



Short communication

Efficient and selective conversion of glycidol to 1,2-propanediol over Pd/C catalyst



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ABSTRACT

The present work deals with the catalytic hydrogenolysis of glycidol to 1,2-propanediol. Reactions were carried out in a closed steel reactor using noble metal based heterogeneous catalysts (Pd, Rh, Pt) under hydrogen pressure (1–8 bars) in the temperature range of 25–140 °C. Pd/C shows the highest glycidol conversion (96%) under solvent free conditions after 24 h with high selectivity to 1,2-propanediol (93%). The effect of the solvent was also investigated and it was demonstrated that ethanol reduces drastically oligomer production enhancing selectivity up to 99% with a significant reaction time reduction (6 h). The Pd/C catalyst shows high recyclability and could be reused several times (9 cycles) without losses in activity and selectivity.

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1. Introduction

The future of humanity is in the sustainable development which is strictly linked with the reduction of the use of non-renewable resources. This trend is nowadays highlighted by legislative interventions that favor or impose the use of bio-resources (see for example in European Directive 2009/28/EC about renewable energy and Horizon 2020 Program about research investments). In this framework a great industrial development has been obtained in the biodiesel production (22.5 billion liters were produced worldwide in 2012 [1]). The biodiesel is mainly produced by transesterification of triglycerides with methanol. A co-product of biodiesel is glycerol and today around 2 million of ton of glycerol are on the market. The glycerol glut has produced a reduction in glycerol price with a strong consequence on the economic sustainability of biodiesel production. However this situation has put on the market a new cheap raw material and a great number of new uses of glycerol has been proposed [2,3]. The production of propanediols (1,2 propanediol (1,2-PD) and 1,3 propanediol (1,3-PD)) by hydrogenolysis of glycerol has received particular attention [4–9]. The reaction of hydrogenolysis of glycerol is characterized by the necessity of high hydrogen pressure (1–25 MPa), high reaction temperature (400–500 K), and also by problems related with the selectivity (1,2-PD, 1,3-PD, 1 Propanol, 2 Propanol, ethylene glycol, ethanol can be formed in the hydrogenolysis reaction) [10,11]. Pd based catalyst

has been successfully employed in glycerol hydrogenolysis to 1,2-PD both in the presence and in the absence of added hydrogen [12,13].

Generally, 1,2-PD is derived from propylene oxide [14], moreover, alternative synthetic routes have been investigated such as vapor phase catalytic hydrogenation of lactic acid [15]. 1,3-PD is currently produced from ethylene oxide (Shell route) or acrolein (Degussa–DuPont route) by catalytic routes.

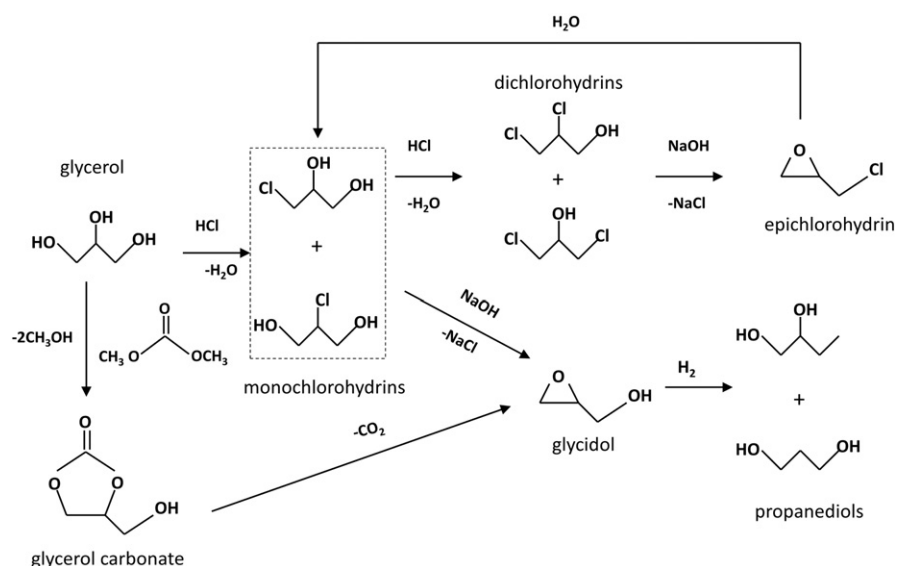
Both 1,2-PD and 1,3-PD are value added products used in many applications therefore the synthesis of these chemicals from glycerol by using less harsh reaction conditions is a highly desirable target. In this scenario the use of alternative path to obtain the desired diols from glycerol seems to be a promising strategy. Indeed the hydrogenation of glycidol can give the desired diols in good yield under moderate reaction conditions. Glycidol can be obtained from glycerol by different ways (see Scheme 1) by decarboxylation of glycerol carbonate [10] or by basic treatment of monochlorohydrins [16].

Monochlorohydrins can be obtained by selective hydrochlorination of glycerol [17] or by hydrolysis of epichlorohydrin [18]. Despite glycerol carbonate is an interesting product for the industrial chemistry its practical application is still under development [19], on the contrary the production of epichlorohydrin from glycerol is now an important industrial reality [2].

The production of glycidol could be integrated in the epichlorohydrin plant also to solve the low reactivity of 2-chloro-1,3-propanediol in the formation of dichlorohydrins [16]. As a matter of fact the rate of conversion of this product to dichlorohydrins is very low and to avoid its accumulation a purge of the recirculation stream is necessary in the epichlorohydrin industrial plant. The purge stream is rich of monochlorohydrins that can be recovered by hydrolysis to glycerol or

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Scheme 1. Reaction pathway for glycerol conversion to epichlorohydrin.

in the new proposed process that can be converted to glycidol. It can be estimated that in an epichlorohydrin industrial plant (from the kinetics of the hydrochlorination reactions [16]) around 5% of glycidol in respect to production of epichlorohydrin can be produced by this way. This means, for example, that an industrial plant of 100,000 tons/y of epichlorohydrin can produce 5000 tons/y of glycidol, and consequently the same quantity of propanediols.

There aren't many data about glycidol hydrogenation, however in a patent application [20], it has been shown that the hydrogenation of glycidol can give place to high yield of 1,3 propanediol (50–65%) using mild reaction conditions 0.8–1.6 MPa, 373 K, metal based catalysts (Ni, Co, Ru) and solvents. Furthermore, a single reaction is reported by Sajiki et al. [21] where an efficient selective conversion (89% yield) of glycidol to 1,2-propanediol (selectivity 100%) is obtained using Pd/C-ethylenediamine complex in methanol for 22 h at a hydrogen pressure of 1 bar using a glycidol/catalyst weight ratio of 10 (calculated TOF = 2.9 h^{-1}).

Noble metals based heterogeneous catalysts (Pd, Rh, Pt) are commonly preferred in hydrogenation reactions and in the reductive ring-opening of epoxides to the corresponding alcohols [22,23].

In this paper a systematic catalytic screening has been done to individuate the best catalyst for glycidol hydrogenation under solvent free conditions. Moreover the effect of reaction conditions (temperature, time, hydrogen pressure) and of the solvent (chloroform,

toluene, tetrahydrofuran, ethanol, methanol, hexane, diethyl ether, dichloromethane) has been investigated.

2. Material and methods

2.1. Materials

The catalysts used in this work were purchased from Sigma-Aldrich (5% Rh/C, 10% Pt/C, 10% Pd/C, 0.5% Rh/Al₂O₃, 0.5% Pt/Al₂O₃, 0.5% Pd/Al₂O₃). Glycidol 96%, 1,2-propanediol 99.5%, 1,3-propanediol 98%, Al₂O₃ and activated charcoal were purchased from Sigma-Aldrich. All the solvents were distilled before reactions and the catalysts were not pretreated before reaction.

2.2. Catalytic reactions

Solvent free hydrogenation of glycidol was carried out in a pressure reactor (maximum operation pressure 8 bars) of 150 mL capacity equipped with a pressure gauge, safety valve, valves for gas inlet and outlet and a thermometer for temperature sensing. Glycidol (96% of purity, Sigma-Aldrich) was distilled before the experiments. Reactor was equipped with glass vials containing 5 mL of glycidol, an appropriate catalyst amount in order to obtain a glycidol/catalyst mass ratio of 100 and a magnetic stirrer. Experiments were carried out

Table 1
Glycidol hydrogenation under solvent free conditions^a.

Experiment	Catalyst/support	Conversion (%)	TOF ^d (h ⁻¹)	1,2-propanediol (%)	1,3-propanediol (%)	Oligomers (%)
1	No catalyst	13.8	–	<1	<1	>99
2	Rh/Al ₂ O ₃ ^b	65.1	4.1	74.5	<1	25.3
3	Pd/Al ₂ O ₃ ^b	59.0	3.9	79.6	<1	19.8
4	Pt/Al ₂ O ₃ ^b	37.8	4.5	56.9	<1	42.8
5	Rh/C ^c	95.2	6.3	21	1.8	77.2
6	Pd/C ^c	96.1	6.6	93.1	<1	6.7
7	Pt/C ^c	96.7	8.1	68.9	2.7	28.4
8	C ^c	89.6	–	<1	<1	99.0
9	Al ₂ O ₃ ^c	95.4	–	<1	<1	99.2

^a Reaction conditions.

^b 1.0 g of catalyst, 0.5 mL of glycidol, 8 bars H₂, 80 °C, 24 h.

^c 0.5 g of catalyst, 5 mL of glycidol, 8 bars H₂, 80 °C, 24 h.

^d TOF was calculated considering all the metal sites on the surface active in catalysis, in such a way the reported TOF is the lowest possible.

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