



# Hydrogenolysis of polyols promoted by supported palladium catalysts

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REGGIO CALABRIA

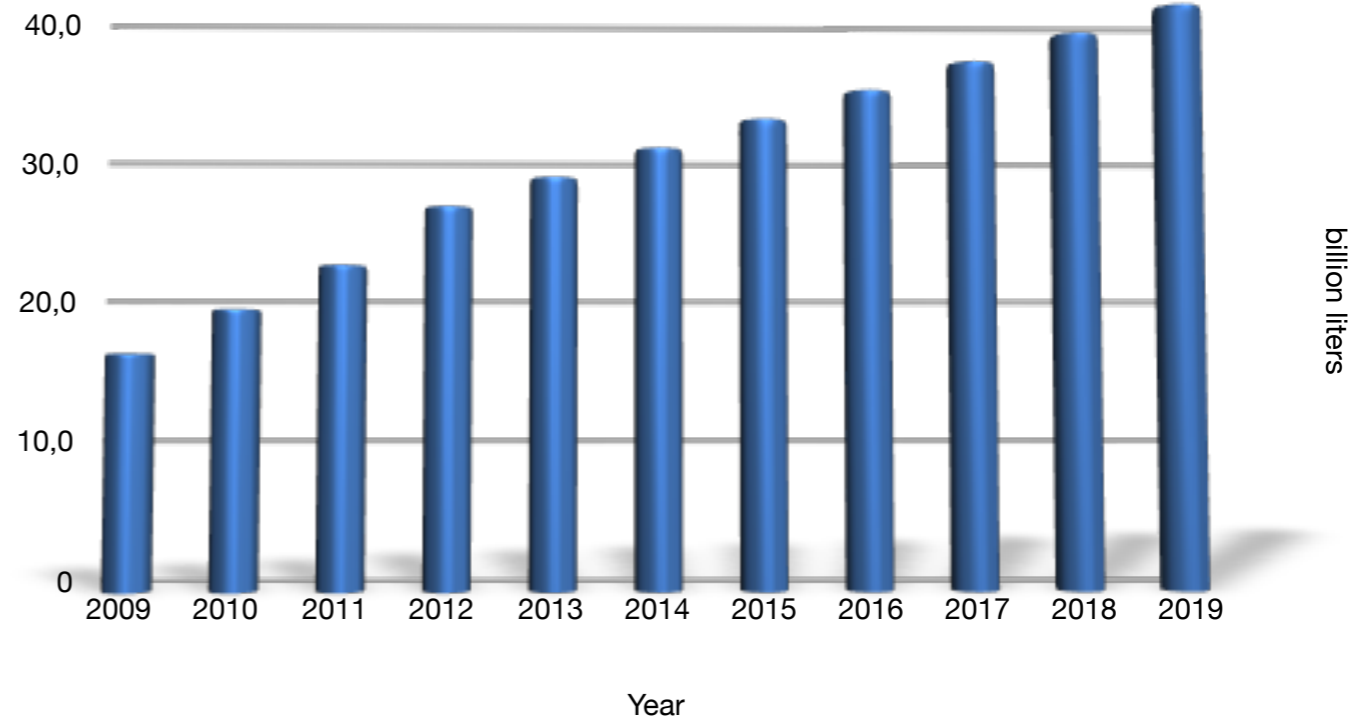


## C3 polyol: the case of glycerol

Biodiesel world production by feedstock

### ► The “case” of glycerol

- Glycerol is a simple polyol (C3 polyol)
- Glycerol is also the main byproduct in biodiesel production (for every 9 kg of biodiesel, about 1 kg of glycerol is formed)
- Today over 200 major fleets of the United States (including the United States Post Office, the US Military and the metropolitan transit systems) run on biodiesel. European legislation (EU) making mandatory to mix the products of fossil fuels with biofuel: 2% in 2008, 3% in 2009 and 5.75% in 2010.
- Glycerol production in the United States already reaches more than 350,000 tons per year and in Europe its production has tripled within the last ten years. By 2005 the price of glycerol is in free fall.
- Today, glycerol surplus is dispersed by incineration



	BIODIESEL	DIESEL
Prezzo unitario	€ 1,00	€ 0,80
Accisa	€ 0,08	€ 0,40
IVA	€ 0,22	€ 0,22
<b>Prezzo Totale</b>	<b>€ 1,29</b>	<b>€ 1,32</b>



## C3-C5 polyols derived biomass

### ► Polyols derived biomass - Horizon2020

- One of the main objectives of Horizon 2020 is to accelerate **the conversion of fossil-based European industries** to low carbon, resource efficient and sustainable ones.
- EU and US have encouraged researchers, in the framework of their strategic research programs, to develop technologies to **process abundant and cheaper non-edible biomass** (e.g. lignocellulosic biomass), thereby permitting sustainable **production of fuels and chemicals** without affecting food supplies or forcing extensive changes in land use.
- Lignocellulosic biomass derived polyols represent a noteworthy feedstock since they are easily available and can be converted, via hydrogenolysis reactions, into **valuable products** such as 1,2-propanediol (1,2-PDO), 1,3-propanediol (1,3-PDO) and ethylene glycol (EG).
- However, the studies present in patents and literature encounter low conversion or selectivities and harsh reaction conditions (e.g. high temperatures or H<sub>2</sub> pressures).
- Tackling these problems requires the development of **suitable catalysts, innovative operative conditions** and a deep comprehension of the **reaction mechanisms** involved.



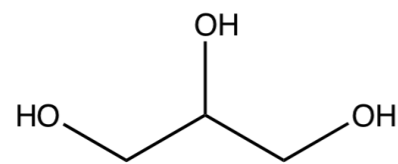


## C3-C5 polyols derived biomass

### ► C3-C5 polyols

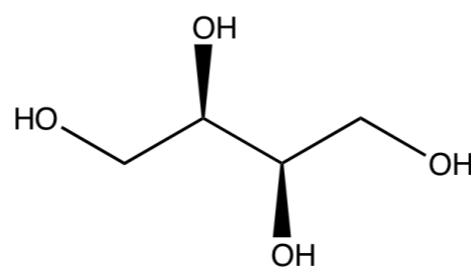
- C3-C5 polyols are characterized by a **shorter chain** and are more "**structurally**" **advantageous** in understanding the hydrogenolysis mechanism in terms of selective formation of ethylene and propylene glycols

C3 polyol

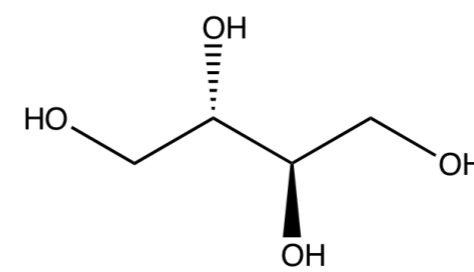


Glycerol

C4 polyols

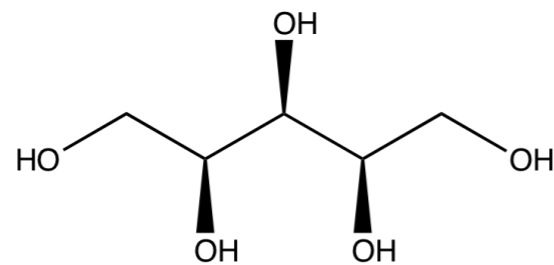


Threitol

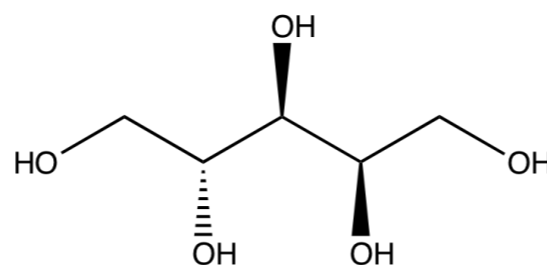


Erythritol

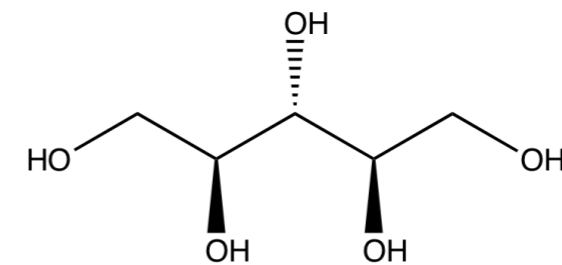
C5 polyols



Xylitol



Arabitol



Rybitol

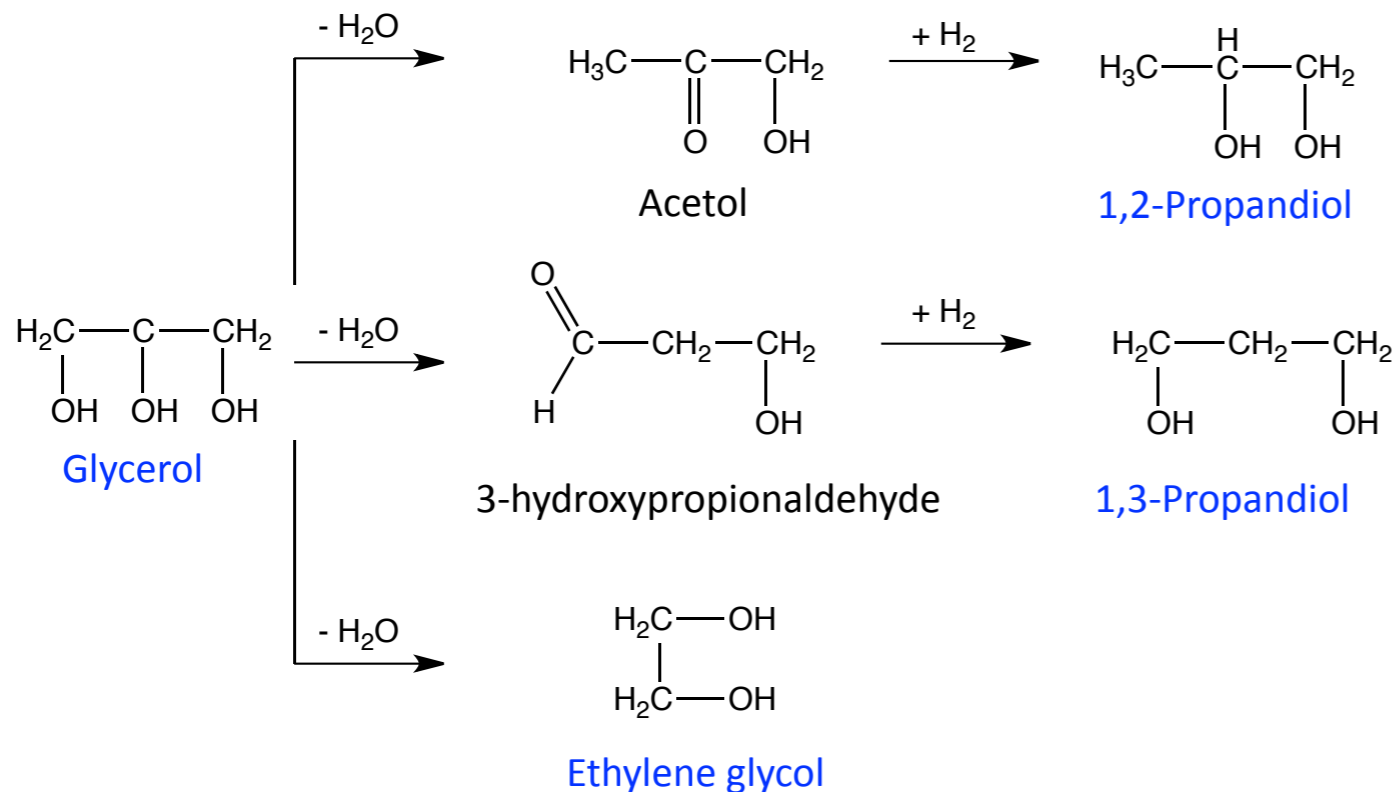




## Glycerol hydrogenolysis

### ► Glycerol hydrogenolysis

- The selective conversion of glycerol to glycols leads the formation of different valuable products such as 1,2-propanediol (1,2-PD), 1,3-propanediol (1,3-PD) or ethylene glycol (EG)



- **1,2-PDO** is an important chemical commodity used for polyester resins, liquid detergents, pharmaceuticals, cosmetics, tobacco humectants, flavours and fragrances, etc.
- **1,3-PDO** is mainly used in specialty polyester fibres, films and coatings.
- **EG** widely used as automotive antifreeze and as polymers precursor. Is also a raw material for synthetic fibres, explosives, etc.

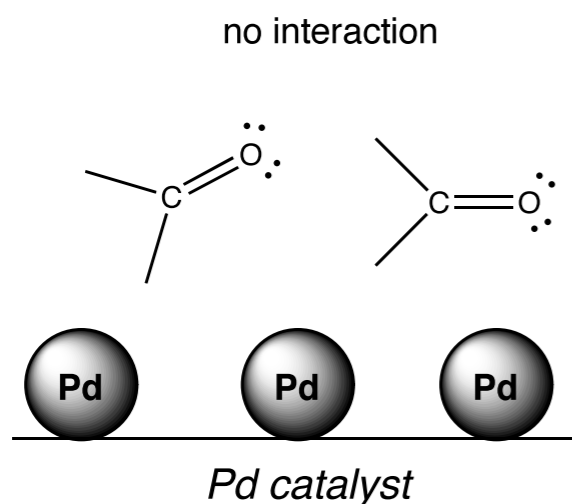




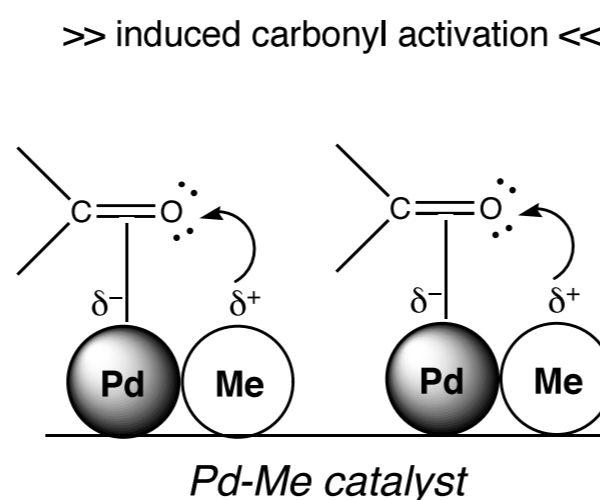
## Glycerol hydrogenolysis

### ► Are palladium catalysts suitable for glycerol hydrogenolysis ?

- In general, Ni, Ru, Rh and Cu are effective for hydrogenolysis reaction. **All the supported Pd catalysts exhibited very low activity under mild conditions** (conversion on Pd/SiO<sub>2</sub>  $\cong$  1%).
- However, co-precipitation technique generally leads to a better interaction between metal and support than that observed using the impregnation method.



(A)



(B)



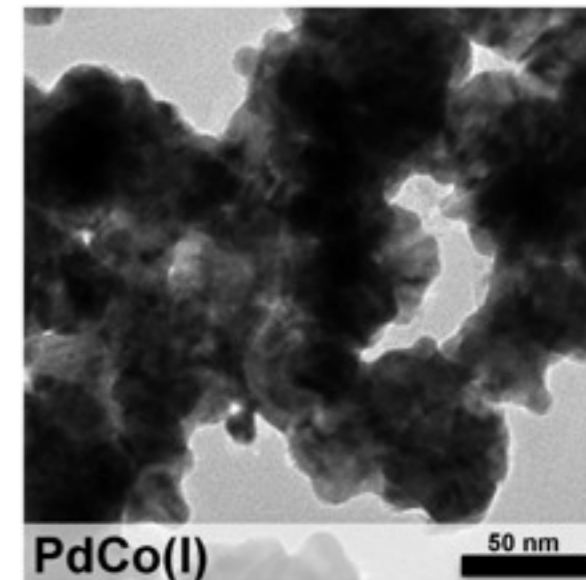
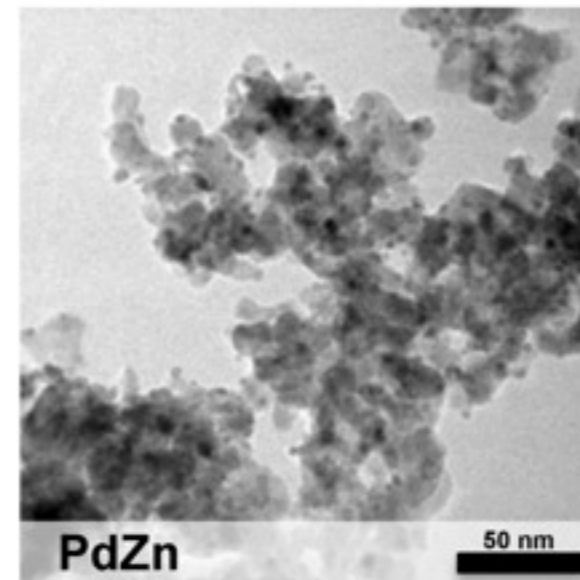
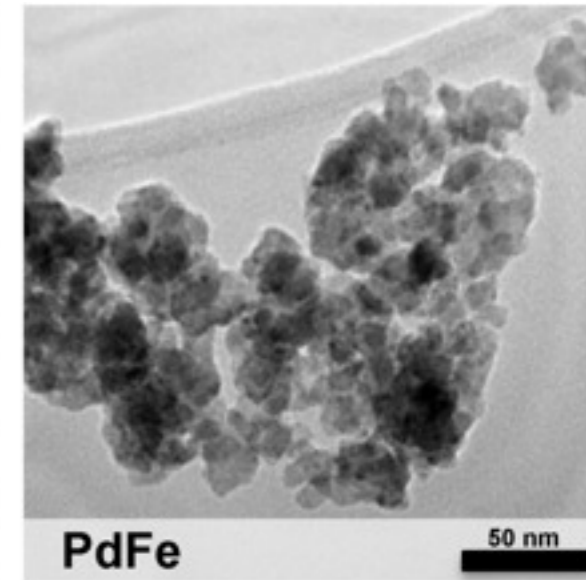
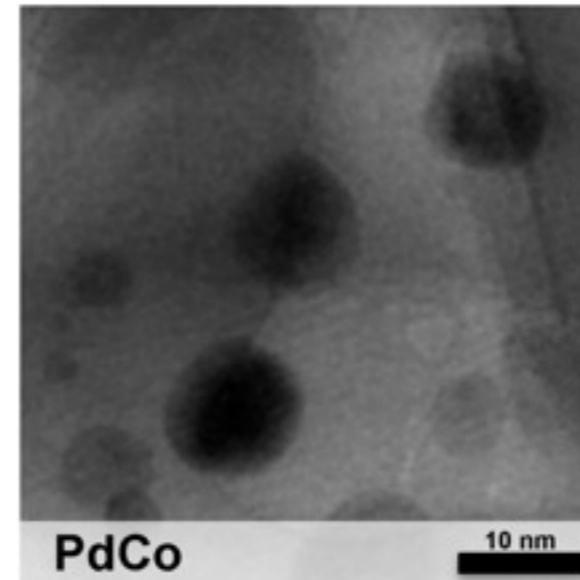


## Catalysts characterization

### ► Main characteristics of supported Pd catalysts

- The PdCo catalyst shows a broad size distribution with a mean diameter of 10.7 nm
- other co-precipitated samples that exhibit a predominance of small metallic particles and a relatively narrow particles size distribution
- PdCo(I) and PdFe(I) samples show a narrow particle size distribution centered around 4 and 7 nm

Catalyst	Support	Pd loading (wt%)		S.A. (m <sup>2</sup> /g)	d <sub>n</sub> (nm)
		Nominal	XRF		
PdCo	CoO	5	37	106	10,7
PdFe	Fe <sub>2</sub> O <sub>3</sub>	5	87	170	2,4
PdZn	ZnO	5	52	85	2,7
PdNi	NiO	5	50	90	4,2
PdCo(I)	CoO	5	45	8	4,3
PdFe(I)	Fe <sub>2</sub> O <sub>3</sub>	5	55	6	7,1



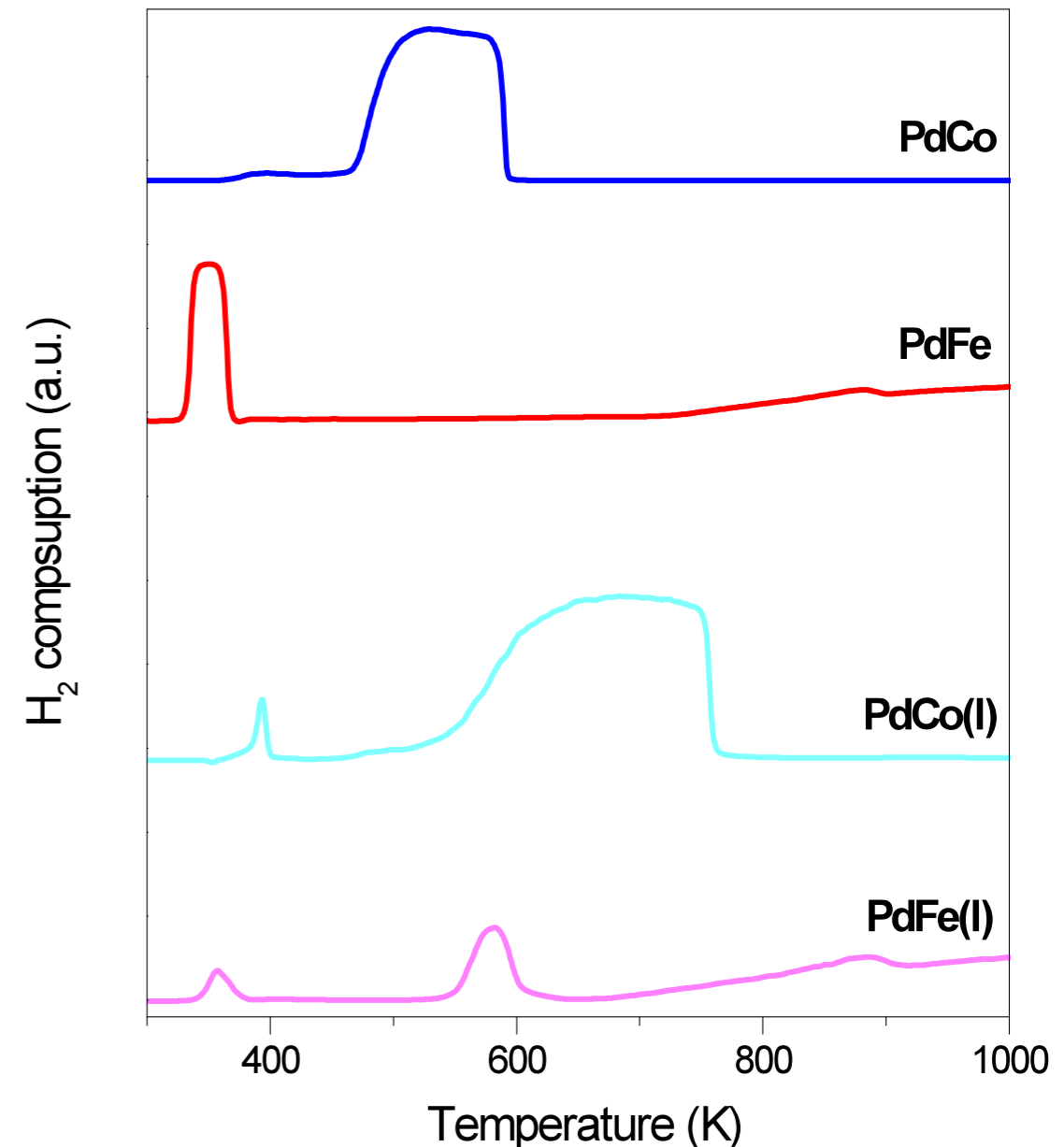


## Catalysts characterization

### ▶ TPR measurement

- ▶ Pre-reduced at 473 K for 2 h
- ▶ No negative peak, attributable to  $\beta$ -hydrides decomposition is observed on the TPR spectra
- ▶ **Impregnated catalyst:**
  - ▶  $\text{Pd}^{2+} \rightarrow \text{Pd}^0$  reduction and is close to that of  $\text{Pd}(\text{acac})_2$ , used as precursor in the catalysts preparation.
  - ▶ The second peak attains respectively to  $\text{Co}^{2+} \rightarrow \text{Co}^0$  and  $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$
- ▶ **Coprecipitated catalyst:**
  - ▶ PdFe shows an intense peak at  $\sim 350$  K including both  $\text{Pd}(\text{II}) \rightarrow \text{Pd}(\text{0})$  and  $\text{Fe}(\text{III}) \rightarrow \text{Fe}_3\text{O}_4$
  - ▶ PdCo shows a broad and intense peak including palladium and cobalt simultaneously reduced

metal-metal or a metal-support interaction occurs







## Catalysts characterization

### ▶ XPS measurement

#### ▶ Impregnated catalysts

- ▶ PdFe(I): haematite structure
- ▶ PdCo(I): CoO structure

Pd 3d<sub>5/2</sub> binding energy values close to value reported for Pd(0) [334.7] → a lack of Pd-support interaction

#### ▶ Coprecipitated catalysts

- ▶ PdFe: magnetite structure

Pd 3d<sub>5/2</sub> binding energy zone for PdNi and PdFe catalysts, can be attributed to a change in electronic density of palladium as consequence of metal-metal or metal-support interaction

Catalyst	Binding energy (eV)						
	Pd 3d <sub>5/2</sub>	Co 2p <sub>3/2</sub>	Fe 2p <sub>3/2</sub>	Fe 2p <sub>3/2</sub>	Fe 2p <sub>1/2</sub>	Zn 2p <sub>3/2</sub>	Ni 2p <sub>3/2</sub>
PdFe	335.2		710.9		724.4		
PdZn	334.9					1021.8	
PdNi	335.7						854.6
PdCo(I)	334.8	780.2					
PdFe(I)	334.8		710.4	718.4	723.8		

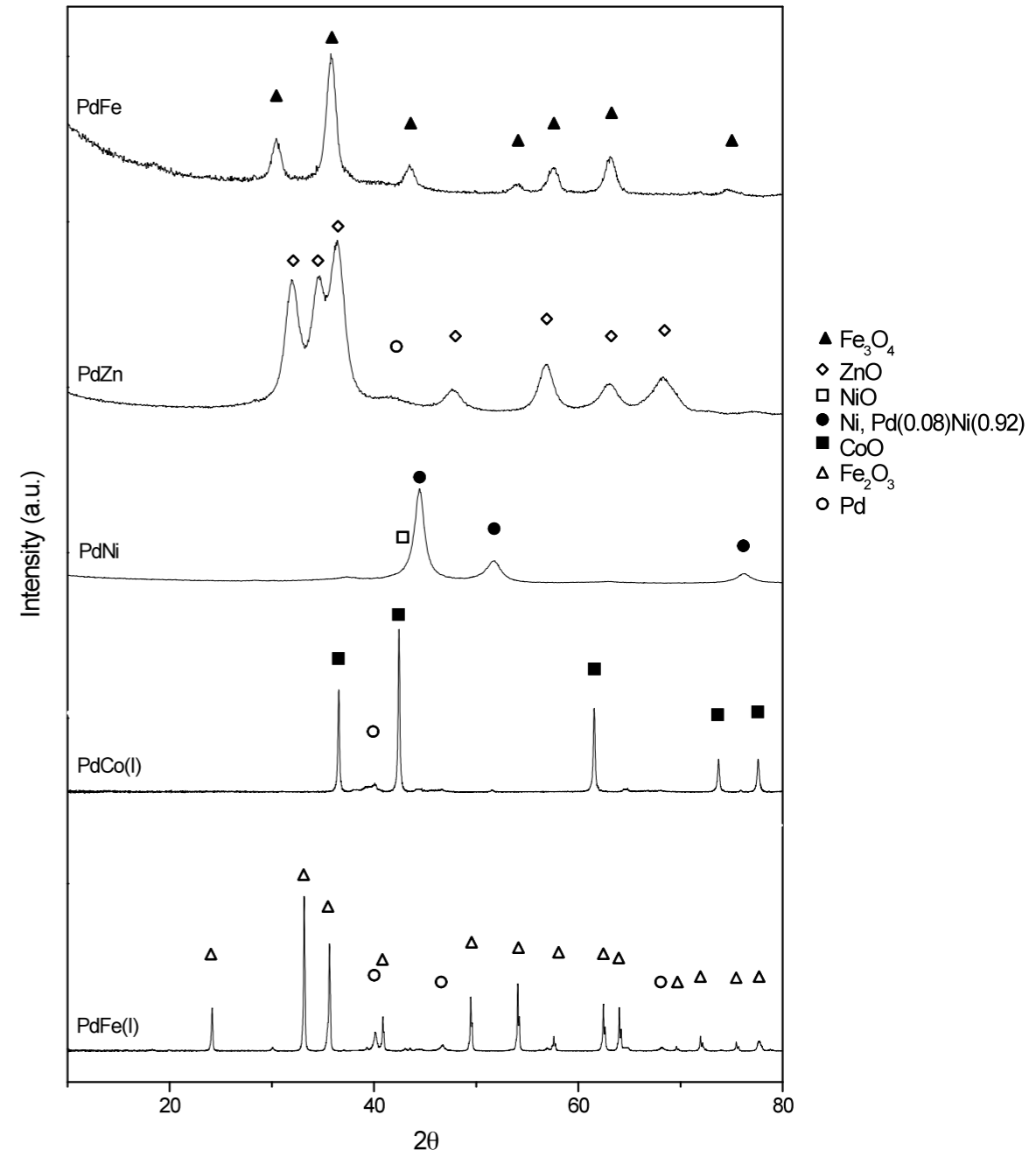




## Catalysts characterization

### ► XRD measurement

- Patterns referring to metal oxides carriers (NiO, ZnO, Fe<sub>3</sub>O<sub>4</sub> on co-precipitated samples and CoO and Fe<sub>2</sub>O<sub>3</sub> on impregnated catalysts) are easily detected.
- the peak located at  $2\theta = 40.1^\circ$  is observed on all catalysts (with the exception of PdNi and PdFe) corresponding to the most intense diffraction line of the (111) plane of metallic palladium
- PdNi, after deconvolution analysis, refer to both metallic nickel and a Pd(0.08)Ni(0.92) alloy





## Glycerol hydrogenolysis promoted by palladium catalysts

### ► Main aims:

- to test the efficiency of supported **palladium catalysts** in the hydrogenolysis of glycerol;
- to investigate the overall **mechanism of the reaction**
- to compare the results obtained with the best performing catalysts, prepared by the co-precipitation technique, with the analogous obtained using the impregnation method.
- To study the **solvent and temperature effect** on the conversion of glycerol and the selectivity
- to test the better performing catalyst on **large scale reaction** in order to verify possible industrial achievements.
- to investigate the production of propylene glycols from glycerol in **absence of added hydrogen**: the hydrogen necessary for the hydrogenolysis will be obtained from the dehydrogenation of the reaction solvent mediated by Pd catalysts





## Glycerol hydrogenolysis promoted by palladium catalysts

### ► Glycerol hydrogenolysis

- T= 453 K - 0.5 MPa H<sub>2</sub> pressure for 24 h - glycerol concentration: 4 wt% - Solvent: 2-propanol
- The activity changes following the order: PdCo > PdFe > PdZn ~ PdNi > PdCo(I) > PdFe(I).
- Generally 1,2-PDO is the main product and only a low selectivity to ethylene glycol (EG) is obtained

Catalyst	Conv. [%]	Selectivity					
		1,2-PDO	EG	1-PO	AC	1,3-PDO	OP
PdCo	100	10,2	1,9	80,9	-	-	7,0
PdFe	100	71,2	3,4	25,4	-	-	-
PdZn	93,6	59,2	-	3,3	19,4	6,3	11,8
PdNi	90,1	84,5	10,1	-	5,4	-	-
PdCo(I)	66,2	37,8	34,5	-	27,7	-	-
PdFe(I)	38,3	26,1	4,9	-	69,0	-	-

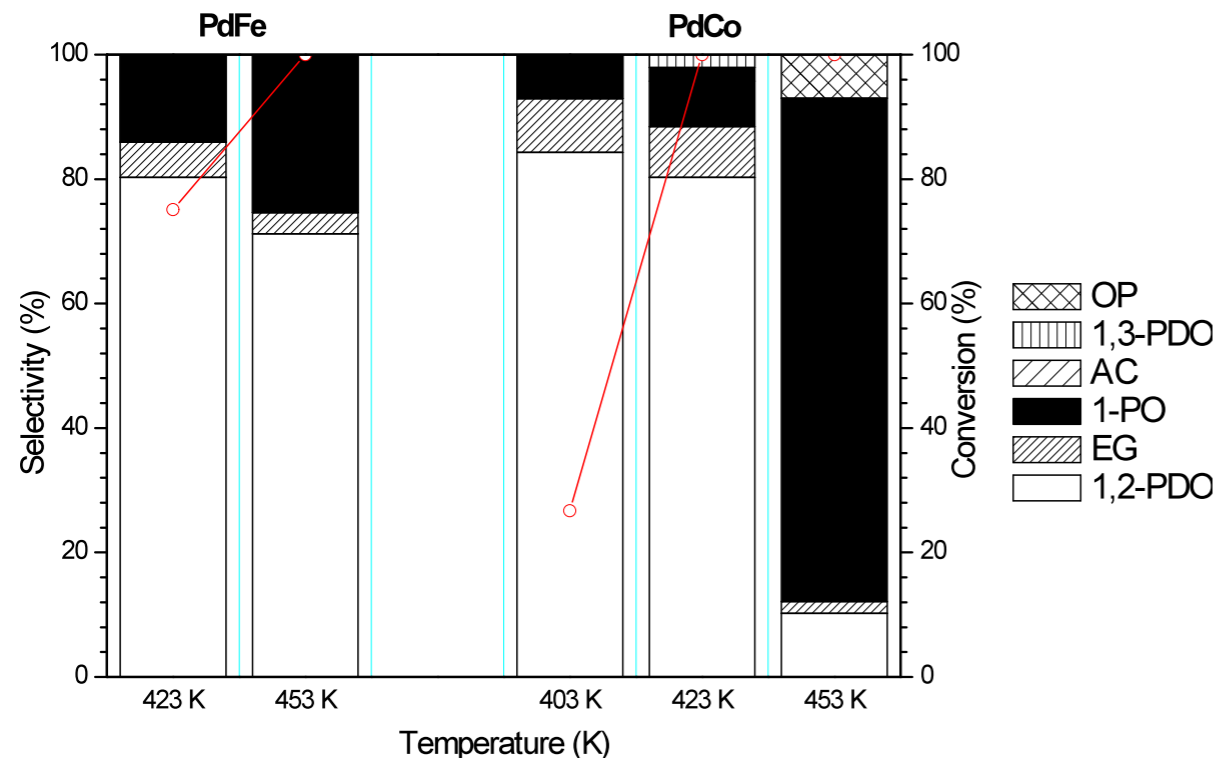
1,2-PDO = 1,2-propanediol; EG = ethylene glycol; 1-PO = 1-propanol; AC = 1-hydroxyacetone; 1,3-PDO = 1,3-propanediol; OP = other products.



# Glycerol hydrogenolysis promoted by palladium catalysts

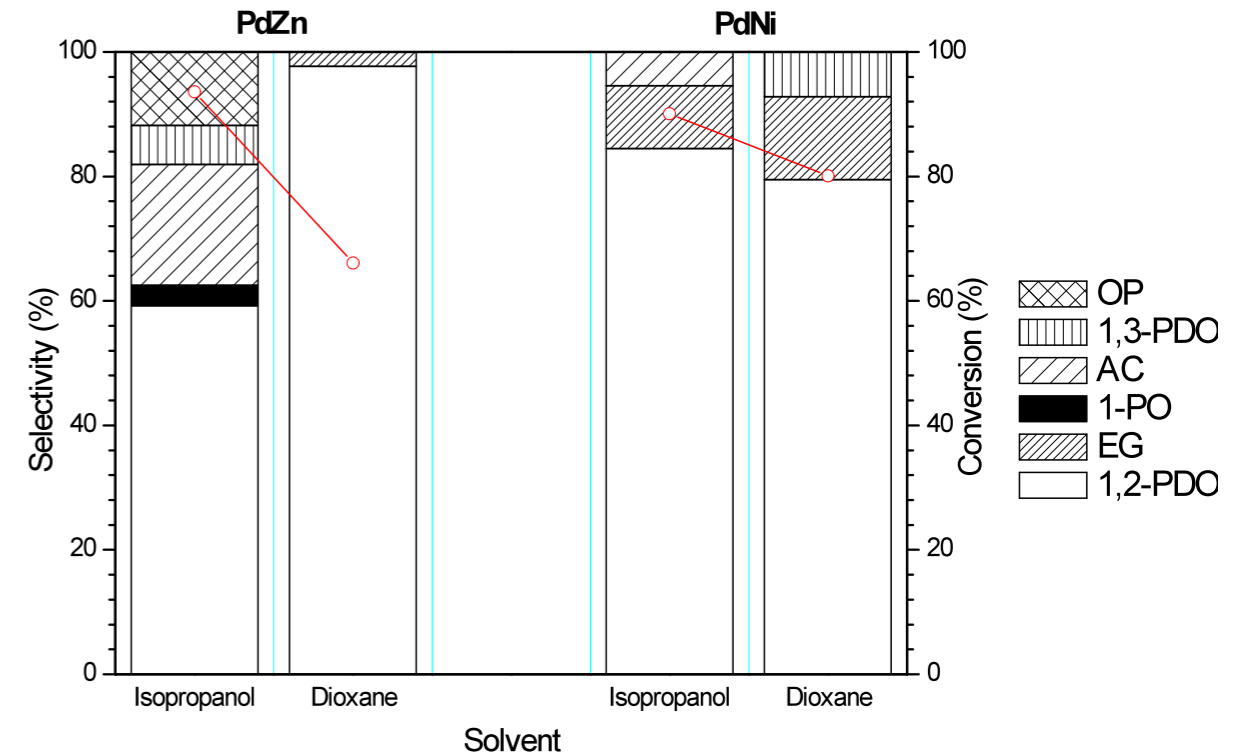
## ► Temperature effect

- At 423 K the conversion of PdCo is very high (100%) whereas that of PdFe drops to ~ 75% PdCo still maintains an appreciable conversion also at 403 K
- The selectivity to 1-PO drastically decreases at 423 K whereas that to 1,2-PDO (~ 80%) increases



## ► Solvent effect

- Good conversion and selectivity with all investigated coprecipitated catalyst using dioxane as solvent
- The hydroxylic and more polar 2-propanol favours the reaction better than the apolar dioxane.

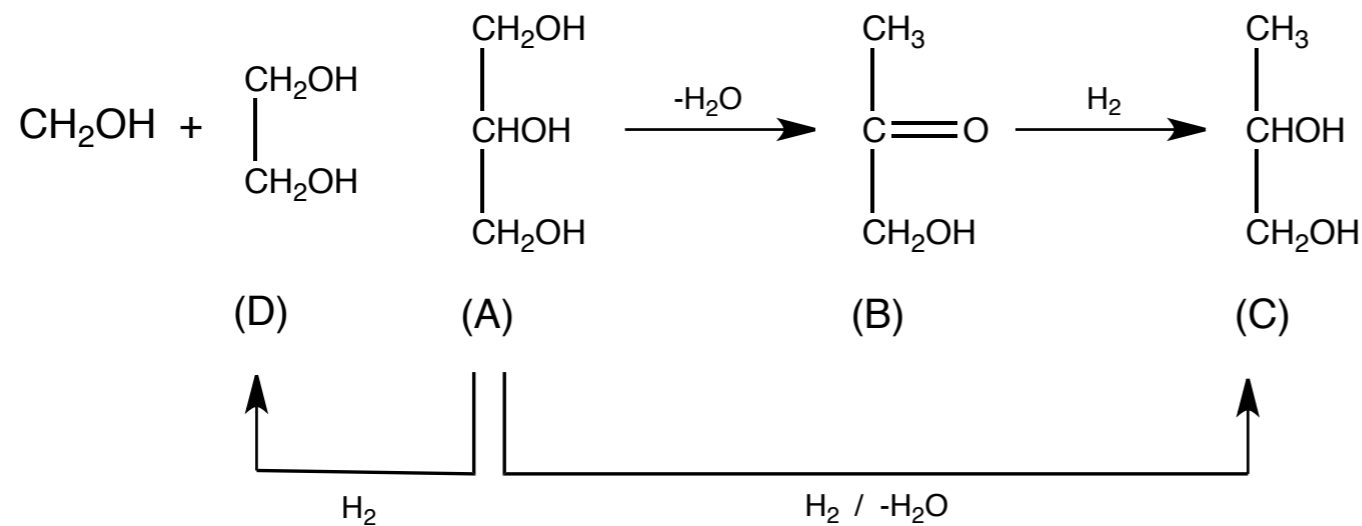




## Glycerol hydrogenolysis promoted by palladium catalysts

### ► The intimate hydrogenolysis mechanism

- how the dehydration process  $A \rightarrow B$  can occur in absence of Brønsted or Lewis acids?
- how a C-OH bond breaking and a C-H bond formation can occur together with the dehydration process?

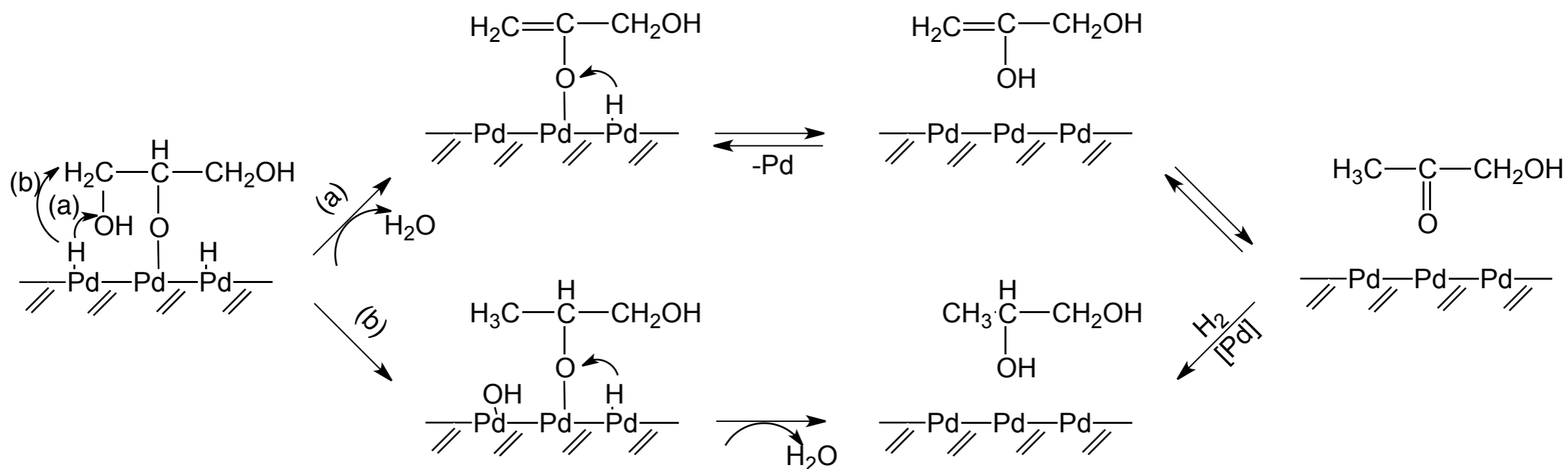




## Glycerol hydrogenolysis promoted by palladium catalysts

### ► The intimate hydrogenolysis mechanism

- an interaction between a palladium bonded hydrogen and a primary alcoholic group leading to a vinylic alkoxide, that rapidly converts to a vinylic alcohol and then rearranges to hydroxyacetone through a keto-enolic equilibrium (**route a**)
- the direct substitution of the carbon bonded OH group by an incoming hydrogen affording directly 1,2-propanediol (**route b**)



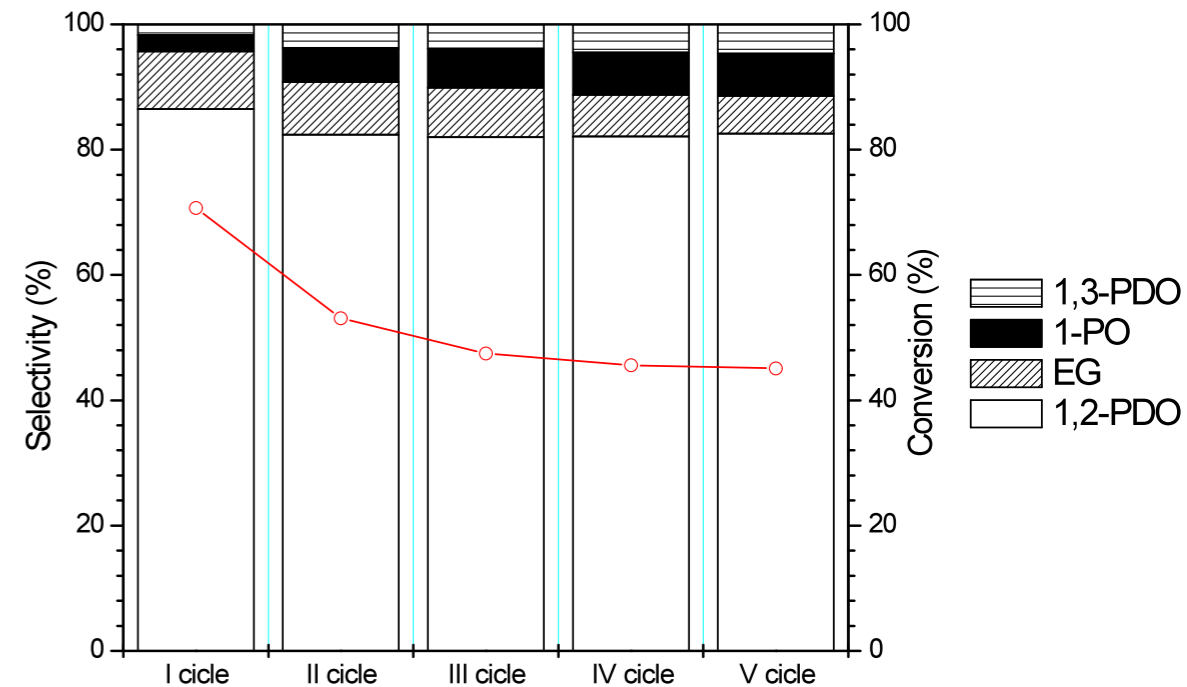


## Glycerol hydrogenolysis promoted by palladium catalysts

### ► Large scale reaction and Recycling of catalysts

- Initial molar ratio of  $H_2$ /glycerol=1 at 4 MPa initial pressure of  $H_2$
- The best conversion (70,7%) was obtained with PdCo.
- A good selectivity towards 1,2-PDO (86,5%) was also detected with PdCo whereas that of PdFe is only 40.2%.
- Further recycles of the catalyst demonstrate potential **practical applicability of the co-precipitated Pd/CoO and Pd/Fe**

Catalyst	Conversion	Selectivity			
		1,2-PDO	EG	1-PO	1,3-PDO
PdCo	70,7	86,5	9,2	2,6	1,7
PdFe	42,8	90,2	2,5	5,7	-



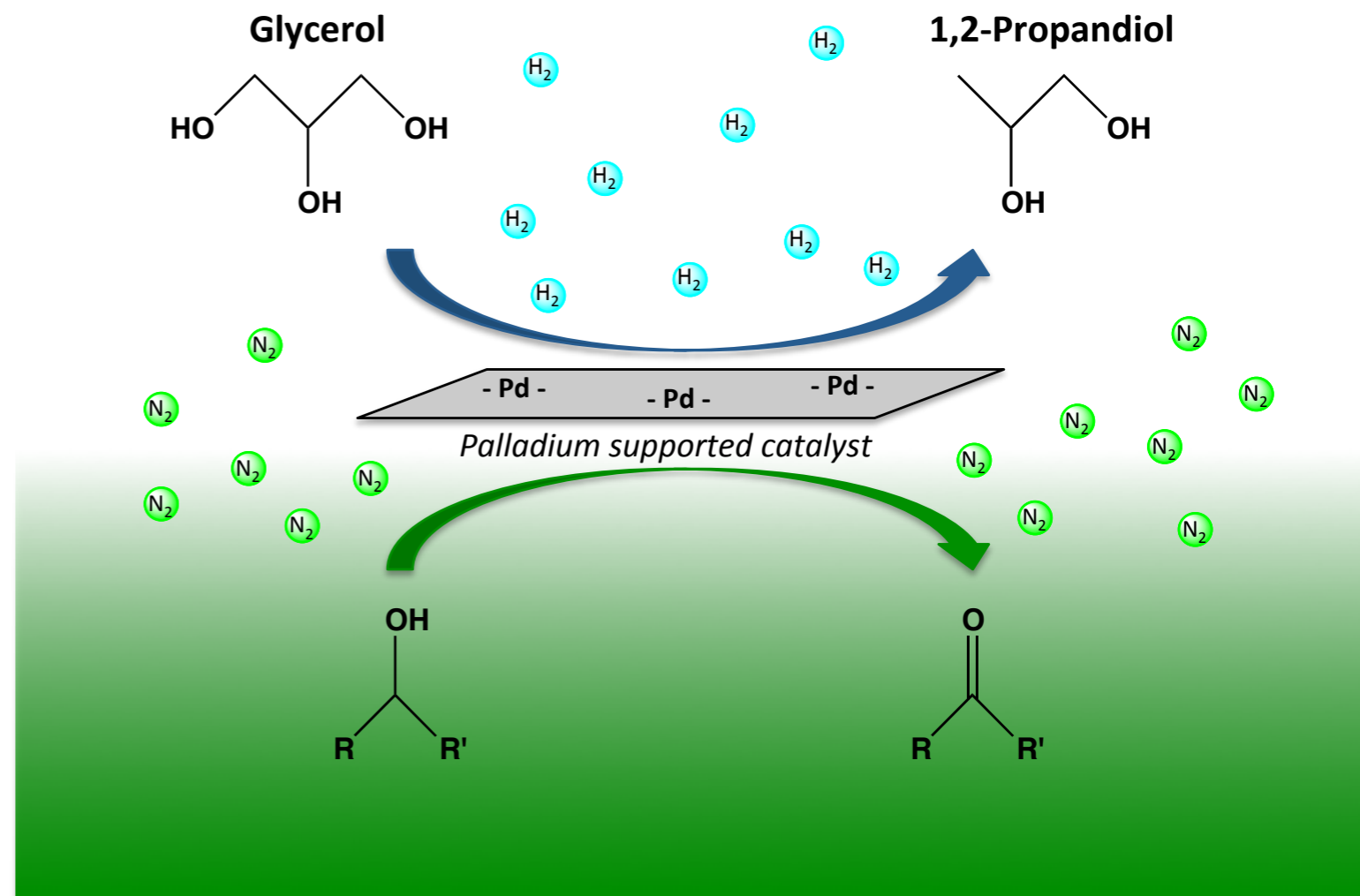




## Selective transfer hydrogenolysis

### ► Selective transfer hydrogenolysis

- In situ hydrogen production, obtained by the **dehydrogenation of the reaction solvent**
- **costs reduction** related to the purchase, transport and storage of the hydrogen;





## Selective transfer hydrogenolysis

### ▶ Selective transfer hydrogenolysis

- ▶ T= 453 K - 0.5 MPa N<sub>2</sub> pressure for 24 h
- ▶ glycerol concentration: 4 wt%
- ▶ Solvent: 2-propanol

Catalyst	Conv. [%]	Selectivity				
		<i>1,2-PDO</i>	<i>EG</i>	<i>1-PO</i>	<i>AC</i>	<i>OP</i>
PdCo	100	66,5	4,6	28,9	-	-
PdFe	100	86,6	4,6	9,0	-	-

### ▶ Large scale reaction

- ▶ T= 453 K - 4 MPa N<sub>2</sub> pressure for 24 h
- ▶ 45 wt% glicerol
- ▶ Solvent: 2-propanol
- ▶ The best conversion (60%) was obtained with PdCo.

Catalyst	Conv. [%]	Selectivity				
		<i>1,2-PDO</i>	<i>EG</i>	<i>1-PO</i>	<i>AC</i>	<i>OP</i>
PdCo	60	55,4	6,4	8,9	9,5	19,8





## Conclusions

- ▶ High conversion and selectivity in the hydrogenolysis of glycerol can be easily obtained by choosing an **appropriate preparation technique of the catalysts**: in co-precipitated samples a good palladium-support (metal) interaction favours a better performance.
- ▶ The best performance, in terms of conversion and selectivity to 1,2-propanediol, was obtained with **co-precipitated Pd/CoO and Pd/Fe<sub>2</sub>O<sub>3</sub> catalysts**
- ▶ **Hydroxyacetone** was detected using PdZn, PdNi, PdCo(I) and PdFe(I) catalysts confirming that it is an **intermediate** in glycerol hydrogenolysis, and is involved in the intimate mechanism.
- ▶ Selective **conversion of glycerol** into 1,2-propanediol, under **inert atmosphere**, is reported for the first time; the hydrogen necessary for the hydrogenolysis reaction derives from the **dehydrogenation of the solvent**
- ▶ The better performing samples (PdCo and PdFe) were tested on a **large scale reaction** at a higher H<sub>2</sub> pressure (4 MPa) and under inert atmosphere. In addition, after several recycles PdCo appears an efficient catalyst suitable to be used on industrial scale.



## Future Perspectives

- ▶ **Objective 1:** to study the selective **hydrogenolysis of biomass-derived C3-C5 polyols** for the production of ethylene glycol and propylene glycols under mild conditions;
- ▶ **Objective 2:** to understand the **molecular aspects of the hydrogenolysis of C3-C5 polyols** to propylene glycols which, at present, are not completely clarified also through a deep examination, by ab-initio calculation, of all possible modes of adsorption of the six selected polyols on the catalytic surface.
- ▶ **Objective 3:** to develop a self-sustainable process for as it concerns hydrogen supply, in order to reduce the costs related to hydrogen purchase, transport, and storage;
- ▶ **Objective 4:** the synthesis and the characterization of innovative **heterogeneous bimetallic catalysts** that, by improving yield and selectivity, would make the reaction economically and environmentally attractive;
- ▶ **Objective 5:** testing of the catalysts and evaluation of the effect on the selective conversion of polyols into propylene glycols of various parameters, such as the nature of the support and of the metal used, the size of metal particles, the reaction temperature and the partial hydrogen pressure;

