

Selective Hydrogenolysis of Glycerol to Propylene glycol over supported Palladium Catalysts: Effect of Support

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Introduction

The growing production of biodiesel by transesterification of vegetable oil, as a renewable source of fuel, leads to a surplus, to great extent, of raw glycerol as reaction by-product [1]. Glycerol is one of the building block chemical that makes it an important biorefineries feedstock [2]. Therefore, the major availability of this compound requires its conversion to new high value-added products, in order to meet a more sustainable economy. The selective conversion of glycerol to propylene glycol is one of the most attractive routes, since it is a clean and economically competitive process that allows the production of commodity chemicals from renewable glycerol instead of from non-renewable petroleum. Propylene glycol can be used as solvent, functional fluid (antifreeze, deicing), precursor in the synthesis of polymers, resins, pharmaceuticals. Supported metal catalysts with and without addition of a modifier, hydrogen pressure of about 2 - 8 MPa and reaction temperatures of 393 – 473 K have been applied for the conversion of glycerol to propylene glycol [3]. However, it seems to be difficult to obtain high conversion of glycerol and/or high selectivity to propylene glycol in milder reaction conditions.

In this work the results obtained by using palladium catalysts supported on different inorganic metal oxides (Fe₂O₃, CoO, CeO₂, NiO, ZnO) for the selective hydrogenolysis of glycerol are reported. The main purpose of this research is the development of a catalytic process with higher efficiency than previous methods.

Materials and Methods

Supported palladium catalysts were prepared by coprecipitation from aqueous solutions of the corresponding inorganic precursors, PdCl₂, dissolved in HCl, and nitrate salts of Fe(III), Co(II), Ni(II), Zn(II) and Ce(III), poured into an aqueous solution of Na₂CO₃ or NaOH (1 M). Then, samples were washed until chloride was removed and dried under vacuum at 353 K for 1 day. After drying, only the Pd/CeO₂ catalyst was calcined at 773 K for 5 h. The nominal Pd loading is 10 wt%.

Hydrogenolysis of glycerol was carried out in a Teflon-lined stainless steel autoclave (250 ml), equipped with a magnetic stirrer and an electric temperature controller, at a stirring speed of 500 rpm. Typical reaction conditions are: 453 K reaction temperature, 0.5 – 4 MPa initial hydrogen pressure, 24 h reaction time, 25 ml of an ethanolic solution of glycerol (1 M), 0.6 g catalyst and 50 ml of ethanol. The products were analyzed by gas chromatography.

Results and Discussion

Data concerning the hydrogenolysis of glycerol over supported palladium catalysts are summarized in table 1. The products of reaction detected are: 1,2-propanediol (propylene glycol, PDO), ethylene glycol (EG) and 1-propanol (PO). Very small amounts of byproducts, deriving from cracking reactions, are also observed. It can be seen from table 1 that the chemical nature of the support deeply affects the activity and selectivity of palladium. In particular, under the experimental condition adopted, Pd/Fe₂O₃ exhibits a remarkable high activity, giving a full conversion of glycerol, and a lower selectivity towards PDO than other catalysts. Higher selectivity to PDO was detected on CoO, CeO₂ and ZnO supported palladium systems. Moreover, it is noteworthy that Pd/CoO shows a high selectivity towards PDO at high conversion of glycerol (95 %). The low selectivity towards EG obtained on all catalysts suggests that C-O cleavage pathway is promoted on Pd systems. Furthermore, runs carried out at lower initial hydrogen pressure (1 and 1.5 MPa) on the more active sample, Pd/Fe₂O₃, lead again to a total conversion of glycerol and show that the selectivity to PDO increases on decreasing H₂ pressure (72 % at 1 MPa). These results, as expected, indicate that H₂ pressure affects the selectivity to PDO. Higher pressure favours PO formation, probably obtained by subsequent hydrogenolysis of 1,3-propanediol. Hydrogenolysis reaction is favoured by acid catalysts [4] and the high activity observed on Pd/Fe₂O₃ is likely due to a major acidity of this system than other samples.

A detailed microstructural characterization of the catalysts is actually in progress in order to clarify the effect of the carrier and to elucidate the different reactivity observed.

Table 1. Catalytic performance of supported 10% palladium samples in the hydrogenolysis of glycerol at 453 K and at 2 MPa of initial H₂ pressure (24 h reaction time)

Catalyst	Conversion (%)	Selectivity (%)		
		PDO	EG	PO
Pd/CoO	94.7	95.2	4.7	0
Pd/CeO ₂	39.3	88.5	5.1	0
Pd/Fe ₂ O ₃	100	53.9	1	44.5
Pd/NiO	23.7	61.6	18.6	0
Pd/ZnO	20.4	100	0	0

PDO = 1,2-propanediol; EG = ethylene glycol; PO = 1-propanol

Significance

CoO supported palladium catalyst has been found to be active for the selective hydrogenolysis to 1,2-propanediol with 94.7 % selectivity at about 95 % conversion, under milder reaction condition (453 K and 2 MPa hydrogen pressure).

References

1. Chiu, C.W., Schumacher, L.G., Suppes, G.J., *Biomass Bioenergy* 27, 485 (2004).
2. Fernando, S., Adhikari, S., Chandrapal, C., Murali, N., *Energy Fuels* 20, 1727 (2006).
3. Feng, J., Fu, H., Wang, J., Li, R., Chen, H., Li, X., *Catal. Commun.* 9, 1458 (2008) and references therein.
4. Miyazawa, T., Kusunoki, Y., Kunimori, K., Tomishige, K., *J. Catal.* 240, 213 (2006).