Produzione catalitica di Bulk Chemicals a partire da Biomasse

Dr. Francesco Mauriello, PhD

Dipartimento DICEAM Università degli Studi "Mediterranea" di Reggio Calabria email: <u>francesco.mauriello@unirc.it</u>

Chemical 2040 themes at a glance

- Chemicals are an integral part of modern daily life. There is hardly any industry where chemical substances are not used and there is no single economic sector where chemicals do not play an important role.
 - Productions of bulk chemicals (Projection 2012-2040)



Chemical 2040 themes at a glance

- Demand growth in Asia Asian chemical markets are clearly the center of gravity for chemical industry growth and investment. A disciplined and realistic strategy to achieve profitable growth is key to success.
- Petrochemical supply growth in the Middle East Middle East economic advantage in petrochemicals will decline over the next decade as low opportunity cost ethane is committed. Understanding feedstock costs and positioning will be critical to future business and investment planning.
 - "Greening" of the chemical industry Sustainability has moved beyond corporate social responsibility and regulatory compliance to become a strategic issue driving business growth. Businesses are beginning to integrate sustainable development principles into top-line growth and investment plans.

Biomass

- **"Biomass"** is biological material derived from living, or recently living organisms. More in general, we can define biomass as a biological material with a organic matrix.
- Promotion of the use of energy from renewable sources: the Directive
 2009/28/EC establishes a common framework for the use of energy from
 renewable sources in order to limit greenhouse gas emissions and to
 promote cleaner transport. To this end, national action plans are defined,
 as are procedures for the use of biofuels.

Green Chemical Markets 2011-20



Lignocellulosic biomass

- The term "biomass" most often refers to plants or plant-based materials which are specifically called lignocellulosic biomass.
 - Plant material consists of lignocellulose
 - cellulose (40-50%) (a polymer of glucose)
 - hemicellulose (10–20%), a polymer of various sugar monomers including glucose, xylose, mannose, galactose, rhamnose, and arabinose,
 - lignin (20–30 %), an aromatic polymer



Lignocellulosic Biomass



Valorization of platform chemicals - Oxygen removal

- Platform chemicals coming from biomass usually contain higher O/ C ratio than most commodity chemicals
- The high presence of oxygen, makes biomass derived chemicals acidic and unstable (high reactivity of the oxygenated functional groups); thus main valorization processes require the removal of oxygen.
- This is a significant aspect, because, in those processes where the starting and target molecule have the same number of carbons it is important to use catalytic systems that present high activity in C-O bond cleavage while low activity in C-C bond breaking!



Hydrogenolysis Reaction

- In terms of an exact definition, hydrogenolysis describes a chemical reaction whereby carbon–carbon or carbon–heteroatom single bonds are cleaved or undergo "lysis" by hydrogen.
 - The definition does not imply any mechanistic considerations, but refers to the stoichiometry of the reaction, which may be summarized as:

$R-X + H_2 \rightarrow R-H + H-X$

where X can represent an alkyl chain or other functional group containing heteroatoms, for example, OH, OR, SH, NH₂, NR, etc.

Cellulose as feedstock

- Cellulose is the major part of lignocellulose and the most abundant biopolymer. Consequently, its utilization for the production of chemicals and fuels would be highly desirable.
- Cellulose is a polymer composed of glucose units linked by β-1,4-glycosidic bonds. Glucose can be easily obtained via the hydrolysis of cellulose.



Cellulose as feedstock

Catalytic hydrolysis of cellulose

Catalyst	Catalyst Pretreatment of cellulose		T/K	Time/h	Conv./%	Yield/%	
						Glc ^b	Olg ^c
Amberlyst 15DRY	Microcrystalline	5.0	373	5	29	0.9	0.6 ^k
C–SO ₃ H-IL	Microcrystalline	2.0	363	2	nd ⁱ	33 ^j	nd ⁱ
$Sn_{0.75}PW_{12}O_{40}$	Ball-milled	0.9	423	2	23	23 ^j	nd ⁱ
$H_5BW_{12}O_{40}$	Microcrystalline ^f	0.3	333	48	nd ⁱ	77	5 ^k
C–SO₃H	Microcrystalline	0.083	373	3	nd ⁱ	4	64
AC−SO ₃ H	Ball-milled	0.9	423	24	nd ⁱ	41	nd ⁱ
SiO ₂ –C–SO ₃ H	Ball-milled	1.0	423	24	61	50	2
CMK-3–SO ₃ H	Ball-milled	0.9	423	24	94	75	nd ⁱ
Fe ₃ O ₄ –SBA–SO ₃ H	[BMIM]Cl	0.7	423	3	nd ⁱ	50	nd ⁱ
Fe ₃ O ₄ –SBA–SO ₃ H	Microcrystalline	1.0	423	3	nd ⁱ	26	nd ⁱ
$CoFe_2O_4/SiO_2-SO_3H$	[BMIM]Cl	1.0	423	3	nd ⁱ	7.0	30 ^j
CP–SO ₃ H	Microcrystalline	0.2	393	10	nd ⁱ	93	nd ⁱ
2.0 wt% Ru/CMK-3	Ball-milled	6.5	503	0.83 ^g	56	24	16
CMK-3	Ball-milled	6.5	503	0.83 ^g	54	16	5
MC	Ball-milled	3.3	518	0.75 ^h	71	41	0.9 ^k

Hydrogenolysis of sugars

- Two types of sugars are can be easily obtained from cellulose and hemicellulose: hexoses (six-carbon sugars), of which glucose is the most common one, and pentoses (five-carbon sugars), of which xylose is the most common one.
 - Glucose and xylose can be easily hydrogenated to yield sorbitol and xylitol.



Sorbitol and xylitol hydrogenolysis

Sorbitol and xylitol hydrogenolysis: These two molecules can undergo C-C and C-O hydrogenolysis in the presence of hydrogenation catalysts, leading mainly to a mixture of ethyleneglycol, glycerol, and 1,2-propanediol. Other (butanediols, lactic acid, methanol, ethanol and propanol) can also be formed.



Source: R. Palkovits et al. Angew. Chem. Int. Ed. 2012, 51, 2564 – 2601

Glycerol

Glycerol can be obtained from hydrogenolysis of sorbitol. However, it is also a byproduct of the production of biodiesel via transesterification. This form of crude glycerin is often dark in appearance with a thick, syrup-like consistency. Triglycerides are treated with an alcohol (methanol) with catalytic base to give ethyl esters of fatty acids and glycerol.



Biodiesel

Biodiesel production and use

- Biodiesel is an alternative fuel similar to 'fossil' diesel.
- Biodiesel can be used in pure form (B100) or may be blended with petroleum diesel at any concentration in diesel engines.
- 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.
 - Biodiesel has higher production costs than conventional fuels tax reductions

	BIODIESEL	DIESEL
Pure sales price	\$1	\$ 0 <i>,</i> 8
Excise duty	\$ 0,08	\$ 0,4
Vat	\$ 0,22	\$ 0,22
Total Price	\$ 1,29	\$ 1,32

Glycerol

The "case" of glycerol

- For every 9 kg of biodiesel, about 1 kg of glycerol is formed
- 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 world production by feedstock

Glycerol hydrogenolysis

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



- **1,2-PD** is an important chemical commodity used for polyester resins, liquid detergents, pharmaceuticals, cosmetics, tobacco humectants, flavours and fragrances, etc.
- **1,3-PD** 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 to PDOs consists of hydrogen addition and removal of one oxygen atom in the form of H₂O. In order to design efficient catalysts, it is fundamental to understand the mechanism of this reaction. Three main reaction mechanisms have been proposed in the literature, depending on whether the reaction runs on acid or basic catalytic sites and with or without the formation of intermediate compounds:
- dehydrogenation dehydration hydrogenation (glyceraldehyde route),
- dehydration-hydrogenation.
- direct glycerol hydrogenolysis

Glyceraldehyde route

One of the first studies related to glycerol hydrogenolysis was developed by Montassier et al. in the late 1980s. They suggested that over Ru/C catalyst glycerol is first dehydrogenated to glyceraldehyde on the metal sites. Next, a dehydroxylation reaction takes place by a nucleophilic reaction of glyceraldehyde with water or with adsorbed -OH species. Finally, hydrogenation of the intermediate yields 1,2-PDO.



The main controversial point of this mechanism is the initial dehydrogenation step, which is thermodynamically unfavored due to the high hydrogen pressures used. Therefore, in order to shift the equilibrium, glyceraldehyde dehydration should be faster than glycerol dehydrogenation. Otherwise glyceraldehyde would be hydrogenated back to glycerol on the metal sites. Several authors observed that the addition of a base notably increased glycerol conversion, and this was related to the fact that bases enhance glyceraldehyde dehydration.

Dehydration-hydrogenation route

Dasari et al. observed the <u>formation of acetol (hydroxyacetone)</u> together with 1,2-PDO using copper-chromite catalyst at 473 K and 15 bar hydrogen pressure. Moreover, glycerol hydrogenolysis to 1,2-PDO occurred even in the absence of water. Since the copper-chromite catalyst was reduced in a stream of hydrogen prior to the reaction, no surface hydroxyl species were present to take part in the reaction. Therefore, the mechanism suggested by Montassier et al. was not able to explain these results. Dasari et al. proposed a new mechanism in which glycerol is first dehydrated to acetol, which is further hydrogenated to 1,2-PDO.



Based on their findings, a two step process was developed. In the first step, acetol is generated from glycerol dehydration by a reactive distillation process, operating at 513 K, slight vacuum and using copper-chromite catalyst. The acetol obtained is then hydrogenated at 15 bar H₂ pressure using the same catalyst. The process was patented in the USA in 2005

Direct glycerol hydrogenolysis

A direct glycerol hydrogenolysis mechanism was recently proposed by Yoshinao et al. The experiments were carried out using Rh-ReOx/SiO₂ and Ir-ReOx/SiO₂ catalysts at 393 K and 80 bar H₂ pressure. The low reaction temperature implies that the dehydration-hydrogenation route was not further possible, due to the endothermic character of glycerol dehydration and the required activation energy, and suggests the energetically more favored direct hydrogenolysis reaction. They suggested a direct hydride-proton mechanism.



Direct glycerol hydrogenolysis

A different direct glycerol hydrogenolysis mechanism was established by Chia et al. trying to explain the hydrogenolysis of different polyols and cyclic ethers over a Rh-ReOx/C catalyst. They concluded from DFT calculations that the -OH groups on Re associated with Rh are acidic. Such acidic Re sites can donate a proton to the reactant molecule and form carbenium ion transition states. In the case of glycerol hydrogenolysis, the first step involves the formation of a carbocation by protonation-dehydration reaction. This carbocation is stabilized by the formation of a more stable oxocarbenium ion intermediate resulting from the hydride transfer from the primary -CH2OH group. Final hydride transfer step leads to 1,2-PDO or 1,3-PDO. The authors also reported that the secondary carbocation is more stable than the primary carbocation. Nevertheless, higher selectivity to 1,2-PDO was obtained (1,3-PDO/1,2-PDO ratio = 0.65).



Glycerol hydrogenolysis promoted by heterogeneous catalysts

Catalyst	Conditions	Main product(s)	Conversion [%]	Selectivity [%]	
CuO-Cr ₂ O ₃	250°C; 200 bar	1,2-PG	_	85 (yield)	
Raney Cu	240 °C, 30 bar	1,2-PG	85	78	
Cu/C	260°C, 40 bar, 65 h	1,2-PG	43	85	
Cu-ZnO, H ₂ WO ₄	180 °C, 80 bar, 90 h	1,2-PG	21	81	
Cu-ZnO	180°C, 80 bar, 90 h	1,2-PG	19	100	
Cu/γ-Al ₂ O ₃	200 °C, 36 bar, 10 h	1,2-PG	34	94	
Cu-H ₄ SiW ₁₂ O ₄₀ /SiO ₂	210°C, 5.4 bar	1,3-PG	84	32	
Na-CuO/SiO ₂	180°C, 90 bar, 12 h	1,2-PG	41	94	
Ru/Al_2O_3 (from $RuCl_3 \cdot H_2O$)	240°C, 80 bar, 5 h	1,2-PG	69	38	
Ru/SiO_2 (from $RuCl_3 H_2O$)	240°C, 80 bar, 5 h	1,2-PG	25	50	
Ru/ZrO_2 (from $[RuNO(NO_3)_3]$)	240°C, 80 bar, 5 h	1,2-PG	40	60	
Ru/SiO_2 (from $[RuNO(NO_3)_3]$)	240°C, 80 bar, 5 h	1,2-PG	22	60	
Ru/hydrotalcite	180°C, 25 bar	1,2-PG	59	86	
Ru/NaY	180°C, 50 bar, 12 h	1,2-PG	10	37	
Ru/γ-Al ₂ O ₃	180°C, 50 bar, 12 h	1,2-PG	34	47	
Ru/SiO ₂	180°C, 50 bar, 12 h	1,2-PG	3	55	
Ru/TiO ₂	180°C, 50 bar, 12 h	1,2-PG	66	47	
Ru/Cs _{2.5} H _{0.5} [PW ₁₂ O ₄₀]	3–14 bar, no external heating	1,2-PG	21	96	
$Ru/C, Nb_2O_5$	180°C, 60 bar, 8 h	1,2-PG	45	61	
Ru/TiO ₂	180°C, 60 bar, 8 h	1,2-PG	46	63	
Ru/C	190 °C, 90 bar, 7 h	1,2-PG	20	22	
Ru/TiO ₂	190°C, 90 bar, 1 h	1,2-PG	20	45	
Ru/C	200°C, 40 bar, 5 h	EG	40	47	
Ru/C, NaOH	200°C, 40 bar, 5 h	LA	100	34	
Ru/C, CaO	200°C, 40 bar, 5 h	LA	85	48	
PtRu/C	200°C, 40 bar, 5 h	EG	42	49	
PtRu/C, NaOH	200°C, 40 bar, 5 h	LA	100	37	
Ru-Re/SiO ₂	160°C, 80 bar, 8 h	1,2-PG	51	45	
$Ru/C + Re_2(CO)_{10}$	160 °C, 80 bar, 8 h	1,2-PG	59	57	
Ru-Cu(3:1)/BEN-TMGL	230 °C, 80 bar, 18 h	1,2-PG	100	86	
Rh-ReO _v /SiO ₂	120°C, 80 bar, 5 h	1,2-PG	98	48	

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/SiO₂≅1%).
- However, co-precipitation technique generally leads to a better interaction between metal and support than that observed using the impregnation method.



>> induced carbonyl activation <<



Pd-Me catalyst

(B)



Glycerol hydrogenolysis promoted by palladium catalysts

- T= 453 K 0.5 MPa H₂ 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	ОР				
PdCo	100	10,2	1,9	80,9	-	-	7				
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	-	-				

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.

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.



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 vynilic 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)



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 demonster potential practical applicability of the co-precipitated Pd/CoO and Pd/Fe

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



Selective transfer hydrogenolysis of glycerol

- 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 of glycerol

Selective transfer hydrogenolysis

- T= 453 K 0.5 MPa N₂ pressure for 24 h
- glycerol concentration: 4 wt%
 - Solvent: 2-propanol

Catalyst	Conv. [%]		S			
		1,2-PDO	EG	1-PO	AC	ОР
PdCo	100	66,5	4,6	28,9	-	-
PdFe	100	86,6	4,6	9	-	-

Large scale reaction

- T= 453 K 4 MPa N₂ pressure for 24 h
- 45 wt% glicerol
- Solvent: 2-propanol
- The best conversion (60%) was obtained with PdCo.

Catalyst	Conv. [%]		S			
	1,2-PDO		EG	1-PO	AC	ОР
PdCo	60	55,4	6,4	8,9	9,5	19,8

Catalytic Transfer Hydrogenation

- Catalytic transfer hydrogenation (CTH) is a process in which hydrogen is transferred from a hydrogen donor molecule to an acceptor. CTH reactions can be of industrial importance as the renewable production, transportation and storage of hydrogen donors can be cheaper than those for molecular hydrogen.
- The best hydrogen donors for heterogeneous CTH include simple molecules like cyclohexene, hydrazine, formic acid and formates.
- Alcohols like 2-propanol (2-PO) or methanol can also be used as hydrogen donors; primary alcohols are generally less active than the corresponding secondary alcohols due to the smaller electron-releasing inductive effect of one alkyl group as against two.

Hydrogenolysis with in-situ generation of hydrogen

Aqueous Phase Reforming (APR)

One interesting option to in situ generate the required hydrogen for hydrogenolysis reactions is through aqueous phase reforming (APR). APR is a quite well known process in which a polyol is converted to hydrogen and CO₂ in the presence of water. The hydrogen generated can be further used in the hydrogenolysis reaction. The specific case for combined glycerol APR and hydrogenolysis to 1,2-PDO is shown in Figure. If the process is perfectly balanced, glycerol is fully converted into 1,2-PDO, being CO₂ and H₂O the only byproduct



Hydrogenolysis with in-situ generation of hydrogen

Aqueous Phase Reforming (APR) of glycerol

	Т	Þ	С	t	$X^{\mathrm{a})}$		
Catalyst	(K)	(bar)	(wt%)	(s)	(%)	Y	Remarks
Noble metal catalysts							
3Pt3Re/C	498	29	10		89	41	WHSV = 5 h ⁻¹ ; $S = 26\%$, H ₂ productivity = 1246 l/(l _{cat} h)
3%Pt/Al ₂ O ₃	538	56			99	51	31% alkane selectivity; LHSV = 0.64 h^{-1}
Pt/Al ₂ O ₃	523	20	10		n.a.		0.5 mL/min, 300 mg catalyst, $S(H_2) = 95\%$; only TOFs are presented; Ar in feed
Pt-Re/C	498		10		68		200 mg catalyst 20 mL/min N ₂ , WHSV = 6 h^{-1}
3%Pt/Al ₂ O ₃	498	29	20		90	56	50–160 mg catalyst, 3–38 wt% Pt, 26–45 bar
Pt/Al_2O_3	513	35	5-10			75	1–2 g catalyst, 50–100 μ L/min, 30 mL/min N ₂
Pt/Al_2O_3	493	25	5-10		42	40	0.05 mL/min, 1 g catalyst, LHSV = 1.56 h^{-1}
Other monometallic o	catalysts						
Ni/Al ₂ O ₃	498	30					Modified with Mg, Ce, La, Zr, WHSV = $1.25 h^{-1}$, data after 2.5 h TOS
Other bimetallic catal	lysts						
Ce-Ni-Co	493	25	5		58	64	1 g catalyst; feed 50 μL/min
$Ra\text{-}Ni_{14}Sn/Al_2O_3$	538	51.9			100	76	Alkanes 17%; LHSV = 10.3 h^{-1}

^{a)} Carbon conversion.

Lignin hydrogenolysis

Selective cleavage of the CAr-O bond of lignin model compounds has been so far generally limited to the use of homogeneous Ni catalysts.
The molecular catalysts offer a good chemoselectivity in the selective cleavage of CAr-O bonds under mild reaction conditions (80-150°C).
Unfortunately, their removal from reaction media is difficult and uneconomical. Moreover their reuse is rarely practiced.

Heterogeneous catalysts, on the other hand, are not very selective and require higher reaction temperatures or hydrogen pressures, leading to the reduction of arene functionalities and subsequent hydrogen consumption. In recent years, heterogeneous catalysts have found potential application in the selective cleavage of the CAr-O bond preserving the aromatic ring functionality. However the heavy catalyst loading, the high hydrogen pressure and the substrate specificity limit their use at an industrial scale. Hence, the selective CAr-O bond breaking process in lignin model molecules remains extremely challenging, especially in the fine green-chemical industry and in the energy industries.



Lignin hydrogenolysis

Selective, Nickel-Catalyzed Hydrogenolysis of Aryl Ethers

- This process is catalyzed by a soluble nickel carbene complex under just 1 bar of hydrogen at temperatures of 80 to 120°C.
- Hydrogenolysis of lignin model compounds highlights the potential of this approach for the conversion of refractory aryl ether biopolymers to hydrocarbons.



SIPr·HCI

Alexey G. Sergeev, et al. Science 332, 439 (2011);

	R^1 R^2	+ H ₂ (1 bar)	5-20% N 10-40% S NaO ^f Bu, Temp,	li(COD) ₂ , <u>SIPr·HCI</u> <i>m</i> -xylene, Time	+ R ¹ +	HO	2
Entry	Diaryl ether	Ni, mol%	T, °C	Time, h	Conversion, %	Arene, %	Phenol, %
1		20	120	16	100	99	99
2		10	120	32	87	82	87
3		5	120	32	59	59	54
4	Me	20	120	16	100	96	99
5	MeO	e 20	120	16	94	88*	86†
6	Me	20	120	48	100	97	99
7		20	120	48	74	72	73
8	F ₃ C	10	100	16	100	87§	99
9		10	100	16	100	87 ¹¹	92
	F ₃ C ⁻ OM	e					
10	OM	20 e	120	16	100	88¶	80#
11	Me Me	20	120	32	85	85	85

*Anisole (65%) and benzene (23%). †3-Methoxyphenol (83%) and phenol (3%). ‡Trifluoromethylbenzene (64%) and toluene (23%); benzene (4%) as a side product. §Trifluoromethylbenzene (68%) and toluene (19%). ||Anisole (4%) as a side product. ¶Phenol (17%) as a side product.

Green Chemical Markets 2011-20



Green Chemical Market by Region, World Markets: 2011-2020

Chemistry can help to create a more sustainable planet.

Chemist will play a crucial role in the development of a new economy!

Thank you very much for your attention!



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 Pd(Fe) samples show a narrow particle size distribution centered around 4 and 7 nm

Catalyst	Support	Pd loadin	g (wt%)	S.A. (m	d
		Nominal XRF			
PdCo	CoO	5	37	106	10,7
PdFe	Fe	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	5 55		6	7,1









Catalysts characterization

XRD measurement

- Patterns referring to metal oxides carriers (NiO, ZnO, Fe3O4 on co-precipitated samples and CoO and Fe2O3 on impregnated catalysts) are easily detected.
- the peak located at 2t= 40.1° 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





Catalysts characterization

TPR measurement

- Pre-reduced at 473 K for 2 h
- No negative peak, attributable to β-hydrides decomposition is observed on the TPR spectra
- Impregnated catalyst:
 - Pd²⁺ → Pd⁰ reduction and is close to that of Pd(acac)₂, used as precursor in the catalysts preparation.
 - The second peak attains respectively to Co²⁺ → Co⁰ and Fe₂O₃ → Fe₃O₄
- Coprecipitated catalyst:
 - ▶ PdFe shows an intense peak at ~ 350 K including both Pd(II) → Pd(0) and Fe(III) → Fe₃O₄
 - 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	Catalyst			Bind	ing energ	v (eV)		
 PdFe(I): haematite structure PdCo(I): CoO structure 		Pd 3d	Co 2p	Fe 2p	Fe 2p	Fe 2p	Zn 2p	Ni 2p
Pd $3d_{5/2}$ binding energy values close to value reported for Pd(0) \rightarrow a lack of Pd-support	PdFe	335.2		710.9		724.4		
interaction	PdZn	334.9					1021.8	
	PdNi	335.7						854.6
 Coprecipited catalysts PdFe: magnetite structure 	PdCo(I)	334.8	780.2					
	PdFe(I)	334.8		710.4	718.4	723.8		
Pd 3d5/2 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								

