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Effect of Catalyst pretreatment on performance of glycerol oxidation over Pd/Al₂O₃ catalyst

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Highlights

- Oxidation of glycerol with molecular oxygen over Pd/Al₂O₃ was carried out in a batch reactor.
- Effect of oxidative/reductive pretreatment on Pd/Al₂O₃ investigated.
- Pre-reduced catalyst has a lower activity compared to pre-oxidized catalyst.

1. Introduction

Biodiesel, produced chemically by transesterification of triglycerides from vegetable oils and/or animal/waste fats on a commercial scale, is catching on due to pressure on fossil resources. The process produces almost 10-14 wt. % crude glycerol as a by-product, which adds to the existing industrial sources like soaps, fatty acids, fatty alcohols, synthetic glycerol, etc. The emergence of bio-diesel industries from year 2002 dominated the glycerol market with more than 65% production share, and is rapidly growing, leading to glycerol oversaturation and biodiesel price instability. Hence, conversion of glycerol to high-value fine chemicals through various chemical routes like etherification, esterification, dehydration, hydrogenolysis, reforming, oxidation, reduction, etc. has been studied by the researchers over three and a half decades [1]. Here, the focus is on catalytic oxidation process. Various supported noble metal catalysts have been used for oxidation of alcohols in general, and glycerol in particular. In this work, Pd supported on alumina is used as an oxidation catalyst. Different pre-treatments of the catalyst, viz., reduction and oxidation, were used in batch reaction and the performance compared with as-obtained catalyst. The study provides insights into the effect of oxidation state on oxidation performance, and helps rationalize some aspects of metal-support interaction studied earlier in our lab.

2. Materials and Methods

Alumina supported palladium catalyst (Pd/Al₂O₃, 5% metal loading) was obtained from Vineeth Chemicals (Mumbai, India). Two different pretreatments were performed over this as-obtained catalyst: 1.) Reduction using 5% H₂ in Ar, and 2.) Oxidation using 5% O₂ in He. The gases were procured from Med Gas & Equipment, India.

A 100 ml Batch autoclave (Sharad Autoclave, India), equipped with temperature and pressure measurements and agitation speed control, was used for the oxidation reaction. Glycerol was obtained from Merck. 99.9% pure oxygen obtained from Med Gas & Equipment (Mumbai, India) was used for oxidation. 0.6 M aqueous solution of glycerol is prepared in Milli-Q water (Millipore). NaOH (Merck) was added so that NaOH to glycerol mole ratio is 4. Pd/Al₂O₃ was added so that glycerol to active metal mole ratio is 1000. The reaction mixture is initially stirred at 100 RPM under nitrogen atmosphere and heated up to the required temperature. After the required temperature is attained, the nitrogen gas is replaced with oxygen gas and pressurized.

Reaction products were analyzed using HPLC using the method developed elsewhere [2]. The surface area of catalyst was found using BET, and the active metal sites, using CO pulse chemisorption with a TPDRO instrument (Make: Thermo Scientific). SEM and TEM were used to for particle size and morphology studies. XPS was used to analyze the oxidation state of Pd in catalysts with different pretreatments.

3. Results and discussion

While comparing the glycerol (GLY) consumption for the three different catalysts, it was found that the rate of oxidation over the reduced catalyst is the lowest, as observed in Figure 1 (d). Moreover, almost 100% conversion was achieved within 60 min for the oxidized catalyst and catalyst with no pretreatment while reduced catalyst took 180 min to achieve the same. From Figure 1 (a-c), it may be seen that glyceric acid (GA) and Tartronic acid (TA) collectively, are produced at the highest concentration at any given time for all the three catalysts.
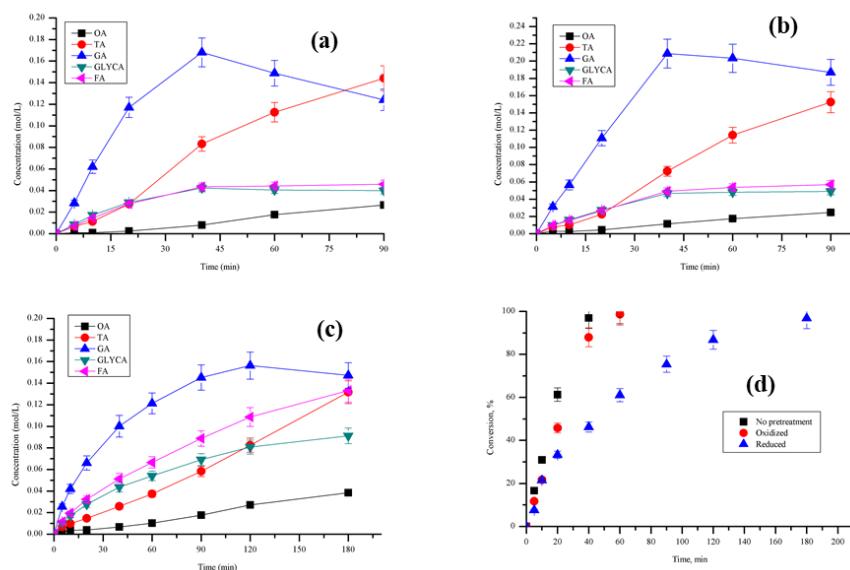

Figure 1. Concentration versus time of different oxidation products for (a) Catalyst without pretreatment, (b) Oxidized catalyst, and (c) Reduced catalyst, and (d) Conversion versus time for all the three type of catalysts.

However, the formation of formic acid was comparable with that of GA and TA in case of reduced catalyst. Moreover, evidence of increase in formation of glycolic acid (GLYCA) and formic acid (FA) in case of reduced catalyst is also observed. These are C-C scission products. Additionally, from the carbon mass balance at complete conversion, the carbon imbalance was found in the following order: Reduced (30%) < Oxidized (37%) < No pretreatment (47%). The imbalance found in all cases indicates the presence of C-C scission reaction in greater extent, probably, leading to CO_2 formation. Moreover, it was observed using CO pulse chemisorption of different pretreated catalysts that reduced catalyst adsorbed CO more than oxidized catalyst, which is need to be understood based on the mechanism of adsorption and bonding between CO and Pd/PdO_x.

4. Conclusions

It is concluded that reduced catalyst shows lower activity in glycerol oxidation compared to the oxidized one. From the metal dispersion values of different catalysts, TOF values were in the order: As-obtained > Oxidized > Reduced.

References

[1]   B. Katryniok, H. Kimura, E. Skrzyńska, J.-S. Girardon, P. Fongarland, M. Capron, et al., Selective catalytic oxidation of glycerol: perspectives for high value chemicals, Green Chem. 13 (2011) 1960. doi:10.1039/c1gc15320j.

[2]   A. Namdeo, S.M. Mahajani, A.K. Suresh, Palladium catalysed oxidation of glycerol—Effect of catalyst support, J. Mol. Catal. A Chem. 421 (2016) 45–56. doi:10.1016/j.molcata.2016.05.008.