



Short Communication

On the role of the atmosphere in the catalytic glycerol transformation over iridium-based catalysts

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ARTICLE INFO

Article history:

Received 18 July 2011

Received in revised form 5 September 2011

Accepted 12 September 2011

Available online 18 September 2011

Keywords:

Iridium catalyst

Glycerol

Lactic acid

1,2-propanediol

Hydrogenolysis

ABSTRACT

Here, we report the transformation of glycerol alkaline solutions in the presence of supported iridium catalysts under either reductive or inert atmosphere at 453 K. It was shown that under H₂, the expected 1,2-PDO issued from hydrogenolysis of the triol was the main product while under He, lactic acid was formed predominantly via Cannizzaro rearrangement.

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1. Introduction

Glycerol is a feedstock available in large amount since it is a by-product in the process of bio-diesel production by transesterification of vegetable oils [1,2]. The selective transformation of glycerol represents one of the most attractive routes as large range of valuable compounds such as acrolein, dihydroxyacetone, glyceric acid, lactic acid, 1,2-propanediol or 1,3-propanediol can be produced [3–5]. Among all potential routes, the reaction of glycerol with hydrogen in the presence of homogeneous or heterogeneous metallic catalysts received a growing attention leading mainly to 1,2-propanediol (1,2-PDO) as a major commodity chemical. This product finds some uses as antifreezing, lubricant, industrial solvent or bulk chemical intermediate for the production of polyester materials [6]. Depending on the reaction conditions, the production of some other compounds was described such as 1,3-propanediol (1,3-PDO) used in polymeric applications [7–12] or ethylene glycol (EG) issued from C–C hydrogenolysis [13–15]. Lactic acid (LA), a central feedstock for chemical industry, applied either in food industry or as a renewable building block for sustainable chemistry in particular in biopolymer synthesis, was also mentioned in few reports [16–20].

Not only the nature of the catalyst is of large importance for the conversion rate of glycerol but also the reaction conditions such as

the addition of acid and alkaline promoters as well as the nature of the gas atmosphere. Depending on these parameters, dramatic changes of selectivity were achieved from a 100% yield to 1,2-PDO up to the formation of 1,3-PDO or LA.

Recently, several reports dealt with the partial dehydroxylation of glycerol under inert gas. D'Hondt et al. described the formation of 1,2-PDO (54%) at 503 K under inert atmosphere in the presence of a Pt/NaY catalyst after 15 h [21]. Roy et al. reported the use of a 1:1 admixture of Ru/Al₂O₃ and Pt/Al₂O₃ catalysts to perform the dehydroxylation of glycerol to 1,2-PDO without hydrogen addition; a 24% yield of 1,2-propanediol was achieved at 493 K after 6 h [22]. It was suggested that hydrogen was produced via liquid steam reforming [23,24] but the exact mechanism is still questionable. Independently, the teams of Lercher et al. [25] and Fierro et al. [26] studied the reactivity of glycerol without added hydrogen in the presence of bifunctional catalysts such as Pt/γ-Al₂O₃ or Pt/ASA (amorphous silico-alumina).

As mentioned previously, the presence of acid or base additives may influence dramatically the product distribution in the final solution. The reaction rate was significantly enhanced in the presence of basic medium and in that case several reports described the concomitant formation of lactic acid together with 1,2-PDO and ethylene glycol as the main products. Montassier et al. described the conversion of glycerol under hydrogen in the presence of Cu Raney® at different pH [16]. They showed that under alkaline conditions (NaOH 1 M), lactic acid was the main product (85% initial selectivity) while it was not observed under neutral conditions. Casale and Gomez patented the

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use of ruthenium catalyst modified with sulphur at 513 K in the presence of NaOH to yield after 2 h, 75% of 1,2-PDO and 13% of LA as the main constituents [17]. The team of Davis reported the presence of lactic acid during hydrogenolysis of glycerol in the presence of bases (CaO or NaOH) over carbon-supported Ru, Pt, Pt–Ru and Au–Ru catalysts [18,19]. However, the selectivity to lactic acid decreased with the conversion to reach 35–38% at complete conversion. Liu et al. investigated TiO₂-supported Au, Pt or Au–Pt catalysts under oxidative alkaline (NaOH) conditions; they obtained a 45% yield of LA using the Au–Pt/TiO₂ catalyst [27]. To our knowledge, this is the best yield ever achieved for the transformation of glycerol into LA using heterogeneous metallic catalysis. Non-catalyzed hydrothermal conversion of glycerol into lactic acid was also reported [28,29].

Few reports mentioned the use of iridium-based catalysts in this reaction [7,16]. According to Montassier's work, Ir/SiO₂ exhibited a lower activity than the corresponding Rh and Ru-based catalysts but it selectively hydrogenolyzed C–O bonds without affecting C–C ones. In this report, the activities and selectivities of glycerol conversion were investigated in the presence of iridium catalysts under inert or reductive atmosphere and the results were compared with rhodium-based catalysts [16,30,31]. We have shown that while 1,2-propanediol is selectively produced under hydrogen pressure, a high selectivity towards lactic acid can be achieved under helium (Scheme 1). The key role of the nature of the atmosphere in the selectivity of the reaction has been highlighted.

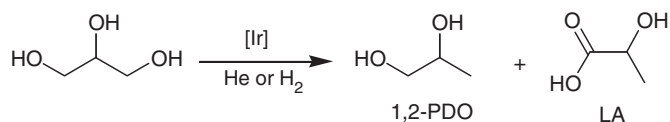
2. Experimental

2.1. Catalyst preparation and characterization

Iridium catalysts supported on carbon were prepared by cationic exchange using [Ir(NH₃)₅Cl]Cl₂ (Alfa Aesar) as metal precursor. MAST carbon (mesoporous synthetic carbon activated at 1123 K under CO₂ atmosphere; S_{BET} = 1220 m² g⁻¹) was first oxidized by treatment with sodium hypochlorite (5% active chlorine) for 20 h at room temperature. The reaction was quenched by the addition of a 1.25 N hydrochloric acid solution. The support was then filtered and washed with demineralized water until complete elimination of chloride ions from the support. 4.95 g of oxidized support were dispersed in 120 mL of 1 M ammonium hydroxide under nitrogen bubbling. 300 mg of the iridium salt (to get 1 wt.%Ir) dissolved in 60 mL of 1 M ammonium hydroxide was added dropwise at room temperature. After stirring under nitrogen atmosphere for 24 h, the suspension was filtered; the catalyst was washed with water until neutralization, and dried overnight at 333 K under vacuum. The solid was reduced according to the following protocol: 2.5 g of solid were introduced in a reduction cell which was purged with argon before the hydrogen flow was adjusted at 12 L/h. The catalyst precursor was heated at 2 K/min up to 573 K and this temperature was maintained for 3 h. After cooling down slowly to room temperature, the cell was then flushed with argon. Iridium loading was determined by ICP analysis (Ir% = 0.6–0.8 wt.% depending on the batch).

For comparison, a commercial 5 wt% Ir/CaCO₃ (Alfa Aesar, S_{BET} = 8 m² g⁻¹) catalyst was reduced following the same protocol as for the Ir/C catalyst. The effective loading was confirmed by ICP analysis.

Powder X-ray diffraction (XRD) analysis were performed with a Bruker D8A25 Advance diffractometer (λ = 1.54184 Å) using a one dimensional multistrip fast detector (LynxEye) with 191 channels



Scheme 1. Main products formed during catalytic transformation of glycerol in the presence of supported iridium catalysts.

on 2.94° at 50 kV and 35 mA. Transmission electronic spectroscopy images were obtained using a JEOL 2010 LaB6 microscope operating at 200 kV.

2.2. Catalytic reaction and analytical method

Initial screening of catalysts was conducted in a Slurry Phase Reactor 16 (AMTEC), designed to conduct several experiments in parallel, for 12 h using 6 mL of a sodium hydroxide aqueous solution of 5 wt.% glycerol, in the presence of 30 mg catalyst at 1000 rpm. However this system did not allow to perform sampling and in order to establish the kinetic profile, the reaction was performed in a 200 mL stainless steel autoclave equipped with a graphite-stabilized Teflon® container and designed to sample the liquid phase. 100 mL of 5 wt.% glycerol in NaOH 1 M were introduced in the vessel with 500 mg catalyst and the reactor was flushed with helium and heated at 453 K. When the temperature was reached, the atmosphere was adjusted to 30 bar and the stirring (1500 rpm) started corresponding to time zero of the reaction. For reaction under hydrogen, the reactor was purged with H₂ and the pressure was adjusted to 50 bar at the desired temperature since this pressure was used in previous study [12]. Samples of the reaction medium were taken out regularly and analyzed by HPLC on a CarboSep 107H column (0.5 mL/min 0.005 N H₂SO₄, T = 313 K). 1,3-PDO, 1,2-PDO, ethylene glycol, 1-propanol, 2-propanol, ethanol, methanol, acetol, lactic acid, formic acid and acetic acid were analyzed. GC-MS analysis confirmed the identification of lactic acid and 1,2-propanediol. The Total Organic Carbon (TOC) of the aqueous solution was measured using a Shimadzu TOC-5050A analyzer. The comparison of the measured TOC and the calculated TOC obtained by chromatographic analysis allowed to verify the carbon balance based upon glycerol consumed and products formed in the aqueous phase. Also, the difference between the TOC measured and the initial TOC concentration gave an estimation of carbon-containing gaseous products formed during the reaction. It was checked that similar results were achieved in both reactors.

The gas phase was also collected in a gas bag at the end of the reaction and analyzed using a GC-MS (Agilent Technologies, 5975 C) 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.

The conversion (Conv(%)) of glycerol was defined as the number of mol of glycerol consumed with respect to the initial number of mol of glycerol. The selectivity in a given product *i* was calculated according to the following equation:

$$Sel_i^t(\%) = \frac{X_i^t \times n_{C_i}}{X_{gly}^t \times 3} \times 100$$

Yields were similarly expressed as: $Y_i^t(\%) = \frac{X_i^t \times n_{C_i}}{X_{gly}^0 \times 3} \times 100$. Or, $Y_i^t(\%) = Conv(\%) \times \frac{Sel_i^t(\%)}{100}$ where X_i^t and X_{gly}^t : mol of product *i* and mol of reacted glycerol at reaction time *t*, respectively, X_{gly}^0 initial amount of glycerol, and n_{C_i} standing for the number of carbon atoms of product *i*.

To evaluate the leaching of metallic species in solution, the reaction medium was filtered and the iridium amount was determined by ICP/AES analysis. It was shown that there was no leaching of iridium at the end of the reaction whatever the support.

3. Results and discussion

3.1. Characterization of iridium catalysts

XRD of 0.6% Ir/C and 5% Ir/CaCO₃ catalysts did not show any diffraction peak characteristic of the iridium phase, indicating that the

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