having the most diluted donor, hydrogen generation is promoted regardless of the type of donor and catalyst. This can be observed when Pd/C was used with formic acid, thus, reducing the concentration 13 times and increasing the *TOF* increasing almost 9 times. It is possible that the catalyst undergoes a fast deactivation when it is saturated with molecules of absorbed donors causing its poisoning, as reported by other works (Hu et al., 2014).

Table 1. Results of the First Stage: Essays in Batch 200 °C, 625 RPM, >26.5 bar.

Catalyst	Donor	AP/Donor	A[mV · s]	%H ₂	TOF[h ⁻¹]	Y × 10 ²
1% Pt/USY (CBV 712)	Ethanol 80%	1 mg/g	2.806	0.43	0.75	0.015
1% Pt/USY (CBV 720)	Ethanol 80%	1 mg/g	0.139	0.02	0.04	0.001
1% Pt/USY (CBV 780)	Ethanol 80%	1 mg/g	6.375	0.96	1.68	0.033
5% Pd/C	Ethanol 80%	0.0015 m	3.401	0.52	3.12	0.018
5% Pd/Al ₂ O ₃	Ethanol 80%	0.0015 m	0.593	0.09	0.54	0.003
5% Pt/Al ₂ O ₃	Ethanol 99.9%	0.0015 m	0.569	0.09	0.46	0.003

Table 2. Results of the Second Stage: Essays in Batch 200 °C, 625 RPM.

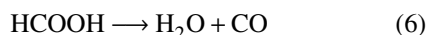
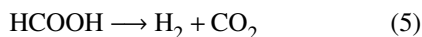
Catalyst	Donor	AP/Donor	A[mV · s]	%H ₂	TOF[h ⁻¹]	Y × 10 ²
5% Pd/C	Formic 26.5 M	0.003 m	2.139	0.33	0.55	0.01
5% Pd/C	Ethanol 2 M	0.027 m	5.685	0.86	2.11	0.22
1% Pt/Zeolite USY	Ethanol 0.45 M	0.150 m	10.26	1.53	3	1.73
5% Pt/Al ₂ O ₃	Ethanol 1 M	0.150 m	58.641	7.8	6.89	3.97
5% Pd/C	Formic 2 M	0.150 m	85.904	10.83	4.78	2.75

3.1.3 Third stage

In the third stage, significantly greater atmospheres of hydrogen were obtained than in the previous two, as shown in Table 3.

It is observed that the ratios catalyst to donor are lower than those of the second stage, however, the sampling times were longer. This leads to a greater conversion and, therefore, to an improvement in the amount of hydrogen generated. The use of pure or diluted formic acid in organic solvents improves the generation of hydrogen. The catalysis Pt/C is slightly higher than that of Pd/C and ratios greater than 0.007 m are not necessary, as no significant change is observed. With respect to hydrogen generation the *TOF* of 5% Pt/C is 40.25 h⁻¹ while 5% Pd/C is 29.34 h⁻¹, but the efficiency of the latter is 50% higher than the former.

Gases other than hydrogen were detected because parallel reactions developed or because by-products appeared during the catalytic transfer. In the case of formic acid, the decarboxylation reaction generated by hydrogen competes with the decarbonylation reaction generated by the carbon monoxide detected to a lesser extent. This can be observed in the decomposition reactions for formic acid, as shown in eqs. (5) - (6):



In the case of ethanol, methane and monoxide were detected as other products additional to hydrogen in the methanation reaction, as shown Eq. (7). In eqs. (8) and (9), there are other decomposition reactions for ethanol that were not important.

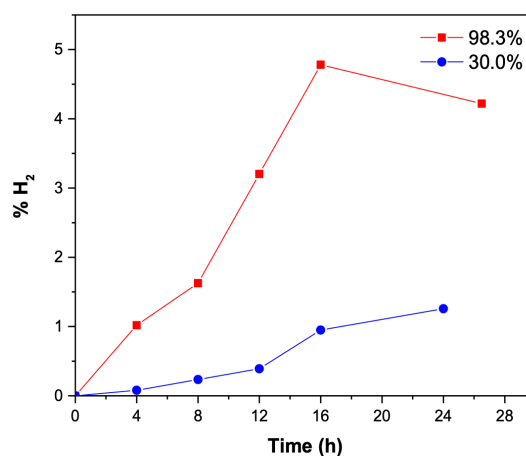
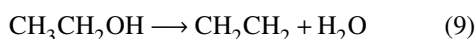
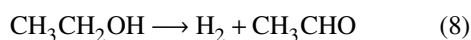
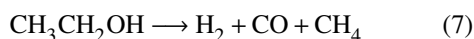


Fig. 2. Evolution of the Generated Hydrogen Concentration using Ethanol with 5% Pd/C at 0.012 m, 200°C, 625 rpm.

3.1.4 Fourth stage

In this stage, 5% Pd/C was used as catalyst.

- Ethanol

Fig. 2 shows the evolution of the concentration of hydrogen gas in the atmosphere. For ethanol 30%, the highest value oscillates around 1% and occurs at 16 h. The generation of methane is also highlighted, since it presents a significant increase (almost 14 times) in the discharge, compared to the first 4 hours.

The Figure also shows that after 16 h, the concentration of hydrogen is close to 5%, or almost 5 times that when ethanol 30% was used. Methane is also generated, but to a lesser extent than in the previous one, as it only quintuples in the discharge, compared to the first 4 hours. Additionally, monoxide was generated, though this did not occur with ethanol 30%, which quadrupled at the end compared to the first 4 hours.

Table 3. Third Stage Results Essays in Batch 200 °C, 625 RPM, 8 h.

Catalyst	Donor	A[mV · s]	%H ₂	Other gases	TOF[h ⁻¹]	Y × 10 ²
5% Pd/C	Formic acid 99.6%, 0.022 m	241.177	35.9	CO	4.69	3.8
5% Pt/C	Formic acid 99.6%, 0.007 m	215.302	30.4	CO	12.49	3.22
5% Pt/C	Formic acid 30%, 0.007 m	85.67	10.7	CO	14.6	3.76
5% Pt/C	Ethanol 99.9% 0.007 m	23.572	3.4	CO, CH ₄	2.16	0.56
5% Pt/C	Ethanol 30%, 0.007 m	44.234	5.4	CH ₄	11.39	2.94
5% Pt/C	Formic acid 30%, iso-octane, 0.007 m	193.3	26	CO, CH ₄ , other	35.47	9.14
5% Pd/C	Formic acid 30%, heptane, 0.014 m	249.938	37.9	CO	25.85	13.33
5% Pd/C	Formic acid 30%, hexane, 0.021m	234.001	34.3	CO	15.6	12.06
5% Pt/C	Formic acid 99.6%, 0.007 m	252.325	38.4	CO	15.78	4.07
5% Pt/C	Formic acid 5%, 0.007 m	12.4	1.9	CO	15.55	4.01

The autogenous pressure or increase in pressure due to the generation of gases in the case of 30% ethanol was 10 bar that occurred at the first hour of reaction. Meanwhile, in the case of 98.3% ethanol was 17 bar at the half hour of reaction.

- Formic Acid

Regarding the previous trials where ethanol was used as a donor, hydrogen generation from formic acid is much higher, as shown at the beginning in Fig. 3. A high generation of hydrogen was found, reaching a maximum of 50% at 12 h (third gas sample) in the case of 5% and the highest recorded, at the first 8 hours of reaction, with a presence of around 65% in the Gas Phase (see Figure). The presence of CO was also detected from the beginning, which did not exceed a 50% increase during the process for formic acid 5% and growth during the first 8 h, then a later, although slight, decrease, for formic acid 30%. The highest autogenous pressure was 37 bar at 12 h of reaction for the case of 30% formic. For reactions involving hydrogen, the activity pattern may be broadly assessed as Pd over Pt.

The activity in the generation of hydrogen can sometimes be related with the d-character and lattice parameters of metals. The d-character percentage of the palladium is 46% and of the platinum is 44%, while the lattice parameter is 0.388 nm for palladium and 0.392 nm for platinum. In consequence, the specific activity of the thin metallic films is approximately 10^{-10} molecules.cm⁻²s⁻¹ for the first and 10^{-20} molecules.cm⁻²s⁻¹ for the second (Trim, 1980). Then, for the above reasons, the results obtained are confirmed, where palladium had a better catalytic activity for the generation of hydrogen with respect to platinum. Palladium is an unusual metal, often both active and selective.

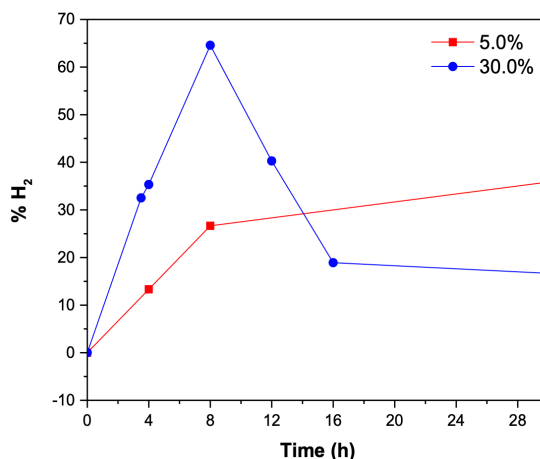


Fig. 3. Evolution of the generated hydrogen concentration using formic acid with 5% Pd/C at 0.012 m, 200°C, 625 rpm.

According to the Volcano plot for the decomposition of the formic acid for hydrogen generation over transition metals, the palladium is more appropriate than the platinum. Then, in the next stage, they will be tested with the formic acid - Pd/C system, supported by the experimental results obtained so far (Liu *et al.*, 2015).

3.1.5 Fifth stage

According to the above results, formic acid was used as a donor and Pd/C as a catalyst. Fig. 4 shows how the generation of hydrogen changed with respect to the molality of the active phase of the catalyst (%5 Pd/C) in the donor (30% formic acid). In the case of more formic acid, the system pressure increased from 5 bar at 15 °C, to 70 bar at 300 °C during 6 h. That is to say that the autogenous pressure reached a value close to 60 bar.

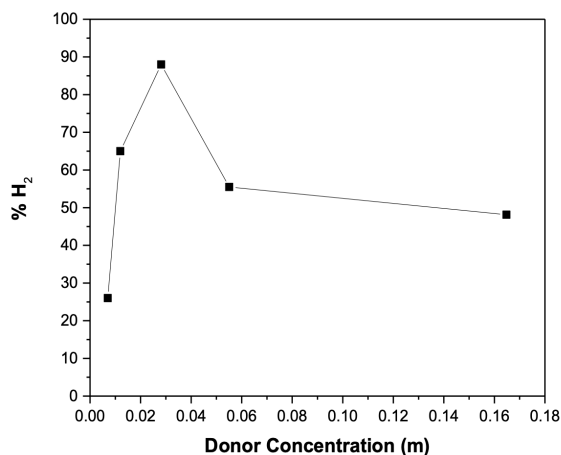


Fig. 4. Generated hydrogen with formic acid 30% and 5%Pd/C.

According to Fig. 4, the maximum generation of hydrogen (88.0%) was achieved with a molal concentration of 0.028 m, where the *TOF* was 49.21 h^{-1} and the yield was 0.5. From 0.007 m to this value, the hydrogen generation increases because for a certain amount of formic acid, the catalyst increase implied a greater number of available active sites. However, after this value (0.028 m), the increase in the concentration of the catalyst compared with the donor generates a reduction in the generation of hydrogen, which, after being noticeably increased after 0.055 m, changes in the reduction to be small and stabilizes around 50%.

Then, the best generation of hydrogen has a *TOF* of 49.21 h^{-1} from formic acid 30% (7.0 M) with 5% Pd/C at 300°C and 8 h. Meanwhile, other works have reported different values of *TOF*, although of the same order. A *TOF* of 6.9 h^{-1} and a hydrogen yield of 0.0027 were determined through an essay of formic acid 2.0 M with Pd/C catalyst at 30°C during 2 h (X. Wang *et al.*, 2014). A research with Pd/C catalysts 1% and 10% obtained 255.6 h^{-1} and 180 h^{-1} , respectively, using formic acid (5 vol.%) at 100°C (Bulushev *et al.*, 2010). Hu *et al.* reached the highest *TOF* of 339-563 h^{-1} , but for formic acid (4.0 M) decomposition with commercial catalyst of 10% Pd/C at 60°C and 10 min (Hu *et al.*, 2014). Several researches have tried to improve *TOF* by doping the catalyst, using donor mixtures or with some additive. For example, a *TOF* of 835 h^{-1} was obtained employing formic acid/sodium formate 0.6 M mixture with 2.3% Pd/C at 25°C (Li *et al.*, 2017). The deviation among results is due to the formic acid concentration, reaction time and temperature. As the reaction of formic acid

is exothermic, its disadvantaged is the increase in temperature, as in this work. *TOF* also tends to reduce with longer reaction times (Hu *et al.*, 2014).

3.2 HP DSC tests

The catalysts with better performance in the previous tests (5% Pd/C, 5% Pt/C and 1% Pt/USY CBV 780) were evaluated with ethanol and formic acid. Fig. 5 shows comparatively the thermograms for the decomposition of ethanol. In all three cases, an endothermic peak is observed simply when the catalyst of 5% Pt/C is carried forward at a temperature around 90°C , while with the other two catalysts it occurs between around 205°C . Apparently, a tendency towards an exothermic peak is seen when 5% Pt/C is used and the system exceeds 190°C .

When formic acid is used, it is placed inside the crucible and then brought to temperatures below 8°C , and once it is in solid phase the catalyst is added. Fig. 6 shows the decomposition of formic acid in a comparative manner performed by the three catalysts. When the 1% Pt/CBV 780 catalyst is used, an exothermic peak is observed around 100°C which indicates a decomposition, while the endothermic peak is at 240°C . In the case of 5% Pt/C, there are two small exothermic peaks between 40 and 60°C , and the endothermic peak is near 200°C . Finally, in the case of 5% Pd/C, an exothermic peak is not observed, but a little endothermic line is around 220°C .

The analysis of hydrogen composition of the gas samples for the case of formic acid indicate a greater presence in the case of 5% Pt/C (0.61%), with respect to 1% Pt/C (0.41%) and 5% Pd/C (0.15%).

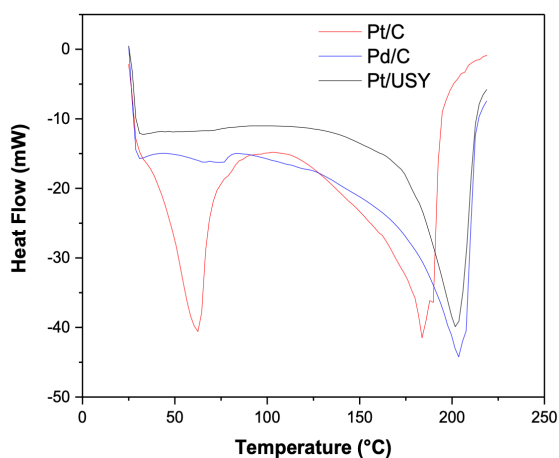


Fig. 5. HP DSC thermogram for tests with ethanol at 50 bar N₂, $10^\circ\text{C}/\text{min}$.

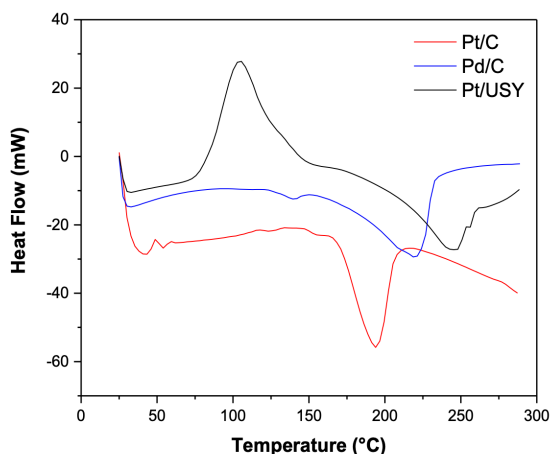


Fig. 6. HP DSC thermogram for tests with formic acid at 50 bar N_2 , 10 °C/min.

3.3 Characterization of catalysts

The best catalytic performance occurred with Pt/C and Pd/C. According to the XRF results, the platinum catalyst contains elements such as platinum (49%), phosphorus (28%), sodium (10%) and some traces of aluminum, silica acid and sulfur in small proportions. This corroborates the infrared spectrum (Fig. 7), which has bands associated with the vibrations of Al-O-Al at 1053 cm^{-1} (Hosseini & Khosravi-Nikou, 2012). For the palladium catalyst, the results of XRF shows 65% of palladium, 22% of sodium and traces of between 0.5 to 0.7% of calcium, sulfur and aluminum. This can be corroborated with the diffractogram (Fig. 8).

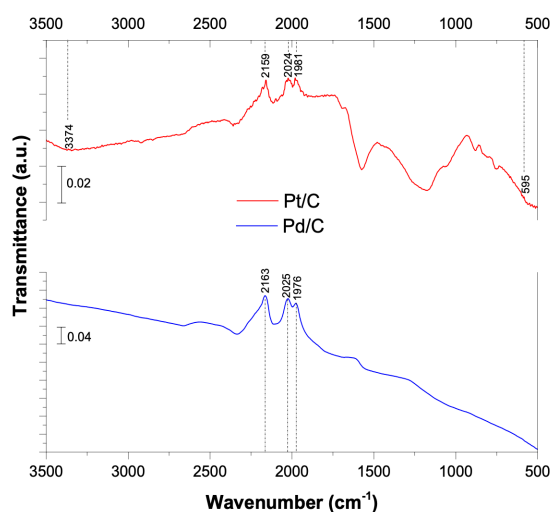


Fig. 7. FTIR both catalysts.

The image of FTIR (Fig. 7) for Pt/C catalyst presents the follow bands: between 459 and 595 cm^{-1} are aginose to Al-O stretches in an octahedral structure, as explained in other studies (Djebaili *et al.*, 2015). There are also bands of carbonyl absorption in CO, which are in the range of 2159 and 2028 cm^{-1} . There is also a small band of Pt in the oxidized sites in 2159 cm^{-1} , while in 3374 cm^{-1} the band corresponds to HOH doubling and OH narrowness. In the water adsorption band, catalysts showed an OH-stretching IR band with a strong band centered at 3345 cm^{-1} . This corroborates the presence of water in the sample, which can come from the atmosphere. These bands are also found in other studies (Ivanova *et al.*, 2007). Low crystallinity and aggregate phases are also observed, it is an amorphous material, which can vary in size, in agreement with FTIR and XRF. This is attributed to metal platinum, as the diffractogram shows phases associated with the components added in the XR.

The catalysts of Pd/C mainly presents bands from 2163 cm^{-1} until 1976 cm^{-1} that correspond to the carbon monoxide adsorption, more exactly 2163 cm^{-1} and 2025 cm^{-1} for linear and bridged bond forms, respectively, between the CO molecule and the metallic surface of Pd (Skoda *et al.*, 1994). Furthermore, this catalyst contains traces of phosphorus, which has the characteristic of transporting and storing energy. Therefore, this element can influence it to be a material with better catalytic behavior. Unlike Pd/C, the Pt/C catalyst is a more amorphous material, where bands can be seen in 2183 cm^{-1} , 2088 cm^{-1} and 2073 cm^{-1} . Cobalt ICOD 00-027-0136 is orthogonal and at high temperatures is a magnetic semiconductor. There are phases of molybdenum platinum in the Pd/C and peaks of 1045 cm^{-1} , 2177 cm^{-1} and 2600 cm^{-1} .

The XDR diffractograms (Fig. 8) of Pt/C and Pd/C have pronounced peaks, suggesting that noble metals were highly dispersed as small crystallites. Generally, peaks less than 30° correspond to the amorphous carbon support, then for both, platinum and palladium, the characteristic peaks of the (002) facet of activated carbon at 2θ were 24.9° and 23.7° , respectively. Both metals presented three characteristic peaks that correspond to the (111), (200) and (220) facets, which indicates that both noble metals deposited in the catalysts had a face centered cubic (fcc) structure (JCPDS standard 05-0681).

In the case of platinum, these XRD peaks are located for values of 2θ in 40.1° , 46.5° and 68.4° , respectively. Furthermore, various impurities were found and phases such as lithium, gallium

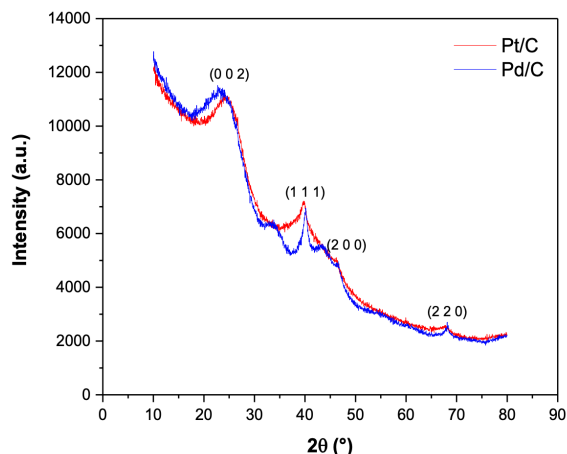


Fig. 8. XRD for both catalysts.

and iodide (ICOD 00-041-089) are observed, which are semiconductors and photocaptors (Yanase & Oi, 2008). Also, cesium phosphate (ICOD PFD 00-026-0398) (G. Zhang *et al.*, 2016) and cobalt (ICOD 00-027-0136) that is orthogonal and at high temperatures is a magnetic semiconductor (Laborium & Section, 1973). The Debye Scherrer shape was used, obtaining a size of $0.065 \mu\text{m}$ in the lithium, manganese, aluminum, molybdenum oxide phase. The catalyst presents phases with other impurities, a peak of molybdenum platinum (1/2) (ICSD PDF 98-008-89803) in 25.9° that is characteristic in other studies and is orthogonal (Roquero, 2011). Bismuth oxide (ICOD PDF) is also found, it is a conductive oxide and it is in cubic phase (Wind *et al.*, 2015). It is also an amorphous material that can give indications of pores. There is absence of platinum oxide peaks, the active phase is in reduced form into bulk, different from the FTIR report.

In case of palladium, the XRD peaks at 2θ of 40.2° , 46.7° , and 68.6° corresponded to the Pd (111), (200), and (220) facets, respectively. Both catalysts, Pt/C and Pd/C exhibited peaks in the region corresponding to (111) facet, which can be attributed to both platinum and palladium, respectively. The distinct peaks at 40.1° and 40.2° (111 planes) and 68.4° and 68.6° (220) can be directly related to the impregnation of both metals, respectively. Therefore, the presence of peaks related to these noble metals depicts successful impregnation of metals in the carbon support. Similar diffractograms have been reported earlier for Pt/C and Pd/C (Al-Muhtaseb *et al.*, 2016).

SEM images (Fig. 9) show sheet forms and a particle size of $0.38 \mu\text{m}$ and $0.17 \mu\text{m}$ for Pt/C and Pd/C, respectively, using Feret diameter.

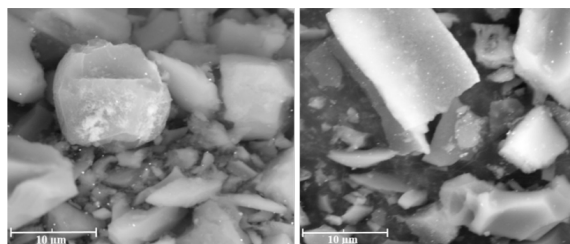


Fig. 9. SEM for both catalysts. 5% Pt/C (left) and 5% Pd/C (right).

This indicates how the size is dispersed in carbon substrates, and additionally it has a sheet form showing that they and their size are dispersed on carbon substrates. Unlike other studies where morphologies are observed in more compact clusters, these ones exhibited a very similar morphology to a porous group composed of many small nanoscale rounded particles (Chiu *et al.*, 2019). The SEM also show morphologies in the form of mines and aggregates and which of them are in the support. Unlike the SEM of the Pd/C, it is less aggregated, but it is inside the sodium catalyst, which is a reductive agent that is also in the Pt/C and can help it to be a better catalyst.

Conclusions

According to the experimentally developed, among the in situ hydrogen generation systems evaluated from a biodonor, the most promising in terms of the amount of hydrogen produced with 88% is formic acid with 5% Pd/C, in a ratio of 28.15 mmol of Pd per kg of formic acid) to 300°C d 500 rpm during 8 h. In this test, the hydrogen *TOF* and yield were 49.21 h^{-1} and 0.5. The behavior of the 5% Pt/C system is similar but it is more expensive. Even when the system that uses formic acid generates more hydrogen than the one that uses ethanol, the non-gaseous product will result in a very high acid value, which can be an inconvenience against the required specifications. The main contribution of this work was to the evaluation of the generation of hydrogen using supported monometallic catalysts, but under the usual conditions of hydroprocessing, which are not so moderate in temperature and pressure with respect to the researches reported in the literature.

Acknowledgements

We thank the Dirección de Investigación y Extensión de la Sede Bogotá and the Vicedecanatura de Investigación y Extensión de la Facultad de Ingeniería, Universidad Nacional de Colombia, for the financing and management of the project: “Producción de biodiésel no éster mediante desoxigenación catalítica de aceite de palma con generación de hidrógeno in situ”.

Nomenclature

A	area of the peak, mV.s
AP	Active Phase in the catalyst
M	Molarity, mol.L ⁻¹
m	Molality, mol.kg ⁻¹
t	Time, h

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