



Catalytic behaviour of four different supported noble metals in the crude glycerol oxidation



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ABSTRACT

The activity of four different noble metals (Ag, Au, Pd and Pt) in the liquid phase oxidation of pure glycerol was confronted with the results obtained with a crude glycerol fraction, received from a large-scale biodiesel production plant. The catalysts were characterized by numerous techniques, giving insight into actual metal loading (elemental analysis by ICP and XRF), surface morphology (nitrogen absorption methods—BET and porosity), chemical state of both the support and the metal (XRD and XPS), and, finally, the metal particle size distribution (TEM microscopy). A good dispersion of totally reduced noble metal particles of a nanometric size (an average metal diameters were equal 3.5 nm, 4.2 nm, 4.7 nm and 21.2 nm for respectively Pd, Pt, Au and Ag) was accompanied with a comparable values of total metal loadings on the alumina support (from 0.95 and 0.96 wt.% for Pt and Pd, up to 0.98 and 1.13 wt.% for Au and Ag supported catalysts, respectively). In terms of initial reaction rate, the most active sample was the Au/Al₂O₃ catalyst, both using pure (12976 mol h⁻¹ mol_{Au}⁻¹) or crude glycerol (1230 mol h⁻¹ mol_{Au}⁻¹). However, comparison of the selectivities and conversions after 1–2 h shows that the most robust and resistant catalyst – toward the impurities present in crude glycerol – is Pd/Al₂O₃, with a loss of conversion less than 50% (in respect to analogous reaction using pure glycerol) and almost unchanged high selectivity to glyceric acid (close to 80–90%). Ag/Al₂O₃ also showed a relatively high resistance to impurities in terms of glycerol conversion, but with a drastic modification of its selectivity. The activity of the two other catalysts was dramatically affected with a conversion divided by ca. 4 and even 10 for the Pt and the Au catalysts, respectively, when using crude glycerol instead of pure glycerol. Finally, the effect of each main impurity (MONG-NM, *i.e.*, matter organic non-glycerol and non-methanol; ash; methanol; sulphur compounds) was independently studied. In any case, the sulphur compounds and MONG-NM were the impurities the most detrimental for the performances of catalysts. Thus, they should be removed in priority from crude glycerol fractions before reaction, while ashes and methanol should not be considered as completely undesirable.

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1. Introduction

Nowadays, glycerol is considered as an important bio-derived platform molecule and a feedstock for biorefineries [1–5]. Its

upgrading by chemical or biochemical transformations has thus attracted much attention, and especially in the last decade [1–19]. Even if the use of glycerol as a raw material for producing a large variety of chemicals is well documented in the literature [1,4,6], only a very few applications have reached industrialization mainly due to the cost of purified glycerol. To reach viability, many processes would need to be adapted to the use of cheap dirty waste by-produced with biodiesel (the so-called “glycerine” or “crude glycerol”), which currently is the main source of glycerol on the market [1–6,20]. As purification of glycerine is a relatively expensive multistep process [1,4,6,20], the possibility of direct transformation of crude glycerol could be very attractive from an

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industrial point of view. Indeed, in the liquid phase glycerol oxidation reaction, in addition to the obvious direct economic benefit brought when using a cheaper raw material, some other indirect economic as well as environmental advantages can be listed: (i) the unreacted base used in the conventional process of biodiesel production (*i.e.*, basic transesterification) could be directly used in a downstream oxidation process, which is often also conducted under basic conditions; (ii) the global amount of waste mineral salts (from base neutralization) should thus be reduced; (iii) the number of purification steps would also be reduced with only one purification downstream for recovering the final product. Unfortunately, as the most of the scientific papers dealing with catalytic conversion of glycerol to value-added products are based on the use of a purified raw material [1,10–19]. Hence, the effect of the different impurities present in crude glycerol streams is still not well known.

The studies where the crude glycerol fractions were used as a raw material are rare [21], especially in the field of glycerol oxidation in the liquid phase. Recently, we compared different grades of glycerine and investigated in details the effect of each major impurity on the performances of platinum supported on alumina in both basic and neutral reaction media [20]. The organic matter non-glycerol and non-methanol (called MONG-NM), comprising mainly of various fatty acid derivatives, was identified as the most problematic contaminant of crude glycerol fraction, showing the highest detrimental effect on the glycerol conversion. The same conclusion was reported later by Chan-Thaw et al. [22], who worked on oxidation of raw glycerol (from edible rapeseed vegetable oil transesterification) using supported Au-Pd nanoparticles. The highest initial activity at 50 °C using non-treated raw glycerol (1672 mol/mol h) was achieved over a 1% Au₆Pd₄/AC catalyst, which also showed the highest activity in a process using commercial pure glycerol (3205 mol/mol h). Gil et al. [23] attempted the oxidation of partially purified glycerol fractions (minimum purity not less than 95.5%) at 60 °C under 5 bar of O₂ over carbonaceous materials-supported gold catalysts. They reported almost 50% of glycerol conversion after 10 h of test with 95.5% glycerol. The performances were much better when using almost pure, neutralized 97.1% glycerol with 60% of conversion after 4 h. Essentially the same conversion was observed using a high-purity 99.5% commercial anhydrous product, but with a higher selectivity to glyceric acid (65% vs. 45% when using the neutralized fraction). Sullivan and Burnham [24] used model titanium-supported gold catalysts. They proved that such catalytic system is very sensitive to impurities present in a crude (68.5%) glycerol fraction. The authors obtained less than 20% conversion after 24 h at 60 °C under air flow at atmospheric pressure; a remarkably enhanced production of formic acid from crude glycerol fraction in comparison to analogous test with pure glycerol and purified fractions (after partial removal of potassium, phosphorous and fatty acid derivatives) was observed without any tentative explanation [24]. Finally, Kondamudi et al. [25] studied photooxidation over a titanium di-silicide catalyst (TiSi₂) at 65 °C under atmospheric pressure, where almost 64% conversion with 100% selectivity to glyceric acid were achieved after 6 h of reaction, using crude glycerol of an unspecified composition.

In the present paper, we evaluated the impact of glycerol purity on the performances of four different noble metals-based catalysts, namely: Ag/Al₂O₃, Au/Al₂O₃, Pd/Al₂O₃ and Pt/Al₂O₃. Three of them, *i.e.*, gold, palladium and platinum supported catalysts, are commercially available and well known for their high activity in the partial oxidation of pure glycerol in the liquid phase. In numerous studies, various research groups investigated the effect of such parameters as: the reaction temperature, the oxygen pressure, the glycerol concentration, the presence of base, the catalyst synthesis method, *etc.* [1,5,10,12–20]. Nevertheless, the effect of glycerol purity was investigated only over gold and platinum catalysts [20,22,24]. As each of the aforementioned

research groups used different glycerol fractions, further using different reaction conditions, it seems quite difficult to draw reliable comparative conclusions on the role of each impurity on catalytic performances modulation over each type of catalyst. From the best of our knowledge, there are no articles concerning oxidation of crude glycerol in the liquid phase using other monometallic catalytic systems, especially those based on palladium and silver.

Herein, the abovementioned catalysts were tested under identical reaction conditions (0.3 M glycerol concentration in the reaction mixture, 60 °C, 5 bars of oxygen, NaOH/glycerol molar ratio equal 4 and glycerol/catalyst weigh ratio of 11), using both commercial anhydrous glycerol and a crude glycerol fraction received from a biodiesel plant. Then, in order to decouple the effect of each impurity and to avoid misinterpretation due to possible interactions and synergism, each of identified and quantified impurity was separately added to pure glycerol solution and the results were compared in terms of glycerol conversion and selectivity to main products. We believe that the outcomes of this study will give elements to decide which type of catalyst should be used for the oxidation of crude glycerol fractions.

2. Experimental

2.1. Materials

Anhydrous glycerol 99% from Sigma-Aldrich and crude glycerol from Orlen Południe S.A. were used for the catalytic tests. The main composition of the crude glycerol fraction is given elsewhere [20] and consists of 47.4 wt.% of glycerol, 29.1 wt.% of methanol (HPLC), 8.6 wt.% of water (Karl Fischer titration), 1.3 wt.% of ash (gravimetric method) and 13.6 wt.% of matter organic, non-glycerol and non-methanol (MONG-NM, calculated according to IUPAC guidelines [26]). The sulphur concentration in the crude fraction (0.1 wt.%) was further determined by portable XOS Sinide OTG analyzer based on Monochromatic Wavelength Dispersive X-Ray Fluorescence (MWD XRF).

Sodium sulfate ($\geq 99.0\%$, ACS reagent from Sigma-Aldrich), methanol ($\geq 99.9\%$ HPLC grade from Aldrich) and thioglycolic acid ($\geq 98.0\%$, pure from Fluka) were used as received without any further purification. The MONG-NM used for supplementary tests was obtained by physical separation from the crude glycerol fraction (hydrophobic top layer of the fraction).

Silver nitrate ($\geq 99.0\%$, ACS reagent), methanol ($\geq 99.9\%$ CH₃OH), formaldehyde (37 wt.% in H₂O) and sodium hydroxide (purum) were all purchased from Sigma Aldrich, and alumina oxide powder (activated basic Al₂O₃, Merck) was used for preparation of silver-supported catalyst.

Commercial 1 wt.% Au/Al₂O₃ catalyst (AUROLite™ from Sterm Chemicals) and 1 wt.% Pt/Al₂O₃ from Sigma-Aldrich were grounded and sieved to obtain fraction 50–125 μm, while 1 wt.% Pd/Al₂O₃ (powder from Sigma-Aldrich) was used as received. No additional pretreatment procedure was applied to these catalysts before testing.

2.2. Catalyst preparation method

The silver supported alumina oxide catalyst was prepared by chemical reduction in the liquid phase. The alumina support powder (fraction 50–125 μm) was suspended in a methanol solution of silver nitrate and, after having adjusted the pH of the reaction mixture to 8 with sodium hydroxide, a 2 M aqueous solution of formaldehyde was used as a reducing agent. The suspension was mixed and heated under the reflux for 90 min. Then, the solid was separated by filtration, washed with distilled water and dried at 110 °C for 24 h prior testing.

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