

Selective transfer hydrogenolysis of glycerol promoted by palladium catalysts in absence of hydrogen

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Selective conversion of glycerol into 1,2-propanediol in the presence of a Pd/Fe₂O₃ catalyst, under inert atmosphere, is reported for the first time; the hydrogen necessary for the hydrogenolysis reaction derives from the dehydrogenation of the solvent (2-propanol or ethanol), promoted by supported palladium, itself reduced “*in situ*” by alcohols.

Catalytic processes converting biorenewable feedstocks to commodities and fuels are actually of large interest for industrial chemical research.¹ Glycerol is widely available from fatty esters and easily obtained, as a byproduct, in biodiesel production.² Selective conversion of glycerol is a clean and economically competitive process and represents one of the most attractive routes, allowing formation of different valuable products, such as 1,2-propanediol (1,2-PDO), 1,3-propanediol (1,3-PDO) or ethylene glycol (EG).^{3,4} So far, conventional hydrogenation catalysts such as nickel, ruthenium and platinum have been used; however, it seems difficult to obtain high conversion of glycerol and/or high selectivity to propylene glycol in mild conditions.^{3,5}

On the other hand: (i) transfer hydrogenolysis, from aliphatic to aromatic alcohols, promoted by nickel raney, is a known reaction⁶ and (ii) oxidated palladium substrates are easily reducible substances.

With the aim to take advantage of the peculiar palladium properties we report, in this communication, on the transfer hydrogenolysis of glycerol in presence of 2-propanol or ethanol at 180 °C, in an inert atmosphere, using the Pd/Fe₂O₃ catalyst. The sample was tested both “as prepared” and reduced with hydrogen at 200 °C.

The *in situ* hydrogen production, obtained by the dehydrogenation of the reaction solvent, ensures several advantages such as:

- costs reduction related to the purchase, transport and storage of the hydrogen;
- use of only one solvent for the entire biodiesel process and for the related chemical valorization of glycerol: ethanol, for example, constitutes a typical solvent for glycerol and is actually used in some innovative biodiesel production cycles.^{7–9}

The nominal 10% palladium catalyst, formulated as PdO/Fe₂O₃, was obtained by the co-precipitation technique from PdCl₄^{2–} and Fe(NO₃)₃, both dissolved in an acid solution,

then precipitated by adding Na₂CO₃ and dried at 80 °C for 1 day. The XRD analysis reveals the amorphous structure of the catalyst.

The experiments were carried out in an autoclave at 5 bar of inert atmosphere using PdO/Fe₂O₃ (600 mg) poured into 50 ml of ethanol or 2-propanol and 25 ml of an alcoholic solution of glycerol (12 wt%). After 24 h, 12 h and 8 h of reaction time at 180 °C (entries 1, 1', 2 and 3, respectively) and at 150 °C (entry 4), the reported results clearly indicate a very high conversion to 1,2-PDO, coupled with a small amount of EG. The other detected products, as expected, mainly were acetaldehyde (derived from ethanol) or acetone (derived from 2-propanol). Relevant data of the investigated hydrogenolysis reaction, determined by GC and GC-MS analysis, are reported in Table 1.

Carrying out the reaction in 2-propanol, using the same supported catalyst, previously reduced for 2 h at 200 °C with H₂, after 8 h and 4 h (entries 5 and 6, respectively) at 5 bar of inert atmosphere, the results confirm the high yield, in a short time, to 1,2-PDO.

In order to confirm the reduction reaction involving the solvent, analogous studies were carried out adding 600 mg of the catalyst to 50 ml of pure ethanol or 2-propanol at 180 °C for 24 h, in an inert atmosphere: acetaldehyde or acetone, besides very small amounts of other products, were formed.

The most interesting peculiarity of the reported results rests on the evidence that:

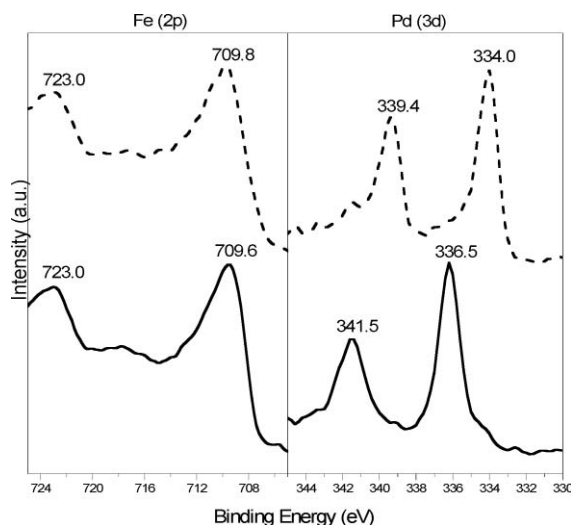
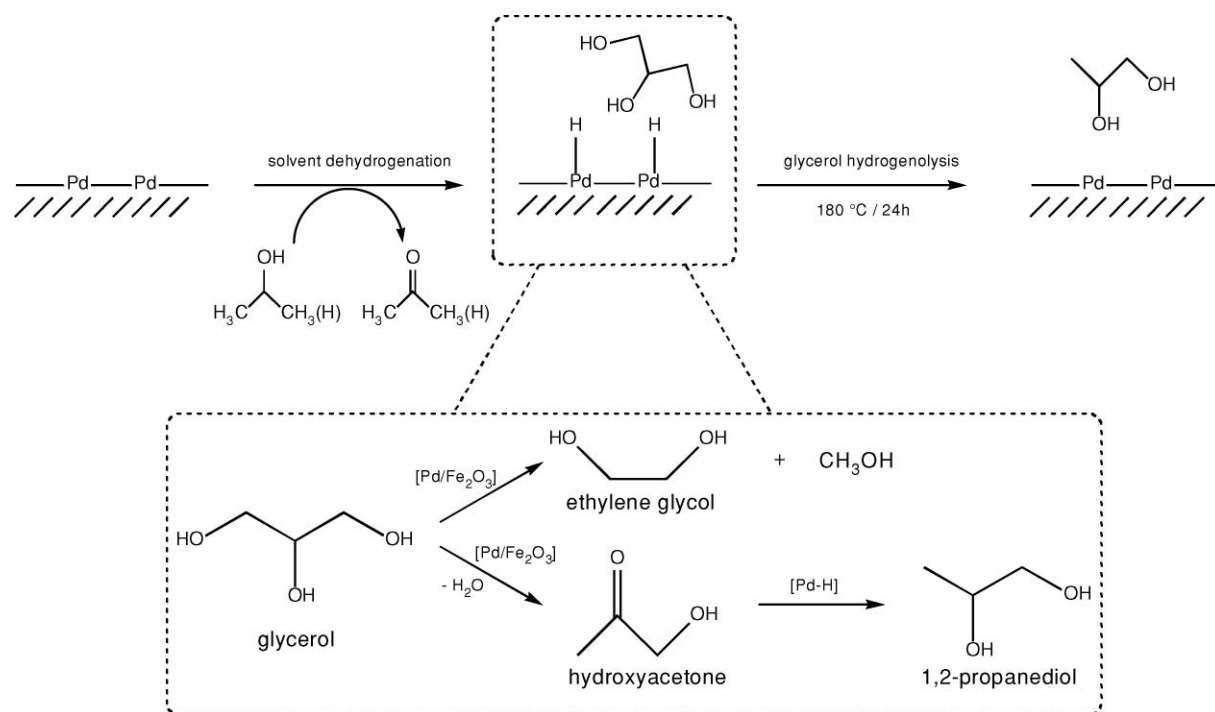


Fig. 1 X-Ray photoemission spectra (Ar ion source) of Pd/Fe₂O₃ catalysts before (full line) and after (dash line) hydrogenolysis reaction.

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Scheme 1 Proposed transfer hydrogenolysis reaction pathway for the conversion of glycerol to 1,2-propanediol and ethylene glycol with Pd/Fe₂O₃ catalyst.

Table 1 Selective glycerol conversion on Pd/Fe₂O₃ catalyst in 2-propanol as solvent and at 5 bar of inert atmosphere

Entry	Time/h	Temperature/°C	Conversion (%)	Selectivity (%) ^a			
				1,2-PDO	Acetol	1-PO	EG
1	24	180	100	94	0	0	6
1' ^b	24	180	100	90	0	6	4
2	12	180	96	84	4	6	6
3	8	180	96	87	2	3	8
4	24	150	84	91	0	0	9
5 ^c	8	180	100	84	3	4	9
6 ^c	4	180	87	73	9	3	15
7 ^d	8	180	100 ^d	100	—	—	—

^a 1,2-PDO = 1,2-propanediol, 1-PO = 1-propanol, EG = ethylene glycol. ^b Reaction carried out in ethanol. ^c Reaction carried out with Pd/Fe₂O₃ pre-reduced in H₂ for 2 h at 200 °C. ^d 1-Hydroxyacetone hydrogenation carried out in 2-propanol with Pd/Fe₂O₃ pre-reduced in H₂ for 2 h at 200 °C.

– on decreasing the reaction time or the temperature it is possible to notice formation of a small amount of 1-hydroxyacetone (acetol);

– reaction of 1-hydroxyacetone, in 2-propanol, at 180 °C and 5 bar of inert atmosphere in the presence of PdO/Fe₂O₃, previously reduced at 200 °C with H₂, leads to a full conversion to 1,2-PDO after 8 h of reaction time (entry 7 in Table 1);

– acetone is the only other product formed by oxidation of the secondary alcohol.

Fig. 1 reports XPS plots, in the Pd(3d) and Fe(2p) binding energy region, of two different specimens: (a) a fresh sample containing PdO/Fe₂O₃ “as prepared”; (b) the same catalyst after hydrogenolysis reaction (180 °C for 24 h under inert atmosphere).

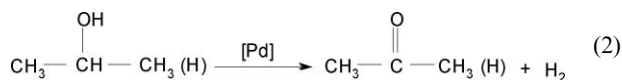
The Pd 3d_{5/2} peak changes from 336.5 eV, observed in the “as prepared” sample, to 334.0 eV of the one filtered from the vessel at the end of the 24 h reaction time performed in an inert

atmosphere. The last value attains to metal palladium particles formed on the catalytic surface, whereas the first belongs to PdO.^{10–11} Furthermore, peaks at 709.6 eV (Fe 2p_{3/2}), 723.0 eV (Fe 2p_{1/2}) and a satellite at 718.8 eV confirm the haematite structure for the iron oxide support.¹²

All the reported experimental results suggest some important conclusions. In particular, under inert atmosphere (entries 1, 1', 2, 3 and 4, Table 1), the following reduction reaction occurs (1):



Accordingly, no proton concentration variation is observed. Besides, data in Table 1 (entries 5, 6 and 7) indicate that a further amount of acetone forms, together with the equimolar amount of H₂ necessary for the hydrogenolysis reaction, through the dehydrogenation process (2):



Conversely, carrying out the glycerol hydrogenolysis in presence of the unsupported PdO, for 24 h and 5 bar of inert atmosphere at 180 °C, only a 32% conversion was detected. In other words, the support plays an important role, allowing the reaction to easily occur.

On the basis of these findings, the mechanism proposed in Scheme 1 should operate; however a minor incidence of a direct hydrogenolysis of glycerol, as inferred from the experiment carried out with unsupported PdO, cannot be excluded.

Recently, a new catalytic cycle allowing glycerol conversion into 1,2-propanediol, in absence of added hydrogen, was experienced.¹³ Furthermore, an interesting reforming cycle involving oxygenated hydrocarbons (glucose, sorbitol, glycerol, ethylene glycol and methanol) was also reported.¹⁴ However, the reducing environment for hydrogenation is generated *via* a liquid glycerol (or other alcohols) steam reforming process in a reaction pathway different than the one proposed in this paper.

In conclusion, the novelty of our work rests on the result, evidenced for the first time, that it is possible to achieve a transfer of hydrogen from an alcohol (ethanol or isopropanol) to another one (glycerol), promoted by a supported palladium catalyst. Therefore, the ensuing hydrogenation reaction occurs in the absence of hydrogen. Furthermore, palladium cations, thoroughly supported, can be reduced “*in situ*” into a given vessel, at a sufficiently high temperature (180 °C) by alcohols, avoiding the pre-reduction of the catalyst with H₂ at 200 °C. In

other words, occurrence of the process, in total absence of added hydrogen, stems from the simultaneous presence of three factors: (i) the easy reducibility of palladium cations; (ii) the high dehydrogenation efficiency of palladium metal and (iii) the use of an appropriate support.

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