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.

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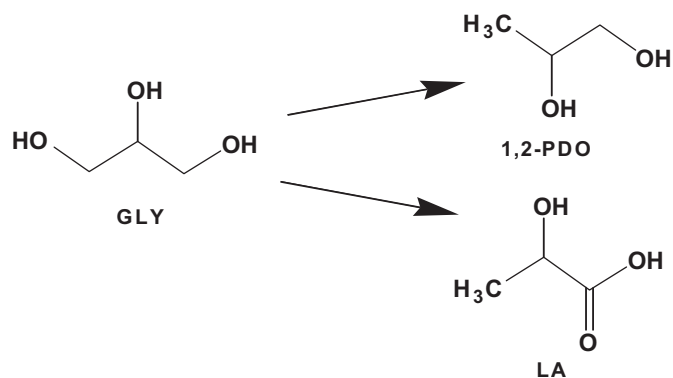
Scheme 1. Conversion of glycerol (GLY) to propylene glycol (1,2-PDO), and lactic acid (LA).

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.

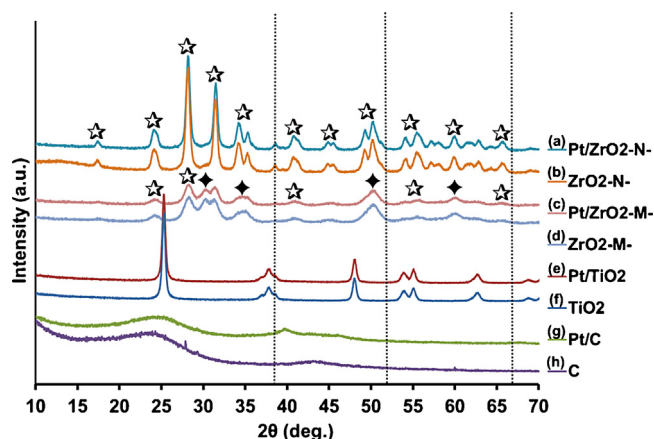The main characteristics of the supports are reported in Table 1.

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 (λ = 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	–