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From glycerol to lactic acid under inert conditions in the presence of platinum-based catalysts: The influence of support

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ABSTRACT

In this work, it was shown that glycerol (Gly) can be effectively converted to lactic acid (LA) under inert atmosphere using a Pt/ZrO_2 catalyst. Starting from pure glycerol, at 180 °C and under a He pressure of 30 bar, we were able to achieve up to 80% yield of LA after a reaction time of 8 h. The catalysts performance of Pt/TiO_2, Pt/C and Pt/ZrO_2 were compared showing that using Pt/ZrO_2 high conversion and stable LA selectivity were achieved during all the process. Further, using Pt/ZrO_2 the LA selectivity was less sensitive to the nature of the reaction atmosphere while using either H_2 or He. While using crude Gly (85% purity), a lower reaction rate was obtained in the presence of Pt/ZrO_2, however high selectivity to LA (~80%) was maintained.

1. Introduction

In the last two decades, due to its large availability, glycerol (GLY) has become an important renewable feedstock for chemicals. The chemical structure of glycerol, with three hydroxyl groups, allows the preparation of a large bench of products by various selective catalytic transformations (e.g. etherification, esterification, oxidation, and hydrogenolysis reactions) [1–4]. Among them, the hydrogenolysis reaction has received a growing attention, since it allows the synthesis of high valuable products (e.g. 1,2-propanediol (1,2-PDO) or 1,3-propanediol (1,3-PDO)) [5,6].

In our group, we carried out this reaction in the presence of supported noble metal catalysts (Rh or Ir) under a wide range of pH (7–10). Under alkaline conditions not only 1,2-PDO was formed but also a significant amount of lactic acid (LA) appeared [7–10].

The catalytic transformation of glycerol into LA has received increasing interest since lactic acid is the most widely occurring hydroxycarboxylic acid with an annual worldwide production of 120,000 tonnes [11]. Most of the applications concern the use of optically pure (or enriched) lactic acid such as in the food industry (as an acidulant, as a preservative or even as an inhibitor of bacterial spoilage), or in the production of polylactic acid (PLA), a biodegradable thermoplastic polymer with medical uses such as implants or sutures. Further, the corresponding racemic PLA is amorphous with poor mechanical and thermal properties. Moreover, racemic lactic acid may serve as a precursor of even higher added-value products such as pyruvic or acrylic acids [12]. The use of ethyl lactate as a green and non-toxic (approved as a food additive by FDA [13]) solvent has also been reported. This solvent is miscible with water and also with some organic solvents, allowing to adjust the polarity of the medium by proper mixing with a co-solvent. Several routes are described to achieve selective transformation of glycerol into LA. The fermentation approach allowed preparing chiral lactic acid under microaerobic conditions. Recent development of metabolically engineering strain of *Escherichia coli* yielded to the production of 75% of D-lactic acid at a 2.78 g L^{-1} h^{-1} productivity [14]. Aerobic catalytic oxidation, in the presence of supported noble metals was also reported [15,16].

The use of platinum-based catalysts in the selective glycerol hydrogenolysis into 1,2-PDO has been described in some papers [4]. Under neutral conditions, Yuan et al. obtained a 92% conversion after 22 h using a 3 bar of H_2 at 220 °C over a Pt catalyst supported on hydrotalcite (HTL) [17]. The selectivity of this process was quasi-exclusively to 1,2-PDO with more than 90%; small traces of ethylene glycol (EG) and propanol (PO) were also detected. Similarly, Pendem et al. reported the use of a Pt/HTL catalyst under 45 bar N_2 at 250 °C. Their results showed a 98% conversion after 3 h with a 1,2-PDO selectivity of 70%. This selectivity was improved to 75% at lower conversion (78%) under 35 bar of N_2 at 225 °C [18]. Moreover, catalytic conversion of GLY to LA has also been studied using a Pt/C

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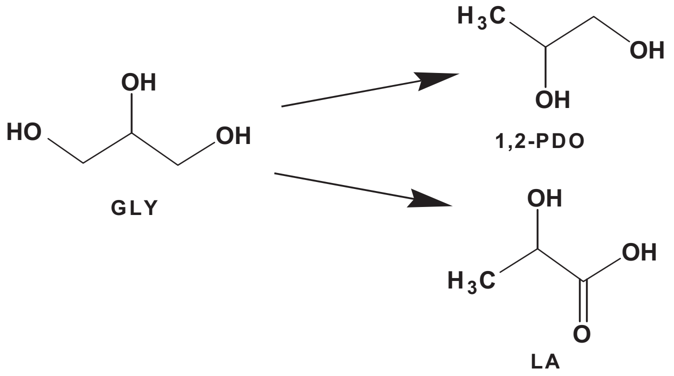

Scheme 1. Conversion of glycerol (GLY) to propylene glycol (1,2-PDO), and lactic acid (LA).

catalyst. Maris et al. achieved, after 5 h, a 92% glycerol conversion at 200 °C under a 40 bar H_2 pressure in the presence of a base (NaOH). The selectivity was pointed to the formation of LA and 1,2-PDO as the main products. Replacing NaOH by CaO led to a full glycerol conversion within 5 h with an improved selectivity to LA up to 58% [19]. Checa et al. obtained a full glycerol conversion with 50% selectivity to LA after 12 h while using Pt/ZnO catalyst under alkaline conditions at 20 bar H_2. Under the same experimental conditions, but replacing H_2 by He, the selectivity to LA was moderately improved to reach 60% [20]. Using $Pt/CaCO_3$, Ten Dam et al. obtained a low glycerol conversion of 25% after 18 h at 200 °C and under a 40 bar H_2 [18]. The selectivity to 1,2-PDO and LA reached 55% and 15%, respectively. In the presence of boric acid, the conversion was increased up to 55% and the selectivity to 1,2-PDO diminished to 20% in favour of LA (60%) [21]. This effect was attributed to the formation of borate ester under alkaline conditions.

Lately, Jin et al. described a new bimetallic catalyst based on Cu and Pd particles supported on graphene. Under their experimental conditions (NaOH:GLY = 1.1; $T = 140$ °C and $P_{N2} = 15$ bar), a 56% glycerol conversion with a high LA selectivity of 88% was achieved after 16 h [22].

In this work, we report the formation of racemic lactic acid (LA) from glycerol (GLY) in the presence of platinum-based catalysts under inert conditions (Scheme 1). In previous works, we highlighted the influence of both: (i) the used atmosphere (H_2 or He), and (ii) the active catalytic phase (Ir, Rh) on both the reaction rate and the selectivity of the reaction [7–10,20]. Zirconia (ZrO_2) has shown a good stability in water, even at high temperature and under elevated pressure [23–25]. For this reason, we have focused our work using this support. The catalytic performance of Pt/ZrO_2 catalysts has been compared to those of some other supported catalysts. Furthermore, the influence of some other experimental conditions (e.g. nature of atmosphere, purity of glycerol) on the reaction rate and the LA selectivity has been investigated.

2. Experimental

2.1. Supports

Two commercial ZrO_2 supports with a specific surface area of 92 and 50 $m^2\,g^{-1}$, were provided by MEL Chemicals ($ZrO_2{}^{M}$) and NORPRO ($ZrO_2{}^{N}$), respectively. A TiO_2 support (Degussa P25), with a $S_{BET} = 50\,m^2\,g^{-1}$ and a carbon support from MAST (40–100 μm), with a $S_{BET} = 1265\,m^2\,g^{-1}$ were also used in this study.

The main characteristics of the supports are reported in Table 1.

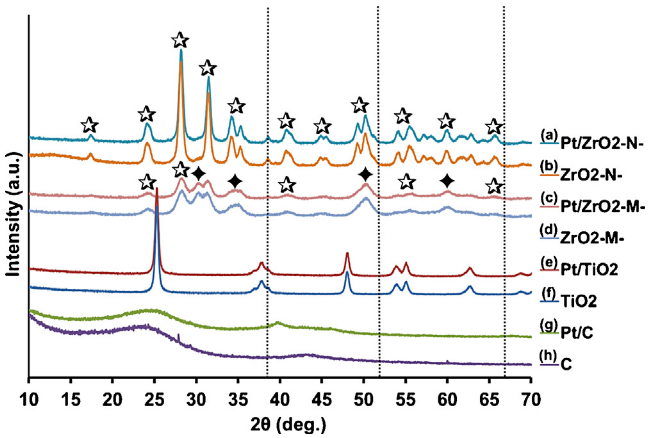

Fig. 1. XRD diffractograms of the supports and the corresponding Pt catalysts. The vertical lines correspond to the reference metallic platinum, ☆: Monoclinic zirconia, ◆: Tetragonal zirconia.

2.2. Catalyst preparation and characterization

The support was dispersed in water and the required amount of platinum (H_2PtCl_6, Alfa Aesar, theoretical amount 1 wt% for ZrO_2 and 3 wt% for C), was added dropwise while stirring under nitrogen flow. After 5 h of impregnation, the slurry was cooled down in an ice bath and a 37 wt% solution of formaldehyde was added dropwise, followed by a 30 wt% KOH solution. After stirring overnight under a nitrogen flow, the suspension was filtered and the solid was washed with water up to elimination of all traces of base (pH test) and chlorine ($AgNO_3$ test). Finally, the catalyst was dried at 100 °C overnight [26].

The ICP analyses were carried out using an ICP-OES Activa (Jobin Yvon) apparatus. Powder X-ray diffraction (XRD) analyses were performed with a Bruker D8 Advance A25 diffractometer ($\lambda = 1.54184$ Å) using a one dimensional multi-strip fast detector (LynxEye) with 191 channels on 2.94° at 50 kV and 35 mA. The crystallographic phases of zirconia (monoclinic and tetragonal) were determined using 'Highscore plus V3' software (Table 1). The diffractograms of the supports and of the corresponding supported platinum catalysts were similar (Fig. 1). The absence of the Pt peaks in the XRD diffractograms suggested that the average diameter of Pt particles was small.

Transmission electron microscopy (TEM) images were obtained using a JEOL 2010 LaB6 microscope operating at 200 kV. TEM analysis confirmed the results of XRD; representative TEM pictures of supported platinum catalysts show the presence of well dispersed small platinum particles, with an average diameter below the 5 nm (Fig. 2); nevertheless some aggregates of Pt were observed on each sample.

2.3. Catalytic reaction and analytical methods

Most of the experiments were carried out with commercial pure glycerol (Aldrich G7893, purity > 99.5%). "Crude" glycerol

Table 1
Summary of the supports used for the preparation of the platinum catalysts.

Support	Supplier	Pt loading (%)	S_{BET} ($m^2\,g^{-1}$)	Ratio tetragonal/monoclinic phases
$ZrO_2{}^{M}$	MELCAT	1.2	92	25/75
$ZrO_2{}^{N}$	NORPRO	1	50	5/95
TiO_2	DEGUSSA	0.9	50	–
Carbon	MAST	2.7	1265	–

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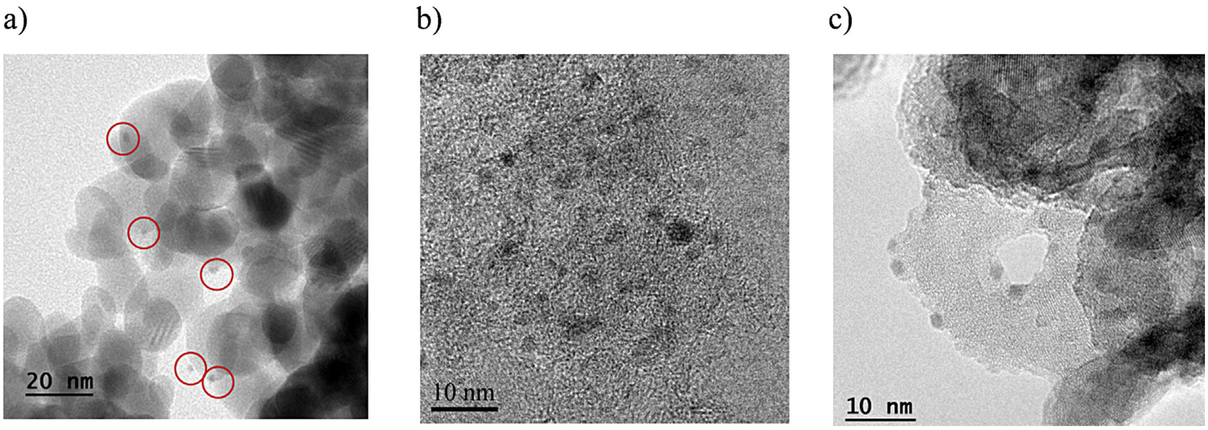

Fig. 2. TEM micrographs of supported platinum particles supported on (a) ZrO_2, (b) C and (c) TiO_2.

was provided by Novance (purity *ca* 85%). The catalytic reactions were performed in a 200 mL stainless steel autoclave equipped with a graphite-stabilized Teflon® container. After introduction of 100 mL of 5 wt% GLY in [1 M] NaOH aqueous solution (molar ratio NaOH/GLY = 1.8 in standard conditions; NaOH/GLY = 1.1 while using crude glycerol), the catalyst was added to achieve the desired Pt/GLY ratio, the reactor was flushed three times with He and then heated up to 180 °C. When the desired temperature was reached, the pressure was adjusted (30 bar of He in standard conditions) and the stirring (1500 rpm) was started setting the t_0 of the reaction. Samples of the reaction medium were taken out regularly, quenched with H_2SO_4 (0.5 M) and analysed by HPLC (Shimadzu) on a CarboSep 107H column (0.5 mL min^{-1} of 0.005 N H_2SO_4, $T = 40$ °C) using both refractive index (RI) and ultra-violet (UV) detectors. The total organic carbon measurements (TOC) were performed using a Shimadzu TOC-5050A to determine the carbon mass balance. The samples were diluted 1/200 before analysis, and the carbon concentration was determined within ±5% accuracy.

In some case, the gas phase was collected in a gas bag and analysed using an Agilent 5975C GC/MSD equipped with Alumina, Poraplot U and 5 Å-Molecular sieve columns and thermal conductivity detectors. Backflush injectors were used for Poraplot U and 5 Å-Molecular sieve columns.

3. Results and discussion

3.1. Influence of the nature of the support

The influence of the supports' nature on glycerol conversion was studied over the four Pt catalysts supported on C, TiO_2 and both ZrO_2. The evolution of the conversion as a function of time achieved at 180 °C under 30 bar of He is reported in Fig. 3.

In the presence of Pt/TiO_2 catalyst, the lowest reaction rate was observed since using this catalyst only 50% GLY conversion was achieved after 8 h corresponding to a calculated initial reaction rate of 0.9 mol h^{-1} $g_{Pt}{}^{-1}$. On the other hand, catalysts prepared on ZrO_2 or C supports exhibited a much higher activity since almost a full GLY conversion was achieved after 8 h, corresponding to an initial reaction rate of 1.9 mol h^{-1} $g_{Pt}{}^{-1}$ and 2.7 mol h^{-1} $g_{Pt}{}^{-1}$, respectively (calculated from the slope of the curves; Fig. 3). As far as the zirconia supports are concerned, they were both mainly composed of monoclinic phase with minor amount of tetragonal phase (5–25%); this resulted in similar evolution of the glycerol concentration within the experimental errors. We attempted to prepare and evaluate platinum catalysts supported on tetragonal zirconia. However, this support was not stable under our experimental conditions and using water as a solvent. Indeed, the tetragonal to monoclinic transformation of ZrO_2 phases was already reported in the presence of water or water vapour even at relatively low temperature (starting at 65 °C) [27]. Further, since significant amount of monoclinic phase was observed we focused only on the use of the stable monoclinic zirconia as support.

As far as the selectivity was concerned, regardless the nature of the support, LA was formed predominantly (Table 2). The other observed products were propanediols and formic acid as well as very low amounts of ethylene glycol, ethanol or acetic acid (≤1%). The mass balance determined by the total organic carbon analysis of the solutions was >95%, indicating that no gaseous compound was produced, and this was confirmed by gas analysis of the atmosphere after 24 h reaction (for selected reactions).

The least active Pt/TiO_2 catalyst yielded the highest initial selectivity to LA (>80%) but at low conversion (15%). However for longer reaction time, we observed a slight decrease in the selectivity and after 24 h, LA yield reached 63% (76% GLY conversion). As a general matter, regardless the nature of the supports the selectivity to LA after 24 h was in the range 75–80% (GLY conversion > 75%) (Table 2).

However, the evolution of the selectivity to LA was affected by the type of the support (Table 2; Fig. 4). In the case of carbon supported catalyst (Pt/C), a moderate selectivity of 60% to LA was observed during the first hours of the reaction, and then it increased progressively to reach 80% after 24 h (Fig. 4a). On the other side, when using zirconia supported catalyst (Pt/ZrO_2), high selectivity to LA in the range of 74–84% was achieved from the beginning of the reaction and it remained almost constant all over the course of the reaction time (Fig. 4b). In both cases, stable selectivity to LA was observed up to *ca* 90–95% GLY conversion, while at nearly full glycerol conversion it increased at the expense of 1,2-PDO.

The differences in the selectivity observed between the two supported catalysts (Pt/C and Pt/ZrO_2) were mainly attributed to the simultaneous formation of 1,2-PDO at various levels. In the presence of Pt/C, the initial selectivity in 1,2-PDO reached 15% before decreasing to 7% at full GLY conversion (Fig. 4a). We have shown independently, that under the tested reaction conditions, 1,2-PDO can be transformed to LA. On the other hand, in the presence of $Pt/ZrO_2{}^M$, 1,2-PDO was produced at negligible level (<5%) and consequently it did not affect significantly the LA selectivity over the reaction.

3.2. Influence of the nature of the atmosphere and the pressure level

The nature of the atmosphere could have a significant influence on the reaction rate and the selectivity to LA [8–10]. This effect was evaluated using $Pt/ZrO_2{}^N$ catalyst and compared to the results

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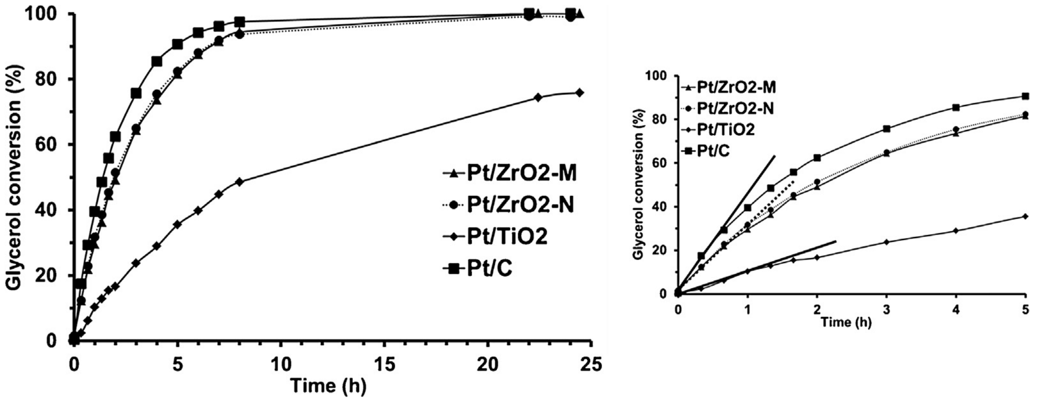

Fig. 3. Evolution of glycerol conversion as a function of time using different supported platinum catalysts. (Reaction conditions: 5 wt% GLY; T = 180 °C; NaOH/GLY = 1.8; Pt/GLY = 2000; P_{He} = 30 bar.)

Table 2
Catalytic transformation of glycerol in the presence of different supported catalysts. (Reaction conditions: 5 wt% GLY; T = 180 °C; NaOH/GLY = 1.8; Pt/GLY = 2000; P_{He} = 30 bar.).

Catalyst	t (h)	GLY conv (%)[a]	Mass balance[b]	Yield (%)[a]	
				LA (Sel[c])	Other products[d]
Pt/ZrO_2^N	2	51	>95%	38 (74)	
	24	95		80 (84)	1,2-PDO = 4; FA[e] = 6; 1,3-PDO = 2
Pt/ZrO_2^M	2	49	>95%	38 (77)	
	24	94		84 (84)	1,2-PDO = 4; FA[e] = 7; 1,3-PDO = 2
Pt/TiO_2	2	17	>95%	15 (87)	
	24	76		63 (83)	1,2-PDO = 6; FA[e] = 3; 1,3-PDO = 1
Pt/C	2	62	>95%	38 (62)	
	24	100		80 (80)	1,2-PDO = 7; FA[e] = 3; 1,3-PDO = 3

[a] Determined by HPLC.
[b] Determined by TOC analyses after 24 h.
[c] Selectivity.
[d] Some other products have been also detected in small amount (<1%; e.g. ethylene glycol, acetic acid and ethanol).
[e] FA = formic acid.

achieved in the presence of the Pt/C catalyst. Regardless the nature of the support, higher conversions were observed under inert He atmosphere compared to the reductive one. In the presence of Pt/ZrO_2^N, after 5 h reaction, 74–82% and 40–50% GLY conversions were achieved under He and H_2 atmosphere, respectively (Fig. 5b). On the other hand, in the presence of Pt/C, 91% and 59% conversions were obtained after 5 h under inert and reductive atmosphere, respectively (Fig. 5a).

The respective yields of the two main products were compared after 5 h reaction (Fig. 6). Under inert atmosphere, irrespective of the catalyst, 60% LA yields were achieved. But as specified previously a larger amount of 1,2-PDO was produced in the presence of Pt/C catalyst (15% vs 5–7% in the presence of ZrO_2^N). On the other hand, under reductive atmosphere, LA was always the main product but to a lesser extent (<35%) and as it was observed under inert atmosphere, the presence of Pt/C favoured the formation of

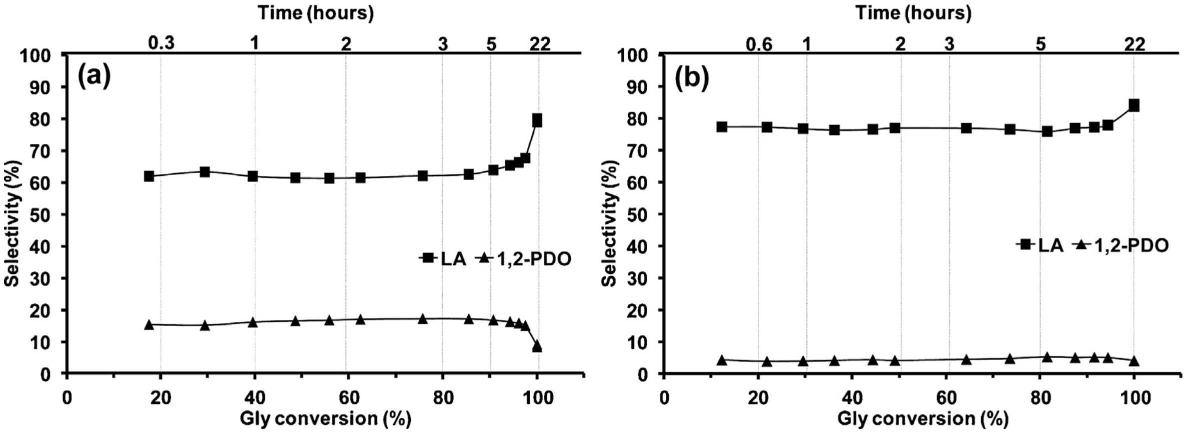

Fig. 4. Selectivities to LA and 1,2-PDO in the presence of (a) Pt/C and (b) Pt/ZrO_2^M under the same experimental conditions as a function of GLY conversion and time. (Reaction conditions: 5 wt% GLY; T = 180 °C; NaOH/GLY = 1.8; GLY/Pt = 2000; P_{He} = 30 bar.)

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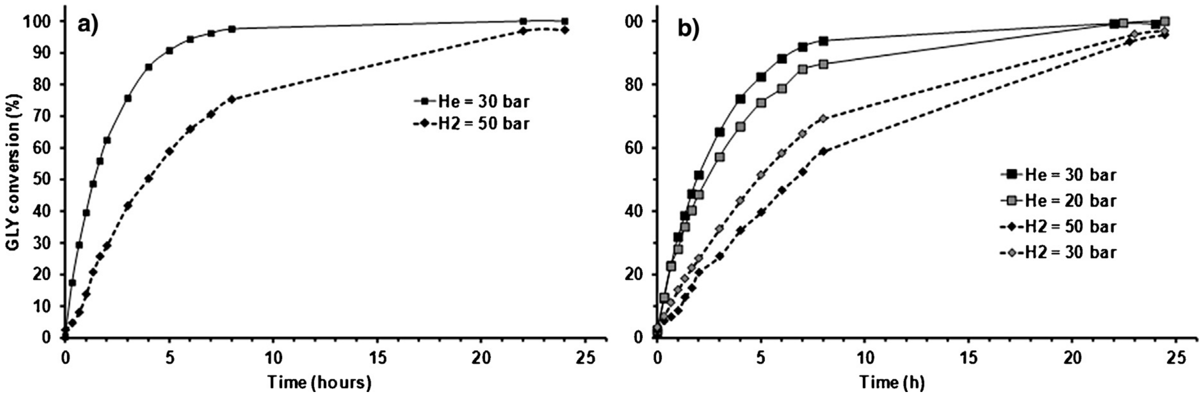

Fig. 5. Conversion of glycerol in presence of (a) Pt/C and (b) Pt/ZrO_2^{N} catalysts, with different He or H_2 pressures. (Reaction conditions: 5 wt% GLY; T = 180 °C; NaOH/GLY = 1.8; GLY/Pt = 2000.)

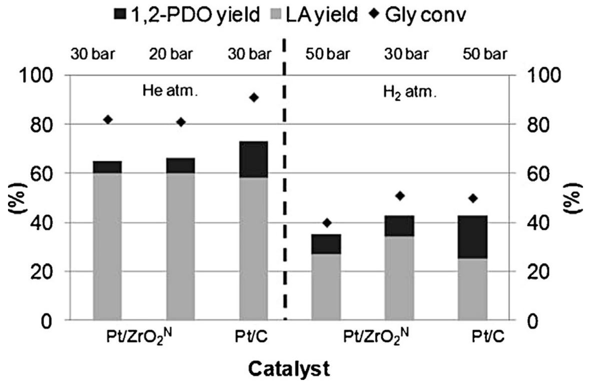

Fig. 6. Influence of the atmosphere on the conversion of glycerol and the yields in 1,2-PDO and LA in the presence of Pt/C and Pt/ZrO_2^{N} catalysts, with different He or H_2 pressures. (Reaction conditions: 5 wt% GLY; T = 180 °C; NaOH/GLY = 1.8; GLY/Pt = 2000, t = 5 h.)

1,2-PDO (21 and 7% under H_2 and He atmosphere, respectively; Fig. 6).

Moreover, the selectivity to the products was affected by the nature of the atmosphere (Fig. 7a and b). Over Pt/ZrO_2^{N}, whatever the nature of the atmosphere, the selectivities to LA and PDO were almost constant during the progress of the reaction (Fig. 7a). Under He atmosphere, 75–80% selectivity to LA was achieved together with selectivity to PDO < 10%. On the other hand, under H_2 atmosphere, the selectivity to LA decreased to 65–70%, while the selectivity to PDO increased up to ~25%.

In the presence of Pt/C catalyst, slightly different behaviour was observed depending on the nature of the atmosphere (Fig. 7b). Under He atmosphere, the initial selectivities to LA and PDO reached 60% and 20%, respectively. During the progress of the reaction, the selectivity to LA progressively increased from 60% to 80% (+20%) while the selectivity to PDO decreased to 8%. Under H_2 atmosphere, the initial selectivity to LA was lower than 50% to reach 56% after 24 h (+6%). In parallel, the selectivity to PDO was in the range 30–40% during the reaction. In that case, some minor by-products were not analysed at low glycerol conversion.

At complete conversion of glycerol, the nature of the used atmosphere has a stronger impact on the yield in LA and PDO in the presence of Pt/C than in the presence of Pt/ZrO_2^{N} (Fig. 7a and b). While using Pt/ZrO_2^{N}, the LA yields reached 78 and 65% after 24 h under He and H_2 atmospheres, respectively. Under identical reaction conditions, in the presence of Pt/C, LA yield reached 80 and 55% under He and H_2, respectively.

In the presence of Pt/ZrO_2^{N}, the influence of partial pressure of gas was evaluated, taking into account that at the considered temperature (180 °C), the inherent partial pressure of water was 15 bar. Under He atmosphere, no significant influence of the pressure on the reaction rate or the selectivities to LA and PDO was observed, the results being similar within the experimental errors (80% GLY conversion after 5 h and 60% selectivity to LA; Fig. 6). On the other hand, under reductive atmosphere, the conversion slightly decreased when higher pressure was used: after 5 h, 40% and 51% glycerol conversions were achieved under 50 and 30 bar of hydrogen, respectively. The influence of the hydrogen pressure on the reaction rate could be due to the fact that a dehydrogenation reaction was proposed as the first step (*vide infra*). Regardless the

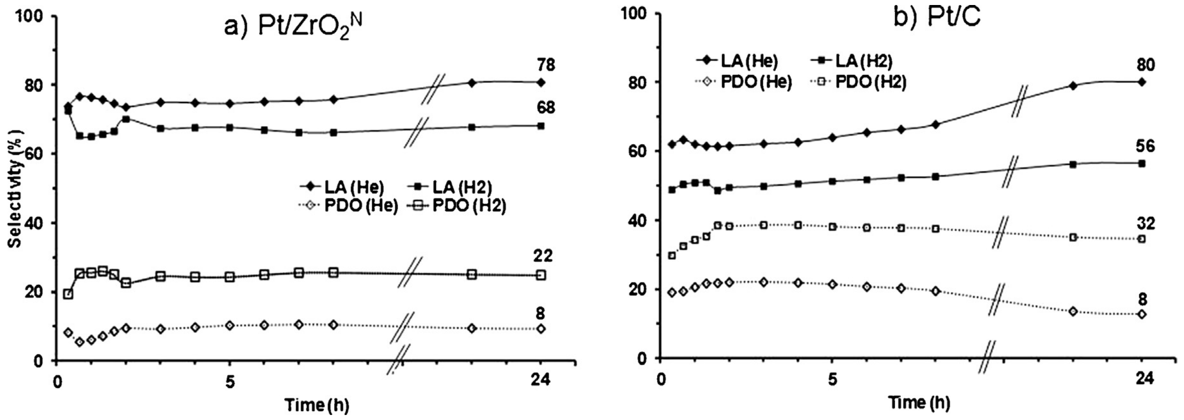

Fig. 7. Evolution of selectivity to LA and PDO in the presence of (a) Pt/ZrO_2^{N} and (b) Pt/C under different atmospheres (He or H_2) as a function of time. (Reaction conditions: 5 wt% GLY; T = 180 °C; NaOH/GLY = 1.8; GLY/Pt = 2000; P = 30 bar of He or 50 bar of H_2.)

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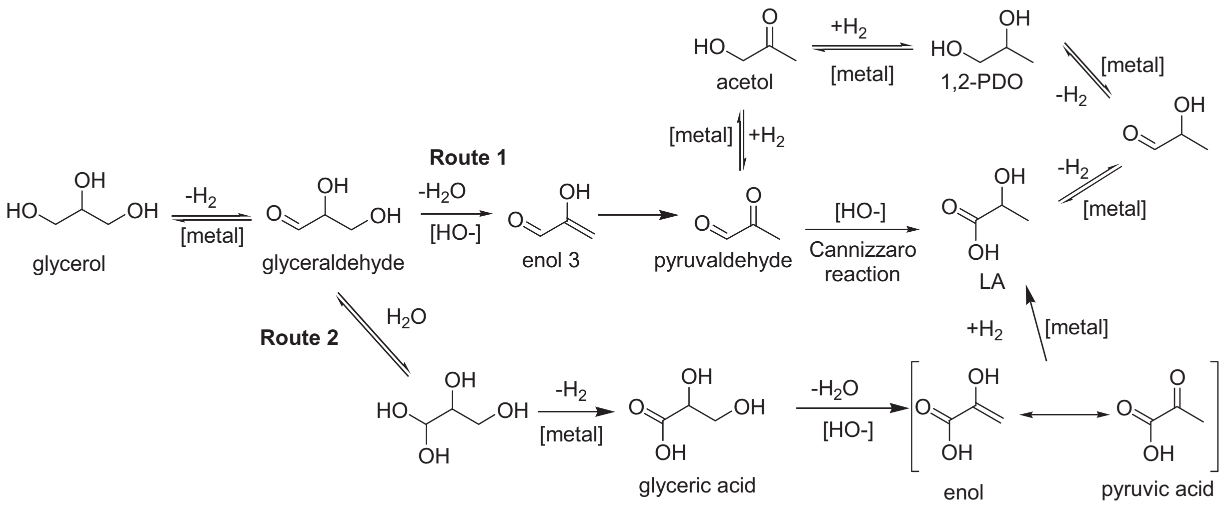

Scheme 2. Proposed reaction pathway for glycerol conversion into lactic acid (LA) and 1,2-propanediol (1,2-PDO) starting with a dehydrogenation step.

pressure, the corresponding selectivity to LA reached 65–67% at *ca* 50% conversion.

To summarize, the influence of the support in the present reaction is not clear. The main change concerns the LA/1,2-PDO selectivity under H_2 pressure while the difference is considerably lower under inert gas (Fig. 6). The evaluation of Pzc of zirconia and carbon has shown that the zirconia support is slightly more acidic than the carbon one (Pzc = 4.9 and 7.2, respectively). However, this parameter should have low impact since the reaction was carried out in alkaline conditions and regardless the nature of the support, the pH decreased from ~13 to ~12 at complete conversion. Further works are under progress to characterize the catalysts in order to understand the role of the support.

We have previously reported the influence of the nature of the atmosphere in the presence of Ir- and Rh-based catalysts for glycerol transformation [8,10]. With these metals, reverse selectivities were achieved when changing from inert to reductive atmosphere: namely, LA was the main product under He while 1,2-PDO was predominant under H_2. In this study, we observed that in the presence of Pt-supported catalysts, LA was the main product irrespective of the used atmosphere. This could be due to the dehydrogenation properties of Pt-based catalysts [26]. Furthermore, according to DFT calculation, it was assessed that the dehydrogenation to glyceraldehyde was the first step of the reaction [8] (Scheme 2). Then, two routes could be involved: either dehydration to enol, then pyruvaldehyde, followed by rearrangement *via* Cannizzaro reaction (route 1); or second dehydrogenation to glyceric acid (*via* the formation of the gem diol) followed by dehydration and hydrogenation (route 2). At the present time, we are not able to discriminate between these different routes. Nevertheless, in some of our experiments, traces of glyceric acid were detected exclusively at the beginning of the catalytic test. These traces supported the route 2; moreover, this route was also discussed by other researches [5,28]. Furthermore, it was established that the Cannizzaro reaction should not be favoured when hydrogen atoms in α-position to carbonyl are present [29]. On the other hand, Lux and Siebenhoffer recently reported that $Ca(OH)_2$ effectively catalysed lactic acid from dihydroxyacetone [30]. Accordingly, we suggest that the reaction occurred mainly through route 2 but further works need to be performed to establish the exact route.

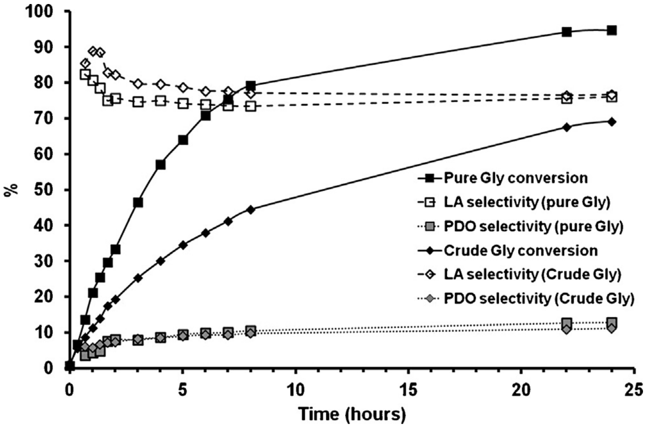

Fig. 8. Evolution of glycerol conversion and selectivities to LA and PDO as a function of time using pure and crude glycerol. (Reaction conditions: 5 wt% GLY; NaOH/GLY = 1.1; GLY/Pt = 2000; T = 180 °C; P_{He} = 30 bar.)

3.3. *Influence of the glycerol purity*

The catalytic transformation of crude glycerol, a by-product from the biodiesel process represents an economic asset because of its lower price. The presence of impurities such as salts, ash, methanol and water could affect the catalyst activity as previously reported in the 1,2-PDO synthesis [31]. As a preliminary study, we compared the performances of the catalyst using pure and crude glycerol. Since the target is to evaluate the catalyst under the most scalable conditions, we performed the reaction using lower base quantity. We have shown previously, that in the presence of Rh-based catalyst, the reaction rate was affected by the pH of the solution [8]. The same evolution was observed in the presence of Pt-based catalyst: using NaOH/GLY ratio of 1.1, 32% glycerol conversion with a 75% LA selectivity was obtained within 2 h (Fig. 8); while in the presence of NaOH/GLY = 1.8, the glycerol conversion and LA selectivity reached 51% and 74%, respectively (Table 2). The higher reaction rate was attributed to the increase of the alkaline contribution of the reaction.

The evolution of the reaction using “pure” and “crude” glycerol sources in the presence of $Pt/ZrO_2{}^N$ catalyst is shown in Fig. 8. Under the same standard experimental conditions (5 wt% GLY; NaOH/GLY = 1.1; pH = 12.7; GLY/Pt = 2000; T = 180 °C; P_{He} = 30 bar), “pure glycerol” gave a full conversion after 24 h with an initial reaction rate of 1.4 mol h^{-1} $g_{Pt}{}^{-1}$. On the other hand, the use of “crude glycerol” resulted in lower initial reaction rate (0.8 mol h^{-1} $g_{Pt}{}^{-1}$) giving a 70% conversion within 24 h. In both cases, similar selectivities of *ca* 80% to LA were achieved at the end of the process (after 24 h).

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Table 3
Composition of glycerol sources.

Glycerol quality	Composition (%)	Inorganic composition (ppm)			
		Na	P	S	Fe
Pure (Aldrich)	>99.5 Gly	4	<2	nd	<2
Crude (Novance)	85% Gly11%H_2O<1% monoester<0.1% MeOH4% ash	6.4×10^3	32	39	7

The analysis of the crude glycerol has shown that the mixture is composed of 85% glycerol, 11% water and 4% ash. The presence of residual monoester (<1%) was also observed. Furthermore, the dark colour of the crude glycerol indicates the presence of other compounds at low level. As far as the mineral content was concerned, the crude glycerol contained mainly Na as impurity issued from the transesterification of vegetable oils (Table 3). Since NaCl was previously reported to act as a poison in glycerol hydrogenolysis [29], this salt was added to the pure glycerol in a NaCl/GLY = 1 molar ratio.

After 24 h reaction, no effect of the addition of NaCl was evidenced either on the glycerol conversion or on the selectivity to LA. This indicates that the lower activity observed when using crude glycerol could not be attributed to the presence of NaCl. Other impurities will be tested to determine the compounds causing the decrease of the activity in the catalytic transformation of ‘crude glycerol’. Decolourization of crude glycerol solution will also be carried out to evaluate the influence of the presence of these by-products on the reaction rate.

4. Conclusion

This work presents an efficient alternative route for the preparation of lactic acid. High yields of LA (~80%) at total conversion were obtained starting from pure glycerol at 180 °C under inert conditions using platinum supported catalysts. Among the supports evaluated (C, TiO_2, ZrO_2), ZrO_2 appeared to be the most efficient for this process. Investigation of the experimental conditions (nature and pressure of the gaseous atmosphere, purity of glycerol) showed that major differences were observed at short reaction times (<10 h) mainly on the selectivity (especially the LA), while after 24 h these differences were mainly negligible. Under the same conditions, despite high selectivity, crude glycerol was converted to LA in a useful 52% yield at 70% conversion after 24 h. Current researches focus on improving the crude glycerol transformation by evaluating the role of the various impurities present in the mixture on the catalytic activity.

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