Catalysis Science & Technology

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/catalysis

Journal Name

ARTICLE

Hydrogenolysis vs. Aqueous Phase Reforming (APR) of glycerol promoted by the heterogeneous Pd/Fe catalyst

Received 00th January 20xx,c
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Francesco Mauriello,[a*] Alessandro Vinci,[a] Claudia Espro,[b] Bianca Gumina, [b] Maria Grazia Musolino[a] and Rosario Pietropaolo[a]

The hydrogenolysis and the aqueous phase reforming of glycerol have been investigated under mild reaction conditions, using water as reaction medium and Pd/Fe as catalyst. The experiments, both in presence of added H_2 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 the dehydrogenation is the prerequisite for the C-C bond breaking (APR) with the latter favoured at higher reaction temperatures. The temperature dependance of the C-C and C-O bond rupture is discussed taking into account the bond energies involved in the competitive hydrogenolysis and APR reactions. Finally, the Pd/Fe catalyst has been also tested in the hydrogenolysis and APR of ethylene glycol in the same temperature range with the aim of claryfing the selective cleavage of C−O and C−C bond in biomass derived C_2-C_3 polyols.

Introduction

A growing attention has been gained to the use of renewable biomass for bulk chemicals production.[1, 2]

Glycerol, the main byproduct in affording biodiesel, is one of the top 12 building block chemicals largely used as bio-feedstock for the production of chemical products.[3, 4] Due to the worldwide expansion of biofuels, today 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 starting renewable 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 formation of propylene diols, ethylene glycol and propanols.[6, 7] Considerable research effort has been directed towards conversion of glycerol into 1,2-propanediol (1,2-PDO) that 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 environmental benefits and the economic viability of biodiesel manufacture.

At the same time, production of hydrogen through the aqueous-phase reforming (APR) of biomass-derived polyols is considered a promising catalytic process.[9-14] Glycerol is an interesting starting substrate for “bio”-hydrogen production since the relative process becomes spontaneous at much lower temperature than that generally used today for the H_2 manufacture from CH_4. An ideal catalyst for H_2 production from glycerol needs to be very active both in the C−C bond breaking as well as in promoting the water gas shift (WGS) reaction thus reducing the CO content.

Furthermore, the H_2 - generated in situ by 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 be considered also 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 in the hydrogenolysis of biomass derived polyols.[6, 7] However, in the last 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 reaction solvent [22, 23] as well as 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,

---

[a] *Dipartimento DICEAM, Università Mediterranea di Reggio Calabria, Loc. Feo di Vito, I-89122 Reggio Calabria, Italy*
Email: francesco.mauriello@unirc.it; Tel: (+39) 09651692278
[b] *Dipartimento DIECII, Università di Messina, Contrada Di Dio, 1 - Vill. S. Agata, I-98166 Messina, Italy*

† Footnotes relating to the title and/or authors should appear here.
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

leading to formation of bimetallic Pd-Fe ensambles, which positively promote the 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 reaction solvent with two different strategic approaches: by using molecular hydrogen as readily available H-source and by using the APR condition producing in-situ H_2.

By using molecular H_2 as direct hydrogen source, at 180°C, 1,2-PDO and EG are the main reaction products in glycerol hydrogenolysis being the Pd/Fe catalyst more active in C–O bond cleavage. Upon increasing the reaction temperature a major tendency of the Pd/Fe catalyst in promoting dehydrogenation/decarbonylation reactions is found. Under inert atmosphere, at 180°C, the H_2 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 a major production of gas phase products and high H_2 selectivity.

Therefore, a 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 aiming at clarifying the competitive occurrence of dehydrogenation and dehydration processes in C_2-C_3 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 salts solution was added dropwise into a 1 M aqueous solution of Na_2CO_3. After filtration, the sample was washed until complete removal of chloride ions and dried for 1 day at 80°C under vacuum. Before reaction, the Pd/Fe catalyst was reduced at 200°C for 2h under 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 (λ=0.15418 nm). Analyses were registered in the 2θ 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) 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 hundred particles visible on the micrographs. From the size distribution, the average diameter was calculated by using the expression: $dn= \Sigma n_i d_i/ni$ where n_i is the number of particles of diameter di.

The H_2-TPR measurement was performed using a conventional TPR apparatus. The dried sample (50mg) was heated at a linear rate of 10°C min^{-1} from 0 to 1000 °C in a 5 vol % of a H_2/Ar mixture at a flow rate of 20 $cm^3\ min^{-1}$. The H_2 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 CO_2, respectively. Signals calibration was done by injecting a known amount of H_2 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 $5x10^{-9}$ mbar. The binding energies (BE) were set taking the C 1s peak at 284.6 eV as reference. Peaks deconvolution and fitting analyses were performed using the peak-fitting software "SPECSURF, 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 PdFe 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 (H_2 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=0.535mm, length=30m) and a capillary column (HP-PLOT/Q, diameter=0.320mm, length=30 m).

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

$$\text{Conversion [\%]} = \frac{\text{moles of reacted substrate}}{\text{moles of substrate feed}} \times 100 \qquad \text{(Eq.1)}$$

$$\text{Liquid Phase Selectivity [\%]} = \frac{\text{moles of specific product in liquid phase}}{\text{sum of moles of all products in liquid phase}} \times 100 \qquad \text{(Eq.2)}$$

$$\text{Gas Phase Selectivity [\%]} = \frac{\text{moles of specific product in gas phase}}{\text{sum of moles of all products in gas phase}} \times 100 \qquad \text{(Eq. 3)}$$

$$\text{1,2-PDO Yield [\%]} = \frac{\text{moles of 1,2-PDO in liquid phase}}{\text{moles of glycerol feed}} \times 100 \qquad \text{(Eq. 4)}$$

3 Results and discussion

3.1 Catalyst preparation and characterization

The Pd/Fe catalyst has been prepared by co-precipitation of palladium chloride (dissolved in HCl) and iron (III) nitrate nonahydrate poured together dropwise into a 1M aqueous solution of Na_2CO_3 followed by calcination and reduction with H_2 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 (Figure 1 and Figure 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 (Figure S1.3).

The H_2-TPR measurement (Figure S1.4) shows only one intense peak at about 80°C including, on the basis of H_2 consumption calculations, both Pd(II) → Pd(0) and Fe(III) → Fe_3O_4 reductions suggesting that Pd nanoparticles are effective in promoting the reduction of the support from hematite to magnetite. Furthermore, the conclusion that palladium particles promote the reduction of Fe^{3+} to the Fe_3O_4 is also confirmed by the XRD analysis on the Pd/Fe catalyst reduced at 100°C (Figure S1.3) that shows signals only related to the magnetite structure.

The presence of partial positively charged metal species is observed with the X-ray photoelectron spectroscopy (Table S1.5 and Figure S1.5) (the Pd $3d_{5/2}$ binding energy is by 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, 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 starting substrate, clearly indicating that the Pd/Fe catalyst is more active in the C–O bond cleavage and less efficient in the C–C bond breaking.

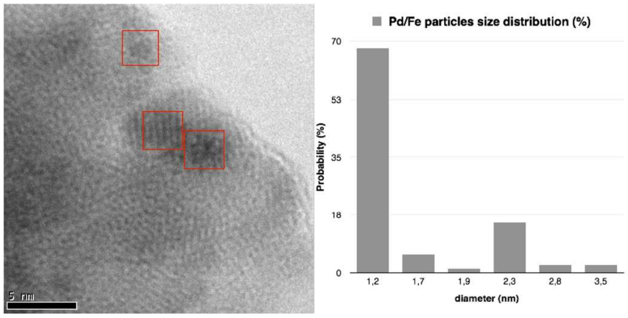


Figure 1. High resolution transmission electron micrograph of Pd/Fe catalyst (left) and particle size distribution of the palladium nanoparticles (right).

The increase of the reaction temperature produces a 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 of note that the amount of EtOH reaches a maximum of 70.5% in the liquid phase products at 240°C.

In reference experiments, 1,2-PDO has been also tested in presence of H_2 (Table S2.1): the reactions provide EtOH as 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 have investigated the hydrogenolysis of glycerol at different reaction time (Figure 2 and Table S2.2). As expected, glycerol conversion and 1,2-PDO yield increase on passing from 6 to 24 hours (Figure 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 (Figure 2 and Table S2.3). A conversion decrease by increasing the hydrogen pressure, in other hydrogenolysis reactions over heterogeneous palladium systems, was ascribed to a competitive adsorption of substrate and H_2 on the catalyst surface. [27]

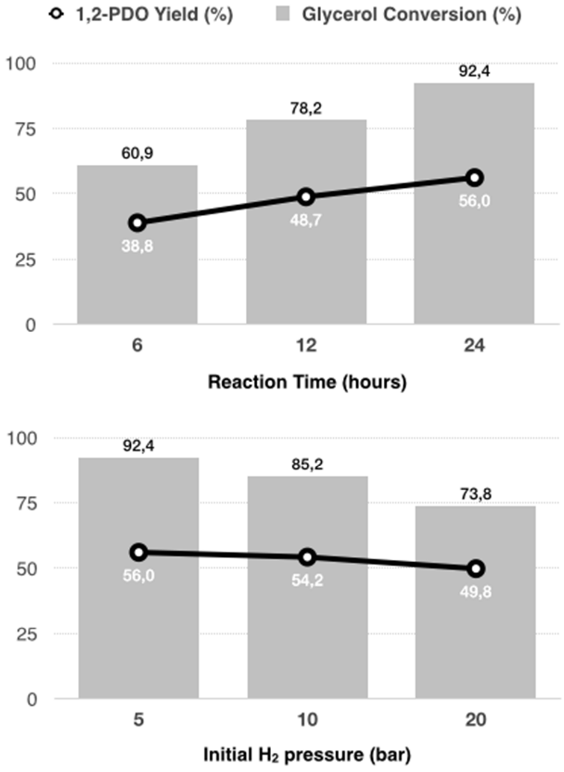


Figure 2. Reaction time (up) and initial H_2 pressure effect on glycerol conversion (%) and 1,2-PDO yield (%) in reaction carried out in presence of added H_2.

Table1. Conversion of glycerol and ethylene glycol promoted by the Pd/Fe catalyst in presence of added hydrogen. Condition: 0,25 g catalyst; 40ml entry solution (4 wt%); 5 bar H_2 pressure, 24 h.

Entry	Temperature (°C)	Conversion (%)	Liquid Phase (%)	Products 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

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

Further recycling of the Pd/Fe catalyst at 180°C in presence of H_2, performed after washing the sample (remaining in the reactor) with pure water, gave, as expected, a lower conversion (Figure S2.4). However, the selectivity did not change appreciably, as already reported, in the past, on using 2-propanol as solvent.[20]

The Pd/Fe catalyst was also tested at higher glycerol concentration (20 wt % of glycerol solution, 1 g of reduced Pd/Fe catalyst, 20 bar initial pressure of H_2, 24 hours of reaction time): a 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 has been also tested in the hydrogenolysis of EG in the same temperature range (Table 1). At all temperatures, reactions proceed more slowly with respect to glycerol. At 180°C, the Pd/Fe catalyst equally cleaves the C–C and the C–O bond of EG allowing the production of methanol and ethanol in a comparable yield. On rising the reaction temperature, an enhanced performance of Pd/Fe for the C–C bond breaking is noticed.

The presence of added H_2 in the catalytic test conducted by using both glycerol and EG as starting substrates doesn't allow a truthful quantitative analysis of gas phase products. However, at all temperature range investigated (180-240°C) a qualitative analysis reveals, together with CO_2, a very low amount of alkanes.

3.3 Reactions under inert atmosphere

The results on 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 gas phase, H_2 is the main product observed (73.4%) together with CO_2 (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 more production of gas phase products. At 240°C a H_2 selectivity of 80.5% in gas phase products is reached.

Significant changes in liquid phase products 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 its further dehydrogenation and hydrogenolysis processes.

Noteworthy CO is never detected 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 Figure 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 liquid state. However, in the temperature range investigated, the quantity of water under vapor conditions should be very low (below 3% at 240°C) allowing us to investigate the C-C bond breaking under reaction conditions very close to those usually adopted for APR reactions.

A combination of aqueous phase reforming and in-situ hydrogenolysis reactions of ethylene glycol is also observed. In line with reactions carried out in presence of added H_2, 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 main reaction product and a selectivity to EtOH (C-O bond cleavage) as lower as the temperature increases. Gas phase products are characterized by a good H_2 production and an insignificant amount of alkanes.

Table2. Conversion of glycerol and ethylene glycol promoted by the Pd/Fe catalyst under inert atmosphere. Condition: 0,25 g catalyst; 40ml entry solution (4 wt%); 5 bar He pressure, 24 h.

Entry	Temperature (°C)	Conversion (%)	Liquid Phase (%)	Products liquid Phase Selectiviy (%)					Gas Phase Selectivity (%)		
				1,2-PDO	POs	EG	MeOH	EtOH	H_2	CO_2	Alkanes
Glycerol	180	89.8	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	-

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

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 presence of H_2 over the Pd/Fe catalyst are substantially in agreement with those obtained, before, on using 2-propanol as solvent which indicate hydroxyacetone (AC) as the reaction intermediate for 1,2-PDO formation. [20, 23] The main difference lays on the higher fraction of EG and EtOH detected in water and not observed in isopropanol where a good selectivity to 1-PO was found (Figure S2.6). Therefore, it can be stated that in glycerol hydrogenolysis it is undesired to use water as reaction medium in order to drive the equilibrium to propanols formation.

Cross-check experiments, under both reaction conditions used in this study (H_2 or He) and within the temperature range investigated (180-240°C), show that pure Fe_3O_4 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 catalytic results, the conversion of glycerol on the bimetallic Pd/Fe catalyst can follow two distinctive routes for 1,2-PDO and EG formation (Scheme1).

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 that is finally hydrogenated into 1,2-PDO. [23]

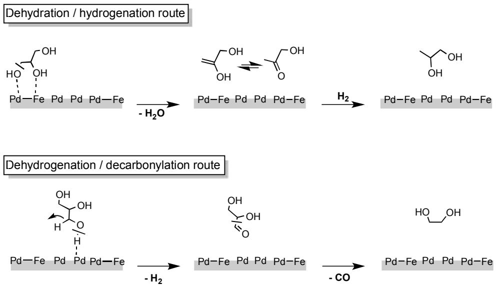
On the other hand, glycerol conversion to EG proceeds via a previous dissociation of a primary alcoholic group followed by C-H bond breaking. The ensuing glyceraldehyde undergoes final C-CO breaking leading to EG and CO formation.

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

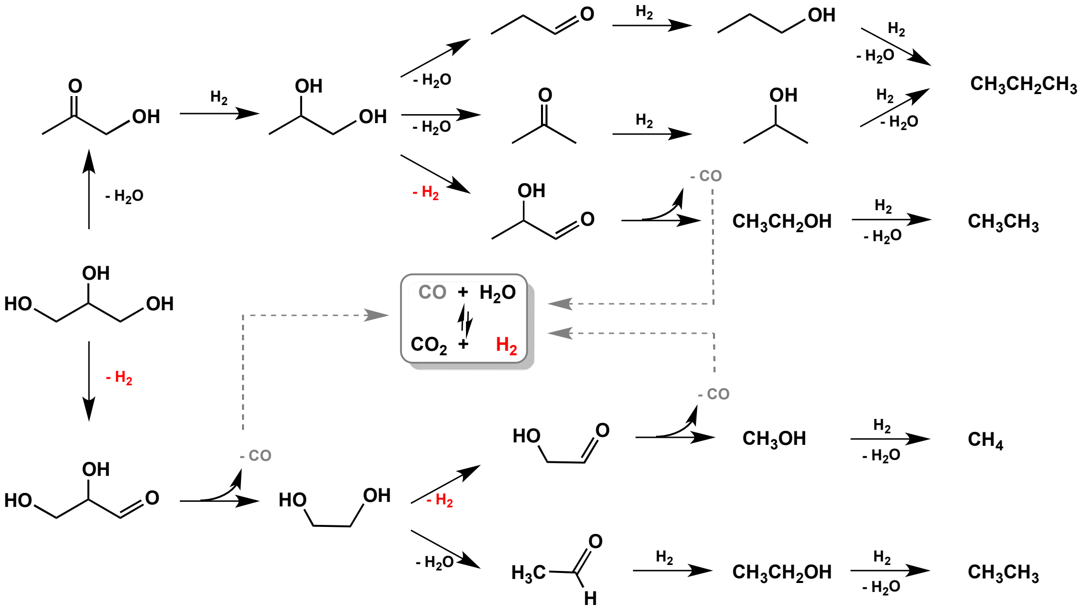
Data reported in Table 2 concerning reactions carried out under inert condition show that, together with H_2, CO_2 and a small amount of alkanes, liquid phase products are formed. The presence of hydrogenolysis products implies that the in-situ produced H_2 directly participates to the hydrogenation 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 dehydration and dehydrogenation reactions are key elementary steps in the conversion of glycerol both in presence and in absence of added H_2.

At 180°C, in presence of H_2 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 a higher reaction temperature, dehydrogenation reactions prevail and dehydration/hydrogenation steps become less important, even when 1,2-PDO is used as starting substrate (Table S3). To this regard, the higher ability of the coprecipitated Pd on 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 been recently observed also 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]



Scheme 1. First steps in glycerol conversion in presence and absence of added H_2: dehydration/hydrogenation and dehydrogenation/decarbonylation routes



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

The temperature dependence of the reaction pathways selectivity can be related to the different bond energy involved in the alternative processes. [29] The dehydration/hydrogenation route implies the previous C-OH cleavage of the primary alcoholic group ($E_{C\text{-}OH} \cong 80$ kcal/mol) [29] followed by the rearrangement of the unstable enol to hydroxyacetone that is finally hydrogenated to 1,2-PDO. [23] Conversely, the dehydrogenation/decarbonylation involves the prior O-H breaking ($E_{O\text{-}H} \cong 104$ kcal/mol) [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 has been detected in reactions carried out by using 1,2-PDO as starting substrate (Table S3) it can be confirmed that the rupture of the O-H bond is a fundamental prerequisite for the C-C cleavage.

Similar conclusions have been also proposed by Lercher and co-workers that suggested a reaction network consisting of parallel routes that include dehydrogenation and dehydration as primary steps in the hydrodeoxygenation and APR of C$_3$ alcohols and polyols. [32, 33]

On this regard, it is worth to underline that the C-CO bond energy value is about 83 kcal/mol quite proximate to that of an internal C-C bond ($E_{C\text{-}C} \cong 85$ kcal/mol). [29] Therefore, the 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 (≅ 95 kcal/mol) bond breaking promoted by 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 dehydration/hydrogenation and dehydrogenation processes (hydrogenolysis vs APR) occurs starting from EG. The catalytic results at 180 and 210°C in presence of H$_2$ show a competition between 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 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]

The whole results allow to draw the overall pathways for describing the hydrogenolysis vs APR reactions starting from glycerol as represented in Scheme 2.

The gas phase composition of 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):

$$C_3H_8O_3 + 3H_2O \rightarrow 7H_2 + 3CO_2 \qquad (1)$$

The explanation for the "apparent" anomaly is that 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 to collect gas-phase products at about 2/3 of the pressure measured at 25°C (Figure S2.5). Therefore, under our sampling condition, it is necessary to take into consideration that CO_2 is much more soluble in water than H_2 ($CO_{2(sol)}/H_{2(sol)} \cong 55$). Therefore the H_2/CO_2 ratio measured is expected to be higher than that predictable on the basis of reaction (1) and as higher as the final pressure (related to the reaction temperature) increases.

In accord with all these considerations, the measured pH values of the liquid phase are 6.10, 5.90 and 5.75 for reactions carried out respectively at 180, 210 and 240°C as expected for the weak acidity of CO2 in water.

Analogous consideration can be done for APR reactions of EG.

Another very important peculiarity of the Pd/Fe catalyst is the absence of CO (as 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 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 that 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 is investigated under both hydrogenolysis and aqueous phase reforming conditions over the bimetallic Pd/Fe catalyst. The beginner alternative processes are found to be the dehydration/hydrogenation and the dehydrogenation/decarbonylation with the latter controlled by the previous O-H breaking followed by the β C-H elimination rather than the direct C–C bond cleavage. At 180°C, the C-O bond is preferentially cleaved allowing the production of 1,2-PDO, while the C-C bond breaking becomes favourable at higher reaction temperatures leading to formation of H_2 in good yield. In analogy, by using ethylene glycol (C_2 polyol) as starting substrate, C-O and C-C bonds are equally cleaved at 180 and 210°C whereas a significant increase of dehydrogenation products is 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, on using the Pd/Fe catalyst, is observed by varying the reaction temperature.

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

Acknowledgements

The financial support by POR Calabria - FSE 2007/2013 - ("Backup" Project) and Mediterranea University of Reggio Calabria is gratefully acknowledged. The authors thank Prof. Pierluigi Antonucci and Ing. Patrizia Frontera for their assistance with GC analysis, Mr. Gaetano Bevacqua and Mrs. Noemi Arcadi for catalytic experiments related to ethylene glycol and 1,2-propanediol.

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, second ed*., 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: M. De Santos Silva, P.C. Ferreira (Eds.), *Glycerol: Production, Structure and Applications*, Nova Science Publishers, Inc, New York, 2012, 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: Environment*., 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 Energ*., 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, K. Asakura, *ACS Catal*., 2011, **1**, 1521.
19 M.G. Musolino, C. Busacca, F. Mauriello and R. Pietropaolo, *Appl. Catal. A: Gen*., 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: Environment*., 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 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. Salciccioli, and D. G. Vlachos, *J. Phys. Chem. C*, 2011, **115**, 18707.

35 M. Salciccioli, W. Yu, M. A. Barteau, J. G. Chen and D. G. Vlachos, *J. Am. Chem. Soc*., 2011, **133**, 7996.