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

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SUPPLEMENTARY INFORMATION

S1. Characterization of Pd/Fe catalyst

S1.1 Main characteristics of the Pd/Fe catalyst

Table S1.1 Main characteristics of the Pd/Fe catalyst.

Catalyst notation	Pd Loading (wt%)	S.A. (m^2/g)	S_{act} (m^2/g)	d_n (nm)
Pd/Fe	8.7	170	2.51	1.8

Pd Loading determined by X-ray fluorescence (XRF) analysis; S.A. = BET surface area; S_{act} = active surface area calculated by CO-pulse chemisorption technique based on an assumption of CO/Pd = 1); d_n = mean particle size from TEM.

S1.2 TEM analysis

Figure S1.2 shows TEM (a, b) and HRTEM (c, d) images of the Pd/Fe catalyst reduced at 180°C.

Only after close inspection, small Pd nanoparticle with diameter in the range of 1.2 (most common measured) - 2.5 nm can be identified. These results are in agreement with XRD analysis where the absence of the (111) diffraction line of metallic palladium in the reduced Pd/Fe sample is indicative of extremely small highly dispersed Pd-particles (the limit of conventional X-ray powder diffraction for the detection of supported nanoparticles is usually 2–2.5 nm).

Tsang and co-workers have recently reported (Nat. Commun. 3, 2012) analogous results on reduced Pd on iron oxide catalyst prepared by an analogous synthetic method as ours: by using high-angle annular dark field scanning TEM, Pd particles ranged in size from ca. 0.5 to 2.5 nm in diameter - with particles of 0.5–1.5 nm being the most commonly measured size - were found.

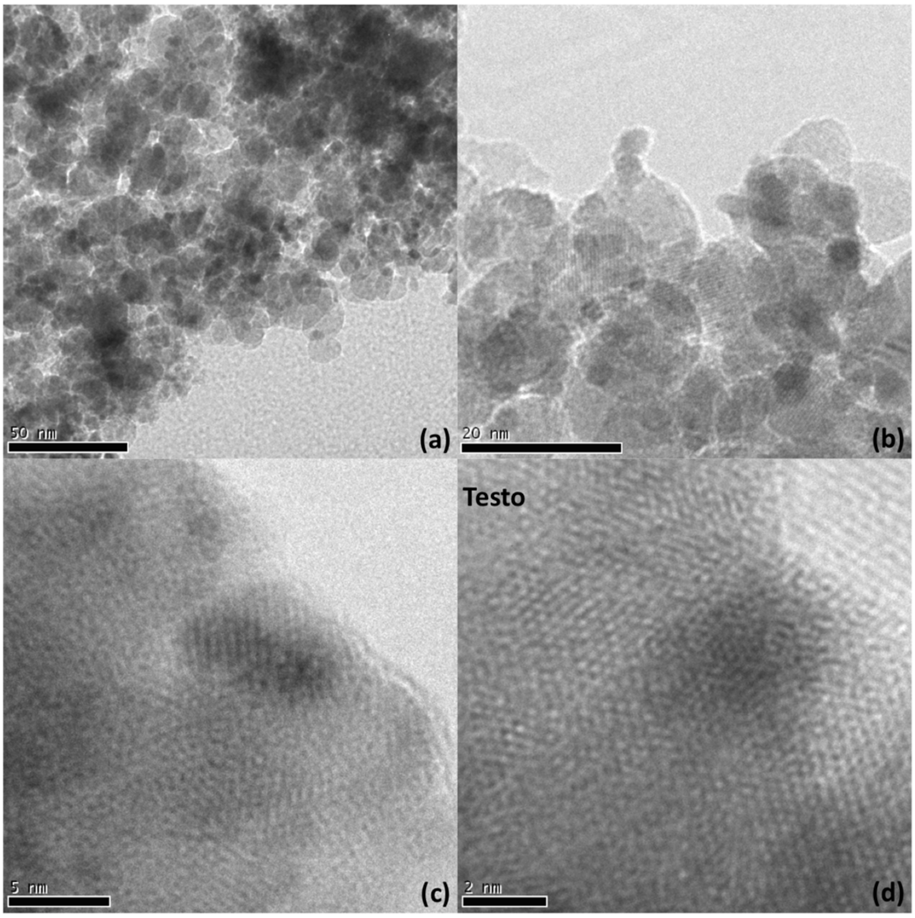

Figure S1.2 TEM (a, b) and HRTEM (c, d) images of the Pd/Fe catalyst reduced at 180°C.

S1.3 XRD analysis

Figure S1.3 XRD shows diffractograms of the Pd/Fe catalyst reduced at 100°C (a), 200°C (b) and after hydrogenolysis reactions (5 bar H_2) carried out using glycerol as starting substrate after 12 hours (c) and 24 hours reaction time (d).

The XRD spectrum of the Pd/Fe catalyst reduced at 100 and 200°C (Figure S1.3) revealed diffraction patterns characteristic of Fe_3O_4. The absence of the diffraction signal of the metallic palladium (111) plane at 2θ = 40.1 is indicative of extremely small highly dispersed Pd-particles consistent with TEM analysis (Pd/Fe exhibits a predominance of very small metallic particles and a relatively narrow particles sizes distribution with diameter values ranging between 0.5 and 2.5 nm, with the 1.2 nm dimension being the most commonly measured size).

Within the reaction time investigated, after 24 hours, no modification of the Fe_3O_4 support structure is observed while the increase of the diffraction peak ascribed to the (111) plane of the palladium is indicative of Pd particles agglomeration.

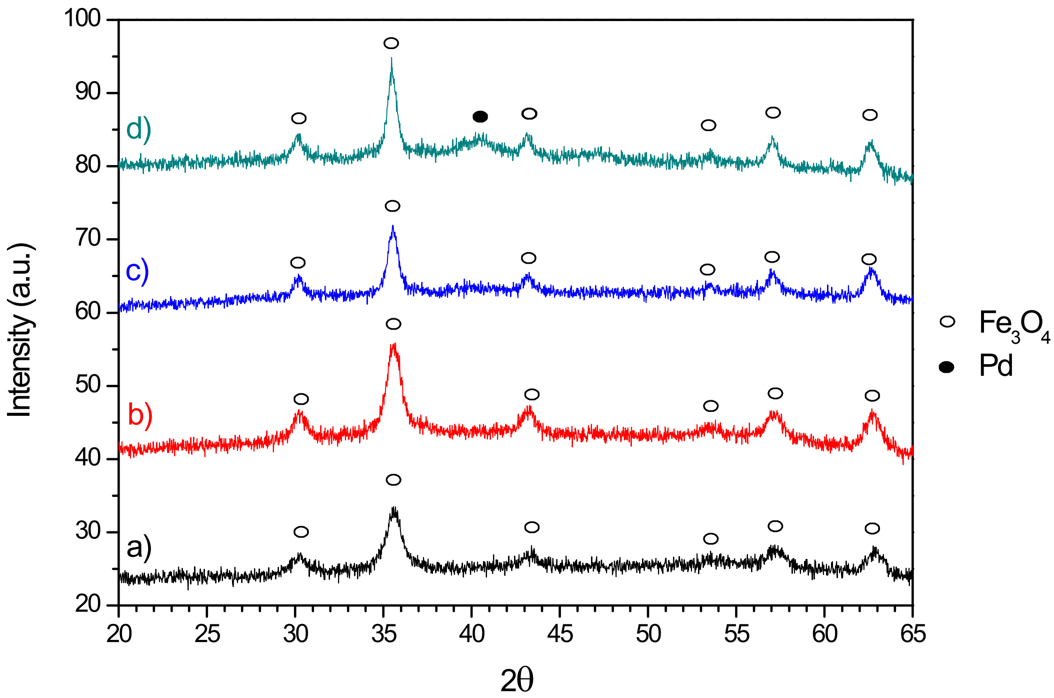

Figure S1.3 XRD of the Pd/Fe catalyst reduced at 100°C (a), 200°C (b) and after hydrogenolysis reactions (5 bar H_2) carried out using glycerol as starting substrate after 12 hours (c) and 24 hours reaction time (d).

S1.4 H_2-TPR profiles

The H_2-TPR profile of the Pd/Fe catalyst shows the main reduction area centered at about 80°C that includes, on the basis of H_2 consumption calculations, both $Pd^{2+} \rightarrow Pd^0$ and $Fe^{3+} \rightarrow Fe_3O_4$ reductions (Figure S1.4 up).

For comparison, the H_2-TPR of pure Fe_2O_3 was performed (Figure S1.4 down). In this case, the reduction profile is characterized by two peaks: the first at about 420°C belonging to the reduction $Fe^{3+} \rightarrow Fe_3O_4$ and the latter at about 690°C related to the subsequent reduction $Fe_3O_4 \rightarrow FeO$.

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.

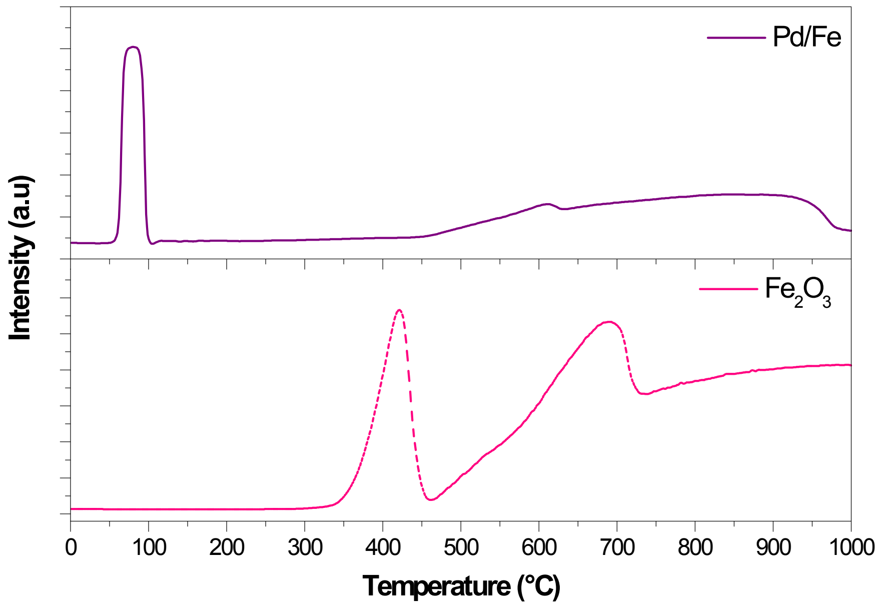

Figure S1.4 H_2-TPR profile of the Pd/Fe catalyst (up) and pure Fe_2O_3 (down)

S1.5 XPS analysis

In the reduced Pd/Fe catalyst the binding energy of the Pd $3d_{5/2}$ level (Figure S1.5 left and Table S1.5) appears at about 0.4 eV value higher than that reported for metallic Pd (334.8 eV), indicating the presence of partial positively charged metal species.

At the same time, the absence of of the satellite peak at about 718.8 eV (Figure S1.5 right and Table S1.5) indicates the Fe_3O_4 support structure.

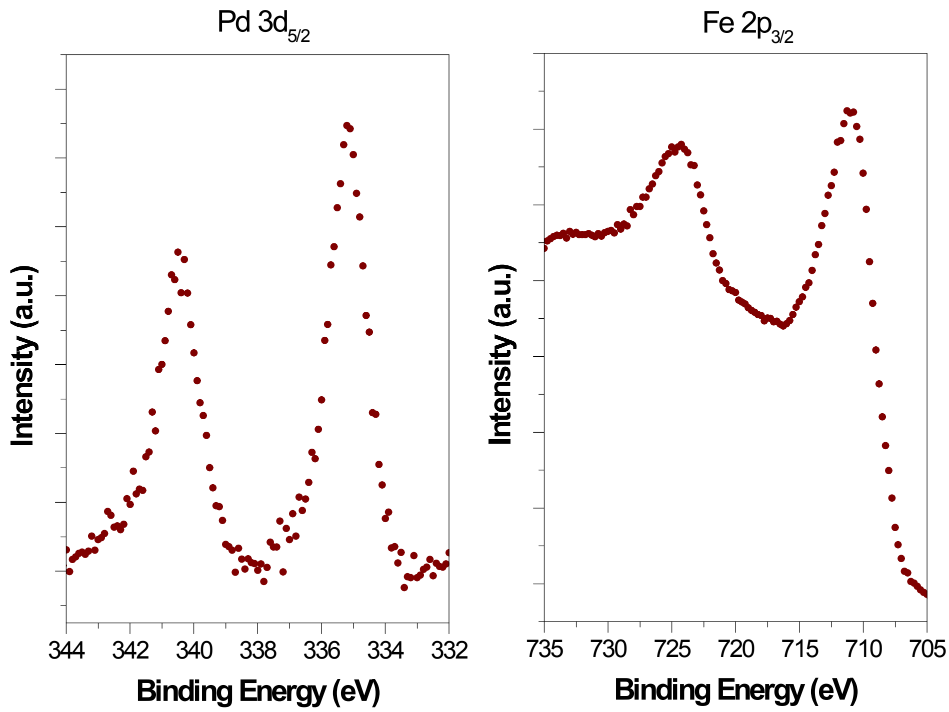

Figure S1.5 XPS Pd $3d_{5/2}$ and Fe $2p_{3/2}$ plots in reduced Pd/Fe catalyst.

Table S1.5 Binding energies values of Pd $3d_{5/2}$, Fe$2p_{3/2}$, and O1s levels determined for the reduced Pd/Fe catalyst

Catalyst	**Binding Energy (eV)**			
	Pd $3d_{5/2}$	**Fe $2p_{3/2}$**	**Fe $2p_{3/2}$ sat.**	**O 1s**
Pd/Fe	335.2	710.7	-	530.2

S2. Catalytic tests

S2.1 Hydrogenolysis of 1,2-PDO promoted by the Pd/Fe catalyst

Table S2.1 Conversion of 1,2-PDO promoted by the Pd/Fe catalyst in presence of added H_2. Condition: 0,25 g catalyst; 40ml entry solution (4 wt%); 5 bar H_2 pressure.

Entry	Temperature (°C)	Conversion (%)	Liquid phase (%)	Products Selectivity in Liquid Phase (%)		
				POs	MeOH	EtOH
1,2-PDO	180	14.2	98.6	5.3	-	94.7
1,2-PDO	210	61.5	72.2	6.1	-	93.9
1,2-PDO	240	78.7	67.7	8.6	1.4	90.0

1,2-PDO = 1,2-propanediol; POs = 1-propanol + 2-propanol; MeOH = methanol; EtOH = ethanol.

S2.2 Hydrogenolysis of glycerol promoted by the Pd/Fe catalyst: effect of reaction time

Table S2.2 Conversion of glycerol promoted by the Pd/Fe catalyst in presence of added H_2 at different reaction times. Condition: 0,25 g catalyst; 40ml entry solution (4 wt%); 5 bar H_2 pressure.

Entry	Reaction Time (hours)	Conversion (%)	Liquid Phase (%)	Products Selectivity in Liquid Phase (%)				
				1,2-PDO	POs	EG	MeOH	EtOH
Glycerol	6	60.9	81.1	78.6	-	16.0	1.2	4.2
Glycerol	12	78.2	79.8	78.1	-	16.0	1.0	4.9

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

S2.3 Hydrogenolysis of glycerol promoted by the Pd/Fe catalyst: effect of hydrogen pressure

Table S2.3 Conversion of glycerol promoted by the Pd/Fe catalyst in presence of added H_2. Condition: 0,25 g catalyst; 40ml entry solution (4 wt%); 24 hours reaction time.

Entry	H_2 Pressure (bar)	Conversion (%)	Liquid Phase (%)	Products Selectivity in Liquid Phase (%)				
				1,2-PDO	POs	EG	MeOH	EtOH
Glycerol	10	85.2	78.2	81.3	-	15.1	-	3.5
Glycerol	20	73.8	78.7	85.7	-	12.9	0.2	1.1

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

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S2.4 Hydrogenolysis of glycerol promoted by the Pd/Fe catalyst: recycling tests

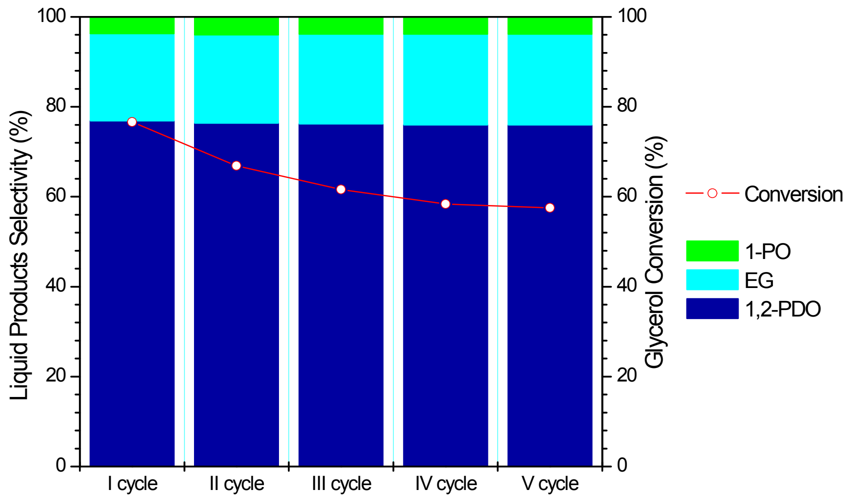

Figure S2.4 Re-use of the Pd/Fe catalyst in the glycerol hydrogenolysis in presence of added H_2. Condition: 180°C; 0,25 g catalyst; 40ml entry solution (4 wt%); 5 bar H_2 pressure.

S2.5 Pressure profiles of the glycerol conversion promoted by the Pd/Fe catalyst under inert atmosphere at 180, 210 and 240°C.

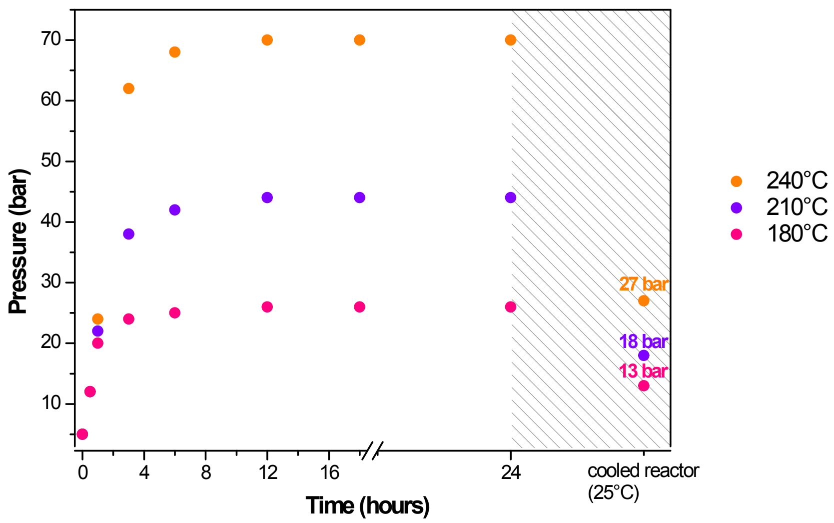

Figure S2.5 Pressure profiles of the glycerol conversion promoted by the Pd/Fe catalyst under inert atmosphere at 180, 210 and 240°C.

S2.6 Hydrogenolysis of glycerol promoted by the Pd/Fe catalyst: effect of reaction solvent

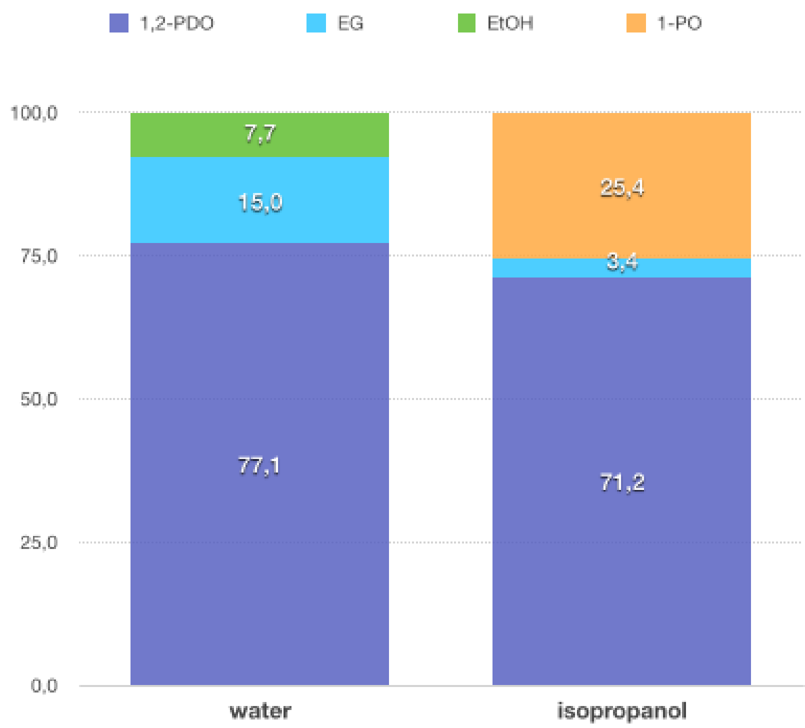

Figure S2.6 Composition of liquid phase products in glycerol hydrogenolysis promoted by the Pd/Fe catalyst in presence of added H_2 (5 bar) by using water (conversion = 92,4%) or isopropanol (conversion = 100%) as reaction solvent.

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