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Hydrogenolysis vs. aqueous phase reforming (APR) of glycerol promoted by a heterogeneous Pd/Fe catalyst†

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The hydrogenolysis and the aqueous phase reforming of glycerol have been investigated under mild reaction conditions, using water as the reaction medium and Pd/Fe as the catalyst. The experiments, in the presence of added H₂ or under inert atmosphere, clearly show that the dehydration/hydrogenation route is the key step in the case of C–O bond cleavage (hydrogenolysis) while dehydrogenation is a prerequisite for C–C bond breaking (APR), with the latter favoured at higher reaction temperatures. The temperature dependence of the C–C and C–O bond rupture is discussed by taking into account the bond energies involved in the competitive hydrogenolysis and APR reactions. Finally, the Pd/Fe catalyst was also tested in the hydrogenolysis and APR of ethylene glycol in the same temperature range, with the aim of clarifying the selective cleavage of C–O and C–C bonds in biomass derived C₂–C₃ polyols.

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Introduction

Growing attention has been gained on the use of renewable biomass for bulk chemical production.^{1,2}

Glycerol, the main byproduct from the production of biodiesel, is one of the top 12 building block chemicals largely used as bio-feedstocks for the production of chemical products.^{3,4} Due to the worldwide expansion of biofuels, at present the production of glycerol has reached over 2 million tonnes that consistently enter the market every year.⁵ This unique situation has made glycerol attractive as a renewable starting material for the synthesis of valuable chemicals.

The conversion of biomass into chemicals and fuels commonly implies oxygen removal. In this context, the selective hydrogenolysis of glycerol has gained more and more attention, leading to the formation of propylene diols, ethylene glycol and propanols.^{6,7} Considerable research effort has been directed towards the conversion of glycerol into 1,2-propanediol (1,2-PDO), which is a high demand chemical, largely used in the production of unsaturated polyester resins, functional fluids, food products, cosmetics and pharmaceuticals.⁸ Currently, the industrial production of 1,2-propanediol mainly occurs through the route of propylene

oxide hydration. Therefore, glycerol hydrogenolysis to 1,2-propanediol represents a sustainable alternative process that would assist both the environmental benefits and economic viability of biodiesel manufacture.

At the same time, the production of hydrogen through the aqueous-phase reforming (APR) of biomass-derived polyols is considered as a promising catalytic process.^{9–14} Glycerol is an interesting starting substrate for “bio”-hydrogen production since the related process becomes spontaneous at much lower temperature than that generally used today for H₂ manufacture from CH₄. An ideal catalyst for H₂ production from glycerol needs to be very active both for C–C bond breaking as well as in promoting the water gas shift (WGS) reaction thus reducing the CO content.

Furthermore, H₂ – generated *in situ* by the aqueous phase reforming of glycerol – has been successfully used for the conversion of glycerol to 1,2-PDO, representing an interesting alternative to the direct use of molecular hydrogen.^{15–18}

Hydrogenolysis and APR reactions involve the breaking of C–C, C–H, C–O and O–H bonds, therefore glycerol can also be considered as a model compound for fundamental studies involving the selective cleavage of chemical bonds of biomass derived substrates.

Heterogeneous palladium catalysts were found to be poorly efficient for the hydrogenolysis of biomass derived polyols.^{6,7} However, in past years, the coprecipitated Pd/Fe catalyst has been deeply investigated^{19–26} for its superior performance in several catalytic reactions including the hydrogenolysis^{20,21} and the transfer hydrogenolysis (CTH) of glycerol using 2-propanol as the reaction solvent,^{22,23} as well as

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in the deoxygenation and aqueous-phase reforming of ethylene glycol (EG).^{24,25} The enhanced catalytic performance shown by the Pd/Fe catalyst can be related to the preparation method used (coprecipitation technique) that ensures a strong interaction between palladium and the iron oxide support, leading to the formation of bimetallic Pd–Fe ensembles, which positively promote C–O and C–C bond cleavage.^{19–26}

In the present work, we extend the studies to the hydrogenolysis and APR of glycerol promoted by the Pd/Fe catalyst using water as the reaction solvent with two different strategic approaches: by using molecular hydrogen as the readily available H-source and by using the APR condition producing *in situ* H₂.

By using molecular H₂ as the direct hydrogen source, at 180 °C, 1,2-PDO and EG are the main reaction products from glycerol hydrogenolysis, the Pd/Fe catalyst being more active in C–O bond cleavage. Upon increasing the reaction temperature, a major tendency of the Pd/Fe catalyst to promote dehydrogenation/decarbonylation reactions is found. Under inert atmosphere, at 180 °C, the H₂ produced by APR is partly consumed in the *in situ* hydrogenolysis process leading to 1,2-PDO. At higher reaction temperatures, glycerol is fully converted with major production of gas phase products and high H₂ selectivity.

Therefore, the dependence of the selectivity in glycerol C–C or C–O bond breaking on the reaction temperature is observed.

Finally, the conversion of ethylene glycol under the same reaction conditions has been also investigated to clarify the competitive occurrence of the dehydrogenation and dehydration processes in C₂–C₃ biomass derived polyols.

2 Experimental

2.1 Catalyst preparation

All chemicals were purchased from Sigma-Aldrich and used without further purification. The Pd/Fe catalyst with a nominal palladium loading of 5 wt% was obtained by using the coprecipitation technique. Anhydrous palladium chloride was dissolved in HCl and iron(III) nitrate nonahydrate was added. The obtained aqueous metal salt solution was added dropwise into a 1 M aqueous solution of Na₂CO₃. After filtration, the sample was washed until complete removal of chloride ions and dried for 1 day at 80 °C under vacuum. Before the reaction, the Pd/Fe catalyst was reduced at 200 °C for 2 h under a hydrogen flow.

2.2 Catalyst characterization

XRD data were acquired at room temperature on a Philips X-Pert diffractometer by using the Ni β-filtered CuKα radiation ($\lambda = 0.15418$ nm). Analyses were registered in the 2 θ range of 10–80° at a scan speed of 0.5° min^{–1}. Diffraction peaks were compared with those of standard compounds reported in the JPCDS data file.

The particle size and the relative morphology were analysed by performing transmission electron microscopy

(TEM) measurements using a JEM-2100F (JEOL, Japan) microscope operating at an acceleration voltage of 200 kV and directly interfaced with a computer controlled-CCD for real-time image processing. The specimens were prepared by grinding the reduced catalyst powder in an agate mortar and then suspending it in 2-propanol. A drop of the suspension, previously dispersed in an ultrasonic bath for 1 hour, was deposited on a copper grid coated by a holey carbon film. After evaporation of the solvent, the specimens were introduced into the microscope column. The particle size distribution was obtained by counting a hundred particles visible on the micrographs. From the size distribution, the average diameter was calculated by using the expression: $\overline{d_n} = \sum n_i d_i / \sum n_i$ where n_i is the number of particles of diameter d_i .

The H₂-TPR measurement was performed using a conventional TPR apparatus. The dried sample (50 mg) was heated at a linear rate of 10 °C min^{–1} from 0 to 1000 °C in a 5 vol% H₂/Ar mixture at a flow rate of 20 cm³ min^{–1}. The H₂ consumption was monitored with a thermal conductivity detector (TCD). A molecular sieve cold trap (maintained at –80 °C) and a tube filled with KOH, placed before the TCD, were used to block water and CO₂, respectively. Signal calibration was done by injecting a known amount of H₂ into the carrier.

XPS measurements were performed on a JPS-9010MC photoelectron spectrometer using an Al Kα (1486.6 eV) radiation source. After the reduction treatment, the sample was introduced into the XPS chamber, avoiding exposure to air. In order to obtain the XPS spectra, the pressure in the analysis chamber was maintained at 5 × 10^{–9} mbar. The binding energies (BE) were set taking the C 1s peak at 284.6 eV as the reference. Peak deconvolution and fitting analyses were performed using the peak-fitting software “SPEC SURF, JEOL” including the spin–orbit splitting and relative intensities of the spin–orbit components fixed.

2.3 Catalytic tests

The reactions were carried out in a stainless steel autoclave reactor (100 mL). In each reaction, 40 ml of an aqueous glycerol solution (4 wt% glycerol solution) and 0.25 g of the Pd/Fe catalyst (previously reduced at 200 °C for 2 h under a flow of hydrogen) were loaded in the autoclave. The reactor was purged with He (99.99%), the system was then pressurized with the desired gas (H₂ or He) and, finally, heated up to the reaction temperature at a linear rate of 2.5 °C min^{–1} until the constant value was reached.

The reactant and products in the liquid phase were analyzed using an off-line HPLC (LC Agilent 1290 Infinity) equipped with a ZORBAX Carbohydrate Analysis Column.

After the reaction, the gas phase products were collected in a gas sample cylinder and analyzed with a GC-TCD-FID (Agilent Technologies, 7890 A) equipped with a molecular sieve column (HP-MOLESIEVE, diameter = 0.535 mm, length = 30 m) and a capillary column (HP-PLOT/Q, diameter = 0.320 mm, length = 30 m).

The conversion, product selectivity in the liquid and gas phases and 1,2-PDO yield were calculated on the basis of the following equations:

$$\text{Conversion [\%]} = \frac{\text{Moles of reacted substrate}}{\text{Moles of substrate feed}} \times 100 \quad (1)$$

$$\begin{aligned} \text{Liquid phase selectivity [\%]} \\ = \frac{\text{Moles of specific product in liquid phase}}{\text{Sum of moles of all products in liquid phase}} \times 100 \end{aligned} \quad (2)$$

$$\begin{aligned} \text{Gas phase selectivity [\%]} \\ = \frac{\text{Moles of specific product in gas phase}}{\text{Sum of moles of all products in gas phase}} \times 100 \end{aligned} \quad (3)$$

$$\text{1,2-PDO yield [\%]} = \frac{\text{Moles of 1,2-PDO in liquid phase}}{\text{Moles of glycerol feed}} \times 100 \quad (4)$$

3 Results and discussion

3.1 Catalyst preparation and characterization

The Pd/Fe catalyst was prepared by co-precipitation of palladium chloride (dissolved in HCl) and iron(III) nitrate nonahydrate poured together dropwise into a 1 M aqueous solution of Na₂CO₃ followed by calcination and reduction with H₂ at 200 °C.

The main characteristics of the Pd/Fe catalyst are reported in Table S1.1.†

The high-resolution transmission electron microscopy reveals a particle size distribution with a majority of particles of 1.2 nm diameter (Fig. 1 and S1.2.†).

Accordingly, Pd nanoparticles are well dispersed on the catalyst surface as revealed also by the absence of the (111) diffraction line of metallic palladium in the XRD spectrum (Fig. S1.3.†).

The H₂-TPR measurement (Fig. S1.4.†) shows only one intense peak at about 80 °C including, on the basis of H₂ consumption calculations, both the Pd(II) → Pd(0) and Fe(III)

→ Fe₃O₄ reductions suggesting that Pd nanoparticles are effective in promoting the reduction of the support from hematite to magnetite. Furthermore, the conclusion that the palladium particles promote the reduction of Fe³⁺ to Fe₃O₄ is also confirmed by the XRD analysis on the Pd/Fe catalyst reduced at 100 °C (Fig. S1.3.†) which shows signals only related to the magnetite structure.

The presence of partially positively charged metal species is observed by X-ray photoelectron spectroscopy (Table S1.5 and Fig. S1.5.†) (the Pd 3d_{5/2} binding energy is 0.4 eV higher than that of metallic palladium) indicating that, in the reduced Pd/Fe catalyst, intimate interactions of palladium nanoparticles with the support are present.^{23,24}

Furthermore, the analysis of the extended X-ray absorption fine structure, carried out on the same catalyst,²⁴ shows a Pd–Fe distance of 2.59 Å and a shorter, distorted Pd–Pd distance of 2.66 Å, confirming the formation of Pd–Fe bimetallic ensembles.

3.2 Hydrogen promoted reactions

Table 1 shows that 1,2-PDO is the main reaction product in the reaction carried out at 180 °C using glycerol as the starting substrate, clearly indicating that the Pd/Fe catalyst is more active for C–O bond cleavage and less efficient for C–C bond breaking.

The increase in the reaction temperature produces higher glycerol conversion accompanied by a lower selectivity towards 1,2-PDO together with an increased amount of ethanol (EtOH), methanol (MeOH), 1-propanol and 2-propanol (POs). It is worth noting that the amount of EtOH reaches a maximum of 70.5% in the liquid phase products at 240 °C.

In the reference experiments, 1,2-PDO was also tested in the presence of H₂ (Table S2.1.†): the reactions provide EtOH as the main product in high yield at all temperatures investigated. These results, coupled with the catalytic tests on EG (see below) suggest that EtOH, found at higher reaction temperatures, arises mainly from the dehydrogenation/decarbonylation of 1,2-PDO.

Having identified 180 °C as the best reaction temperature for the production of 1,2-PDO, we investigated the hydrogenolysis of glycerol at different reaction times (Fig. 2 and Table S2.2.†). As expected, the glycerol conversion and 1,2-PDO yield increase when passing from 6 to 24 hours (Fig. 2).

Upon increasing the initial hydrogen pressure from 5 to 20 bar (180 °C), a decrease in glycerol conversion as well as a lower 1,2-PDO yield is noticed (Fig. 2 and Table S2.3.†). Such a conversion decrease by increasing the hydrogen pressure, in other hydrogenolysis reactions over heterogeneous palladium systems, was ascribed to the competitive adsorption of the substrate and H₂ on the catalyst surface.²⁷

Further recycling of the Pd/Fe catalyst at 180 °C in the presence of H₂, performed after washing the sample (remaining in the reactor) with pure water, gave, as expected, a lower conversion (Fig. S2.4.†). However, the selectivity did

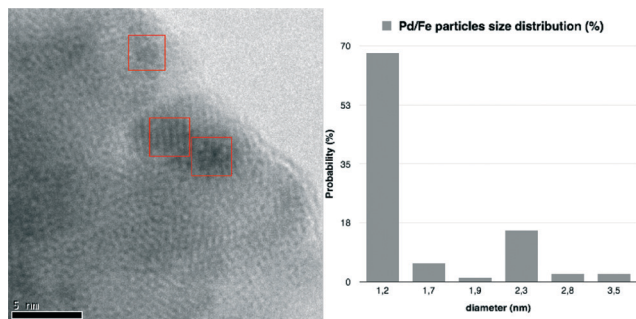


Fig. 1 High resolution transmission electron micrograph of the Pd/Fe catalyst (left) and particle size distribution of the palladium nanoparticles (right).

Table 1 Conversion of glycerol and ethylene glycol promoted by the Pd/Fe catalyst in the presence of added hydrogen. Conditions: 0.25 g catalyst; 40 ml entry solution (4 wt%); 5 bar H₂ pressure, 24 h^a

Entry	Temperature (°C)	Conversion (%)	Liquid phase (%)	Product selectivity in liquid phase (%)				
				1,2-PDO	POs	EG	MeOH	EtOH
Glycerol	180	92.4	78.6	77.1	0.2	15	—	7.7
Glycerol	210	100	67.6	57.7	1.7	9.7	3.8	27.2
Glycerol	240	100	57.2	9.3	10.1	0.5	9.6	70.5
EG	180	11.0	91.6	—	—	—	49.9	50.1
EG	210	31.7	72.7	—	—	—	56.5	43.4
EG	240	72.1	51.7	—	—	—	71.8	28.2

^a 1,2-PDO = 1,2-propanediol; POs = 1-propanol + 2-propanol; EG = ethylene glycol; MeOH = methanol; EtOH = ethanol.

not change appreciably, as already reported in the past, upon using 2-propanol as solvent.²⁰

The Pd/Fe catalyst was also tested at higher glycerol concentrations (20 wt% of glycerol solution, 1 g of reduced Pd/Fe catalyst, 20 bar initial pressure of H₂, 24 hours of reaction time): the selectivity towards 1,2-PDO (83,9%), EG (11,2%), EtOH (4,2%) and POs (0,7%) was detected with a glycerol conversion of 83,9%.

The performance of the Pd/Fe catalyst was also tested in the hydrogenolysis of EG in the same temperature range (Table 1). At all temperatures, the reactions proceed more slowly with respect to glycerol. At 180 °C, the Pd/Fe catalyst

equally cleaves the C–C and the C–O bonds of EG, allowing the production of methanol and ethanol in comparable yields. Upon raising the reaction temperature, an enhanced performance of Pd/Fe for C–C bond breaking is noticed.

The presence of added H₂ in the catalytic test conducted by using both glycerol and EG as starting substrates does not allow a truthful quantitative analysis of gas phase products. However, at the temperature range investigated (180–240 °C) a qualitative analysis reveals, together with CO₂, a very low amount of alkanes.

3.3 Reactions under inert atmosphere

The results for the reactions carried out under inert atmosphere (APR conditions) are summarized in Table 2.

In the case of glycerol, at 180 °C, the liquid products include mainly 1,2-PDO, EG, and MeOH. In the gas phase, H₂ is the main product observed (73.4%) together with CO₂ (26.1%) and a negligible amount (0.5%) of light alkanes (methane, ethane and propane). The hydrogen necessary for the hydrogenolysis reaction derives from the aqueous phase reforming of glycerol itself as well as from the WGS process.

Passing from 180 to 210 and 240 °C, glycerol is fully converted with a higher production of gas phase products. At 240 °C a H₂ selectivity of 80.5% in gas phase products is reached.

Significant changes in the liquid phase product composition are also detected. As expected, the amount of 1,2-PDO decreases while a higher selectivity to EtOH and propanols is observed. Similarly, the ethylene glycol selectivity drops from 12.2% at 180 °C to 6.3% at 210 °C and to 0.2% at 240 °C as a result of the further dehydrogenation and hydrogenolysis processes.

It is noteworthy that CO is never detected, which is indicative of a worthy activity of the bimetallic Pd/Fe catalyst in the water gas shift (WGS) reaction.

The pressure profiles of glycerol conversion promoted by the Pd/Fe catalyst under inert atmosphere at 180, 210 and 240 °C are shown in Fig. S2.5.† It has to be noted that the catalytic tests under inert atmosphere reported in this contribution are at variance with standard APR conditions where higher pressures are used in order to maintain water in the

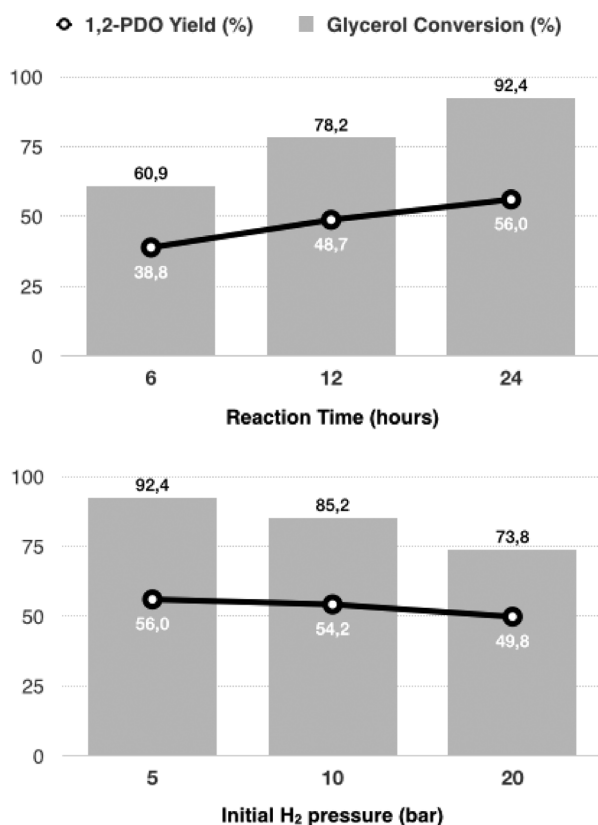


Fig. 2 Reaction time (top) and initial H₂ pressure (bottom) effect on the glycerol conversion (%) and 1,2-PDO yield (%) in the reaction carried out in presence of added H₂ at 180 °C.

Table 2 Conversion of glycerol and ethylene glycol promoted by the Pd/Fe catalyst under inert atmosphere. Conditions: 0.25 g catalyst; 40 ml entry solution (4 wt%); 5 bar He pressure, 24 h^a

Entry	Temperature (°C)	Conversion (%)	Liquid phase (%)	Liquid phase product selectivity (%)					Gas phase selectivity (%)		
				1,2-PDO	POs	EG	MeOH	EtOH	H ₂	CO ₂	Alkanes
Glycerol	180	9.8	76.8	72.8	3.5	12.2	10.5	1.0	73.4	26.1	0.5
Glycerol	210	100	64.7	42.9	5.2	6.3	9.0	36.6	77.8	20.8	1.4
Glycerol	240	100	41.9	9.4	8.7	0.2	8.1	73.0	80.5	17.7	2.4
EG	180	13.3	89.8	—	—	—	60.3	39.7	81.7	18.3	—
EG	210	34.5	73.5	—	—	—	73.3	26.3	81.6	18.4	—
EG	240	66.2	50.9	—	—	—	76.6	23.4	81.2	18.8	—

^a 1,2-PDO = 1,2-propanediol; POs = 1-propanol + 2-propanol; EG = ethylene glycol; MeOH = methanol; EtOH = ethanol.

liquid state. However, in the temperature range investigated, the quantity of water in the vapor state should be very low (below 3% at 240 °C) allowing us to investigate C–C bond breaking under reaction conditions very close to those usually adopted for APR reactions.

A combination of the aqueous phase reforming and *in situ* hydrogenolysis reactions of ethylene glycol is also observed. In line with the reactions carried out in the presence of added H₂, a lower conversion of EG with respect to glycerol is achieved within the temperature range of 180–240 °C. The liquid phase analysis shows MeOH (C–C bond breaking) as the main reaction product and a selectivity to EtOH (C–O bond cleavage) getting lower as the temperature increases. Gas phase products are characterized by a good H₂ production and an insignificant amount of alkanes.

3.4 Hydrogenolysis vs. APR of glycerol: understanding the relationship between C–O and C–C bond breaking

The results of glycerol conversion at 180 °C in the presence of H₂ over the Pd/Fe catalyst are substantially in agreement with those obtained, before, on using 2-propanol as the solvent which indicates hydroxyacetone (AC) as a reaction intermediate for 1,2-PDO formation.^{20,23} The main difference lies in the higher fraction of EG and EtOH detected in water and not observed in isopropanol where a good selectivity for 1-PO was found (Fig. S2.6†). Therefore, it can be stated that in glycerol hydrogenolysis, it is undesirable to use water as a reaction medium in order to drive the equilibrium to propanol formation.

Cross-check experiments, under both reaction conditions used in this study (H₂ or He) and within the temperature range investigated (180–240 °C), show that pure Fe₃O₄ does not give glycerol conversion, suggesting that the presence of palladium is an essential prerequisite for C–O and C–C bond breaking.

Consistent with the catalytic results, the conversion of glycerol on the bimetallic Pd/Fe catalyst can follow two distinctive routes for the 1,2-PDO and EG formation (Scheme 1).

In the reaction pathway leading to 1,2-PDO, the first step is the adsorption of two adjacent alcoholic groups of glycerol on Pd and Fe sites with a subsequent C–OH breaking

promoted by palladium. The unstable enol is then rearranged to AC which is finally hydrogenated into 1,2-PDO.²³

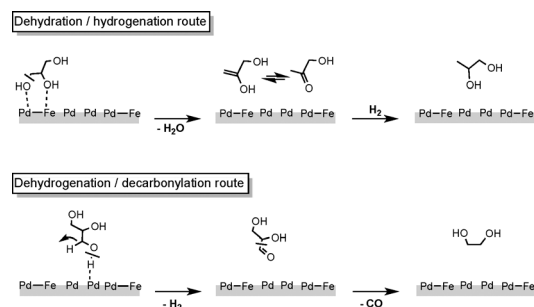
On the other hand, glycerol conversion to EG proceeds *via* a previous dissociation of primary alcoholic groups followed by C–H bond breaking. The ensuing glyceraldehyde undergoes a final C–CO breaking leading to EG and CO formation.

Other possible alternative processes, such as the one affording dihydroxyacetone (derived from the dehydrogenation of the secondary alcoholic group), are discarded since this quite stable compound has never been detected.

Data reported in Table 2 concerning the reactions carried out under inert conditions show that, together with H₂, CO₂ and a small amount of alkanes, liquid phase products are formed. The presence of hydrogenolysis products implies that the *in situ* produced H₂ directly participates in the hydrogenation of the intermediates produced from the dehydration route.

Therefore, it can be stated that hydrogenolysis and APR are competitive processes (hydrogenolysis *vs.* APR) and that the dehydration and dehydrogenation reactions are key elementary steps in the conversion of glycerol both in the presence and absence of added H₂.

At 180 °C, in the presence of H₂ or under inert atmosphere, the Pd/Fe catalyst allows the conversion of glycerol to 1,2-propanediol in a good yield showing an enhanced ability in C–O bond cleavage. Conversely, at higher reaction temperatures, dehydrogenation reactions prevail and the dehydration/hydrogenation steps become less important, even when



Scheme 1 First steps in glycerol conversion in the presence and absence of added H₂: the dehydration/hydrogenation and dehydrogenation/decarbonylation routes.

1,2-PDO is used as the starting substrate (Table S2.1†). To this regard, the higher ability of the coprecipitated Pd on the Fe_3O_4 catalyst (prepared by an analogous synthetic procedure) in the selective C–C bond breaking of biomass derived polyols at a high reaction temperature (250 °C) has also been recently observed by the Tsang research group.²¹ Accordingly, a recent report clearly shows that reaction temperatures lower than 180 °C are more favourable to the production of propanols from 1,2-PDO.²⁸

The temperature dependence of the reaction pathway's selectivity can be related to the different bond energies involved in the alternative processes.²⁹ The dehydration/hydrogenation route implies the initial C–OH cleavage of the primary alcoholic group ($E_{\text{C–OH}} \cong 80 \text{ kcal mol}^{-1}$)²⁹ followed by the rearrangement of the unstable enol to hydroxyacetone which is finally hydrogenated to 1,2-PDO.²³ Conversely, the dehydrogenation/decarbonylation route involves the prior O–H breaking ($E_{\text{O–H}} \cong 104 \text{ kcal mol}^{-1}$)²⁸ followed by the β C–H (with respect to oxygen) elimination and by the consequent C–CO rupture.^{30,31}

Moreover, since a negligible quantity of methanol was detected in the reactions carried out by using 1,2-PDO as the starting substrate (Table S2.1†) it can be confirmed that the rupture of the O–H bond is a fundamental prerequisite for C–C cleavage.

Similar conclusions have been also proposed by Lercher and co-workers who suggested a reaction network consisting of parallel routes that include dehydrogenation and dehydration as the primary steps in the hydrodeoxygenation and APR of C_3 alcohols and polyols.^{32,33}

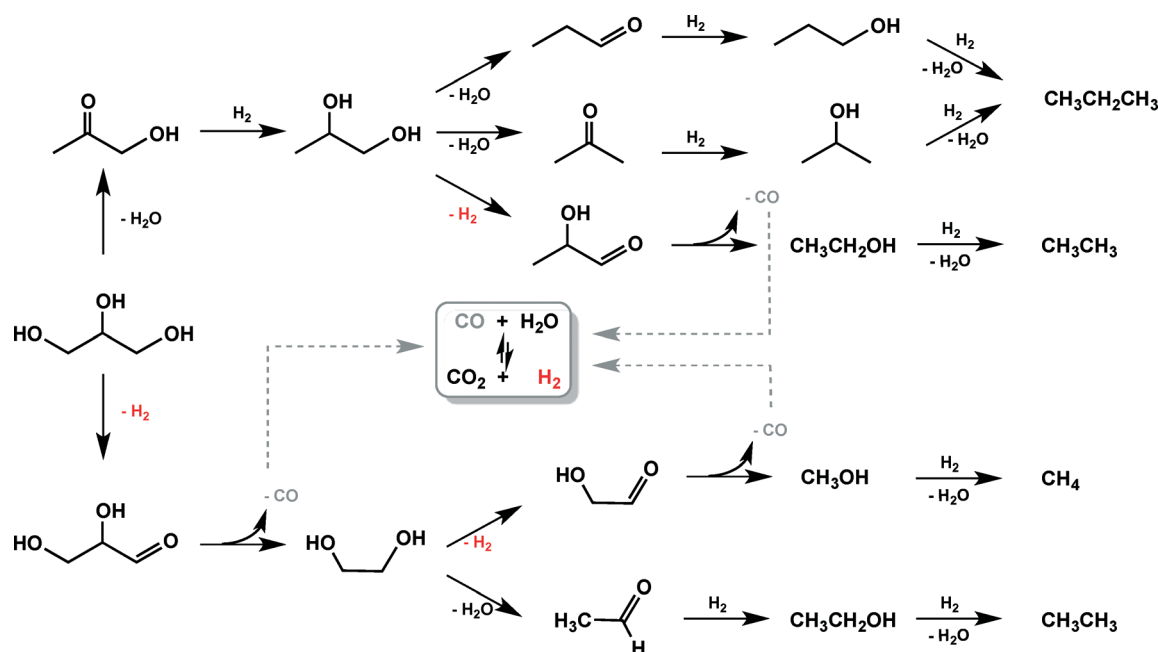
In this regard, it is worth underlining that the C–CO bond energy value is about 83 kcal mol^{-1} , quite proximate to that

of an internal C–C bond ($E_{\text{C–C}} \cong 85 \text{ kcal mol}^{-1}$).²⁹ Therefore, C–CO is cleaved preferentially with respect to the direct breaking of the C–C bond since (i) the terminal C=O group does not undergo steric hindrance and easily interacts with the catalyst metal surface and (ii) its removal is helped by the simultaneous aldehydic C–H ($\cong 95 \text{ kcal mol}^{-1}$) bond breaking promoted by the metal particles. Accordingly, on the basis of theoretical studies, it has been reported that the C–C bond breaking of glycerol on the Pt (111) surface has a very high barrier with respect to that of the terminal C–CO bond cleavage.³⁴

An analogous competition of the dehydration/hydrogenation and dehydrogenation processes (hydrogenolysis *vs.* APR) occurs starting from EG. The catalytic results at 180 and 210 °C in the presence of H_2 show a competition between the CO–H bond cleavage and C–O bond breaking reactions (MeOH and EtOH are almost equally formed) while, at 240 °C, the CO–H bond scission reaction becomes more favourable with a higher production of MeOH confirming the temperature dependence of the dehydration and dehydrogenation routes. Under inert conditions, methanol is the main reaction product obtained in the liquid phase as a result of the prevalence of the dehydrogenation/decarbonylation route.

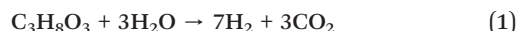
Recent density functional theory (DFT) calculations, complemented with temperature-programmed desorption (TPD) experiments, demonstrate that the decomposition of ethylene glycol on Pt and Pt/Ni surfaces proceeds first through dehydrogenation to reach one of the species with a terminal CO followed by C–C bond cleavage.³⁵

All these results allow the overall pathways for describing the hydrogenolysis *vs.* APR reactions starting from glycerol to be drawn, as represented in Scheme 2.



Scheme 2 Hydrogenolysis *vs.* APR of glycerol: overall reaction pathways.

The gas phase composition of the reactions carried out under inert atmosphere are characterized by a H_2/CO_2 ratio higher than the maximum value theoretically expected for the glycerol APR (1):



The explanation for the “apparent” anomaly is that the catalytic tests are conducted in batch mode with the gas phase products collected in a gas sampler cylinder directly connected to the autoclave reactor. The sampling system adopted allows the collection of gas-phase products at about 2/3 of the pressure measured at 25 °C (Fig. S2.5†). Therefore, under our sampling conditions, it is necessary to take into consideration that CO_2 is much more soluble in water than H_2 ($\text{CO}_{2(\text{sol})}/\text{H}_{2(\text{sol})} \cong 55$). Therefore the H_2/CO_2 ratio measured is expected to be higher than the predicted one on the basis of reaction (1) and even higher as the final pressure (related to the reaction temperature) increases.

In accordance with all these considerations, the measured pH values of the liquid phase are 6.10, 5.90 and 5.75 for the reactions carried out respectively at 180, 210 and 240 °C as expected from the weak acidity of CO_2 in water.

Analogous considerations can be done for the APR reactions of EG.

Another very important peculiarity of the Pd/Fe catalyst is the absence of CO (as a gas phase product) in all experiments. The obvious implication is that the WGS equilibrium is completely shifted towards H_2 and CO_2 formation. Consequently, the Pd/Fe is very efficient in the WGS reaction but poorly effective as a Fisher–Tropsch or metanation catalyst. This is easily understandable considering that both palladium and Fe_3O_4 are known to be efficient catalysts for affording WGS products. Analogous results were also obtained by Dumesic's research group which showed a superior activity of the impregnated Pd/ Fe_3O_4 catalyst with respect to the analogous Pd/ Fe_2O_3 in the APR of EG as a result of the enhanced WGS reaction promoted by the synergistic effect of Pd nanoparticles and magnetite.¹²

Conclusions

The catalytic conversion of biomass-derived glycerol was investigated under both hydrogenolysis and aqueous phase reforming conditions over the bimetallic Pd/Fe catalyst. The starting alternative processes were found to be the dehydration/hydrogenation and the dehydrogenation/decarbonylation with the latter controlled by initial O–H breaking followed by β C–H elimination rather than direct C–C bond cleavage. At 180 °C, the C–O bond is preferentially cleaved allowing the production of 1,2-PDO, while C–C bond breaking becomes favourable at higher reaction temperatures leading to the formation of H_2 in a good yield. In analogy, by using ethylene glycol (C_2 polyol) as the starting substrate, the C–O and C–C bonds are equally cleaved at 180 and 210 °C, whereas a

significant increase in dehydrogenation products was observed at higher temperatures.

Therefore, a change in selectivity in the C–O and C–C bond cleavage of biomass derived C_2 – C_3 polyols, upon using the Pd/Fe catalyst, was observed by varying the reaction temperature.

In all experiments, CO was never detected in the gas-phase products thus revealing an excellent performance of the Pd/Fe catalyst in promoting the water gas shift (WGS) reaction.

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Notes and references

- 1 C. O. Tuck, E. Pérez, I. T. Horváth, R. A. Sheldon and M. Poliakoff, *Science*, 2000, **337**, 695.
- 2 P. Gallezot, *Chem. Soc. Rev.*, 2012, **41**, 1538.
- 3 M. Pagliaro and M. Rossi, *The Future of Glycerol*, 2nd edn, Royal Society of Chemistry, Cambridge, 2010.
- 4 C. H. Zhou, H. Zhao, D. S. Tong, L. M. Wu and W. H. Yu, *Catal. Rev.: Sci. Eng.*, 2013, **55**, 369.
- 5 R. Ciriminna, C. Della Pina, M. Rossi and M. Pagliaro, *Eur. J. Lipid Sci. Technol.*, 2014, **116**, 1432.
- 6 Y. Nakagawa and K. Tomishige, *Catal. Sci. Technol.*, 2011, **1**, 179.
- 7 A. M. Ruppert, K. Weinberg and R. Palkovits, *Angew. Chem., Int. Ed.*, 2012, **51**, 2564.
- 8 F. Mauriello, M. G. Musolino and R. Pietropaolo, in *Glycerol: Production, Structure and Applications*, ed. M. De Santos Silva and P. C. Ferreira, Nova Science Publishers, Inc, New York, 2012, p. 45.
- 9 R. D. Cortright, R. R. Davda and J. A. Dumesic, *Nature*, 2002, **418**, 964.
- 10 G. W. Huber and J. A. Dumesic, *Catal. Today*, 2006, **111**, 119.
- 11 N. H. Tran and G. S. K. Kannangara, *Chem. Soc. Rev.*, 2013, **42**, 9454.
- 12 G. W. Huber, J. W. Shabaker, S. T. Evans and J. A. Dumesic, *Appl. Catal., B*, 2006, **62**, 226.
- 13 A. V. Kirilin, A. V. Tokarev, E. V. Murzina, L. M. Kustov, J.-P. Mikkola and D. Yu. Murzin, *ChemSusChem*, 2010, **3**, 708.
- 14 G. Wen, Y. Xu, H. Ma, Z. Xu and Z. Tian, *Int. J. Hydrogen Energy*, 2008, **33**, 6657.
- 15 A. Martin, U. Armbruster, I. Gandarias and P. L. Arias, *Eur. J. Lipid Sci. Technol.*, 2013, **115**, 9.
- 16 A. Ciftci, D. A. J. M. Ligthart and E. J. M. Hensen, *Green Chem.*, 2014, **16**, 853.
- 17 D. Roy, B. Subramaniam and R. V. Chaudhari, *Catal. Today*, 2010, **156**, 31.

- 18 B. Li, J. Wang, Y. Yuan, H. Ariga, S. Takakusagi and K. Asakura, *ACS Catal.*, 2011, **1**, 1521.
- 19 M. G. Musolino, C. Busacca, F. Mauriello and R. Pietropaolo, *Appl. Catal., A*, 2010, **279**, 77.
- 20 M. G. Musolino, L. A. Scarpino, F. Mauriello and R. Pietropaolo, *ChemSusChem*, 2011, **4**, 1143.
- 21 F. Liao, T. W. B. Lo, D. Sexton, J. Qu, C. T. Wu and S. C. E. Tsang, *Catal. Sci. Technol.*, 2015, **5**, 887.
- 22 M. G. Musolino, L. A. Scarpino, F. Mauriello and R. Pietropaolo, *Green Chem.*, 2009, **11**, 1511.
- 23 F. Mauriello, H. Ariga, M. G. Musolino, R. Pietropaolo, S. Takakusagi and K. Asakura, *Appl. Catal., B*, 2015, **166–167**, 121.
- 24 C.-T. Wu, K. M. K. Yu, F. Liao, N. Young, P. Nellist, A. Dent, A. Kroner and S. C. E. Tsang, *Nat. Commun.*, 2012, **3**, 1050.
- 25 J. Liu, B. Sun, J. Hu, Y. Pei, H. Li and M. Qiao, *J. Catal.*, 2010, **274**, 287.
- 26 D. Scholz, C. Aellig and I. Hermans, *ChemSusChem*, 2014, **7**, 268.
- 27 J. H. Bernas, A. Taskinen, J. Wärnå and D. Y. Murzin, *J. Mol. Catal. A: Chem.*, 2009, **306**, 33.
- 28 Y. Amada, S. Koso, Y. Nakagawa and K. Tomishige, *ChemSusChem*, 2010, **3**, 728.
- 29 Y. R. Luo, *Comprehensive Handbook of Chemical Bond Energies*, CRC Press, Boca Raton, USA, 2007.
- 30 M. K. Weldon and C. M. Friend, *Chem. Rev.*, 1996, **96**, 1391.
- 31 R. M. Rioux and M. A. Vannice, *J. Catal.*, 2003, **216**, 362.
- 32 A. Wawrzetz, B. Peng, A. Hrabar, A. Jentys, A. A. Lemonidou and J. A. Lercher, *J. Catal.*, 2010, **269**, 411.
- 33 B. Peng, C. Zhao, I. Mejía-Centeno, G. A. Fuentes, A. Jentys and J. A. Lercher, *Catal. Today*, 2012, **183**, 3.
- 34 Y. Chen, M. Saliccioli and D. G. Vlachos, *J. Phys. Chem. C*, 2011, **115**, 18707.
- 35 M. Saliccioli, W. Yu, M. A. Barteau, J. G. Chen and D. G. Vlachos, *J. Am. Chem. Soc.*, 2011, **133**, 7996.