Reductive catalytic routes towards sustainable production of hydrogen, fuels and chemicals from biomass derives polyols

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Abstract

Biomass derived polyols represent one of the most attractive resources for modern bio-refineries that need renewable feedstocks directly convertible into building blocks, biofuels and energy carriers reducing, at the same time, CO_2 emissions. To this regard, in the past two decades, the reductive catalytic conversion of polyols via hydrogenation, dehydrogenation, hydrogenolysis and aqueous phase reforming processes has received more and more attention allowing the sustainable production of important products such as glycols, alkanes and H_2. In this contribution, the state of the art in the processing of biomass derived C6 and C5 polyols, namely sorbitol and xylitol, to produce added value chemicals, fuels and energy (H_2) is reviewed highlighting the most reliable and promising catalytic systems used so far merging, at the same time, the reaction conditions adopted for obtaining a target products starting from sorbitol and xylitol. The final aim is to provide a simple and comprehensive guide to academic and industrial researchers for the development of both the future generation of catalysts and greener chemical processes to be used in the valorization of biomass derived sorbitol and xylitol as biorefinery platform feedstocks.

1. Introduction

In the last decade, we have witnessed a significant change in the identity of industrial chemistry with its inexorable transition from fossil to renewable feedstocks. To this regard, the worldwide attention is focusing on the use of lignocellulosic biomasses for the sustainable production of biofuels and bioderived chemicals [1-6]. The reason can be easily explained if we look at the chemical composition of the key components of biomasses (cellulose, hemicellulose and lignin) that have the potential for the sustainable production of several building block intermediates for modern biorefineries [7]. Cellulose and hemicellulose are mainly formed of C6- and C5-sugars, respectively, while lignin is mainly composed by phenolic units. Such a wealth of chemical functionalities represents, at present, the most promising alternative to petroleum resources [9-12].

Surely, cellulose and hemicellulose are an important feedstock for the sustainable production of biobased building blocks since their relative polysaccharide fractions account for up to 70% of the total biomass composition. However, with respect to petroleum feeds, cellulose and hemicellulose fractions are characterized by a higher content of oxygen-functionality (e.g -OH, -COOH, -C=O) which prevents their direct use in traditional refinery processes [7].

Traditionally, catalytic valorization of C6 (cellulosic) and C5 (hemicellulosic) sugars were carried out after using well established and standardized physico-chemical pre-treatments that allow a complete separation of lignocellulose fractions [13]. At present, integrated reductive catalytic processes (the so called “lignin-first” biorefinery approach) for simultaneous depolymerization of cellulose, hemicellulose and lignin fractions from lignocellulosic biomass are getting more and more attention [14]. Whatever the technological approach for the (pre)treatment of biomass is chosen, once cellulose and hemicellulose are deconstructed by acid or reductive catalyzed hydrolysis, glucose and xylose can be easily hydrogenated into the corresponding C6 and C5 polyols (sorbitol and xylitol, respectively) (Figure 1) [15, 16].

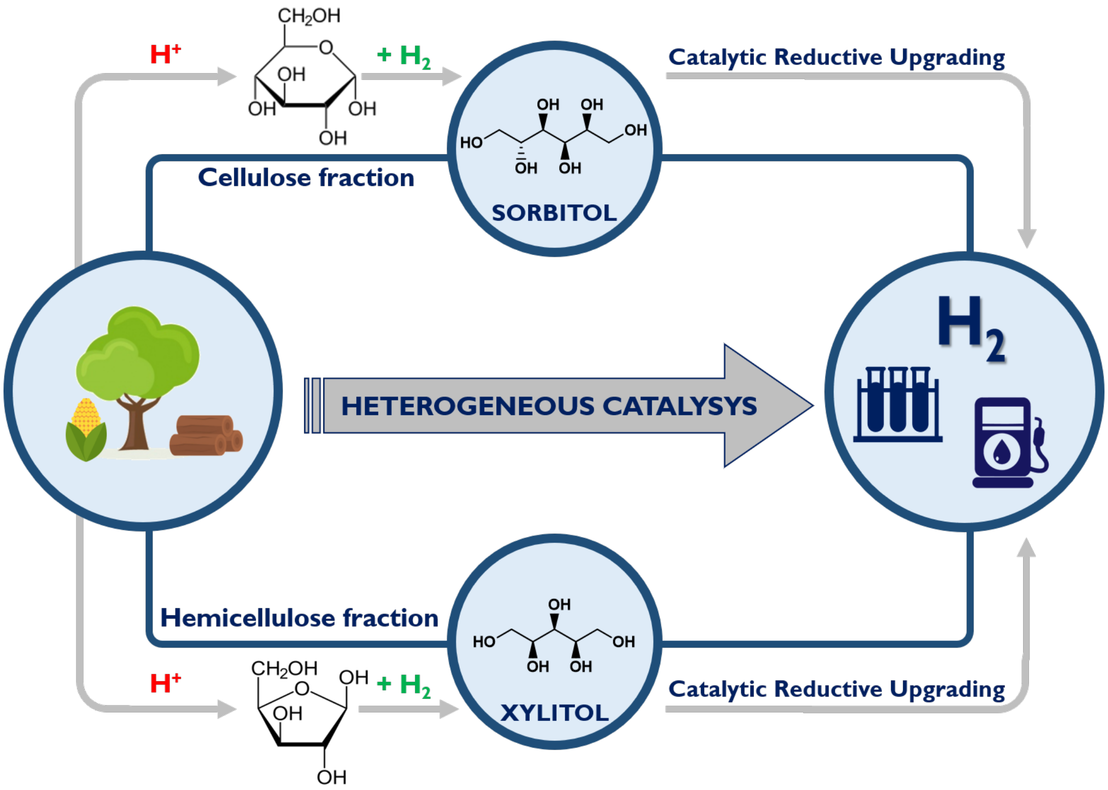

Figure 1. Cellulose and hemicellulose upgrading into H_2, fuels and chemicals via C6 (sorbitol) and C5 (xylitol) polyols.

Biomass derived polyols are characterized by the presence of at least two hydroxyl groups and can be considered an important class of chemical compounds and intermediates with sorbitol (C6 polyols), xylitol (C5 polyols) and glycerol (C3 polyol) being included in the list of the 12 most promising bio-derived platform molecules [17, 18]. C6-C2 polyols, including 1,4-butanediol (1,4-BDO), 1,2- and 1,3-propylene glycol (1,2-PDO and 1,3-PDO) and ethylene glycol (EG), are widely used as ingredient or additive in food (xylitol is the most used sweetener characterized by a lower calories content and reduced glycemic index with respect to sucrose) pharmaceutical and cosmetic industry as well as cheap monomers for the manufacturing of polymers, coatings, adhesives, etc (sorbitol has been successfully used for years for the production of polyurethanes) [19]. EG, habitually adopted as antifreeze agent, is a key component in the production of bio-PET while other bio-based diols, besides their direct applications, are currently used as co-monomers in bio-elastomeric polymers [20].

If compared with fossil feeds, polyols are not directly suitable for classical refinery processes because of the high presence of oxygen. This “*oxygen-overfunctionalization*” makes polyols acidic and difficult to selectively convert into target compounds owing to their high reactivity. Therefore, modern catalytic technologies could face the need of the efficient reduction of the oxygen content in bio-polyols allowing the production of H_2, fuels and added value compounds that can be directly placed on the chemical market [21-27]. Glycerol (GLY), being also the main by-product in biodiesel production, is certainly the most investigated biobased polyol with many important contributions published in the course of the years focused on its reductive catalytic upgrading into added value compounds [28-34].

The main focus of this review is to show recent progress and future challenges on the conversion of bioderived C6 and C5 polyols into energy (H_2), fuels (linear alkanes) and chemicals (alcohols), highlighting the fundamental reductive catalytic processes that drive their conversion into desired products (e.g., hydrogenation/hydrogenolysis, reforming, retro-aldol condensation, etc.) as well as an overview on the recent advances in the preparation of tailored heterogeneous catalysts adopted in the last years to achieve this goal (Figure 2).

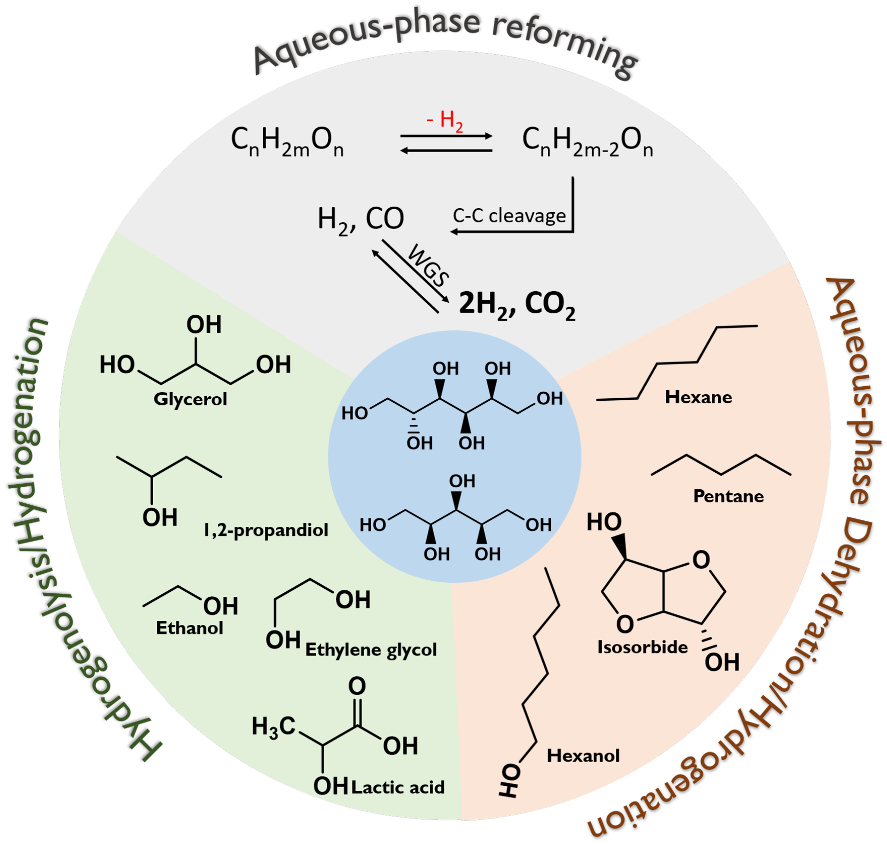

Figure 2. Production of energy (H_2), fuels and added value chemicals from sorbitol and xylitol via reductive catalytic processes.

2. Chemical processes for the reductive upgrading of biomass derived polyols

The catalytic conversion of biomass-derived polyols to fuels and chemicals involves the presence and/or combination of various types of reactions, including C-O and C-C hydrogenolysis, hydrogenation, dehydrogenation, dehydration, liquid and gas-phase reforming. In Figure 3, a qualitative diagram of the temperature and pressure ranges of in wich polyols are typically processed is sketched.

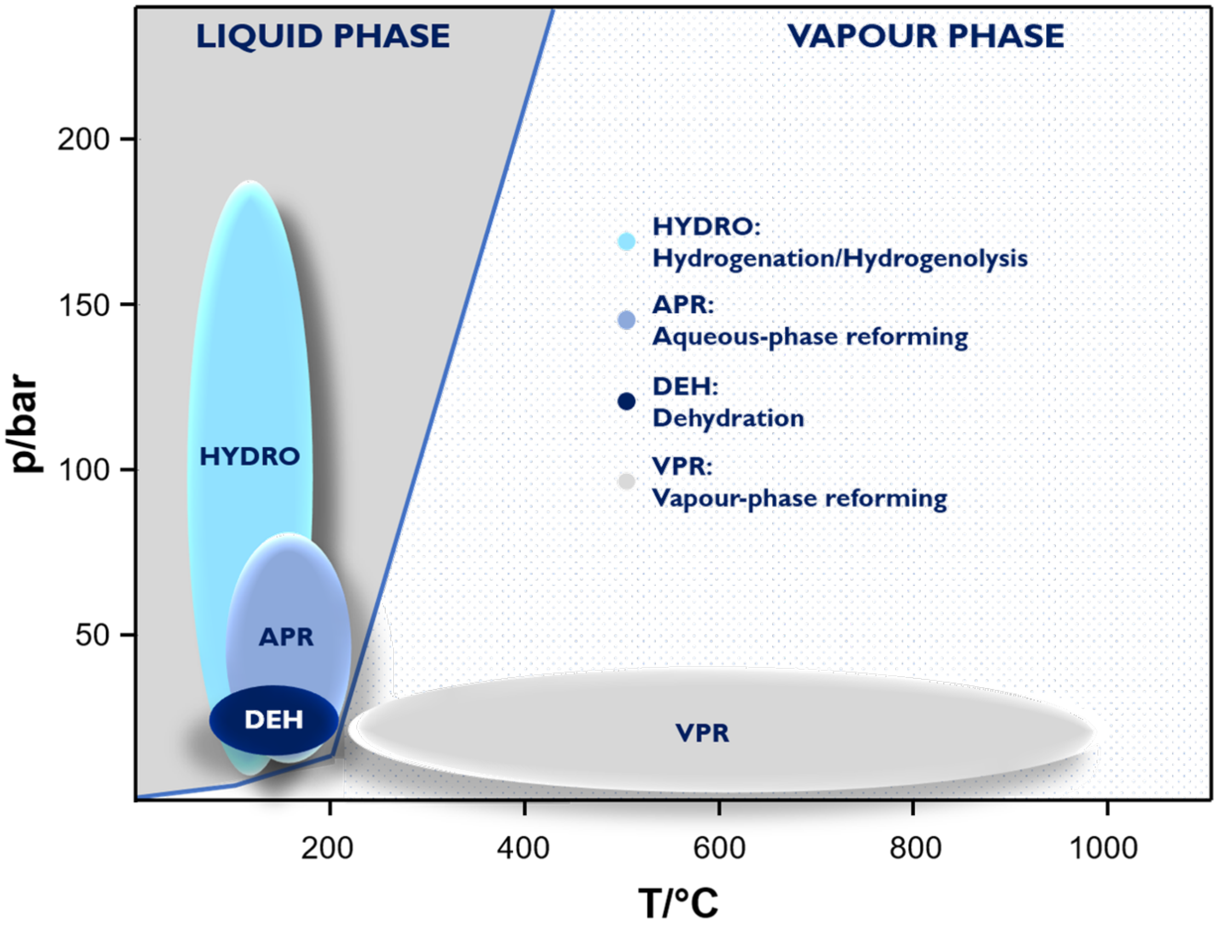

Figure 3. Typical reaction conditions adopted for the catalytic reductive processing of biomass derived polyols (adapted from ref. 27).

2.1 Hydrogenolysis and transfer hydrogenolysis reactions

In hydrogenolysis reactions, carbon–oxygen and/or carbon–carbon bonds can be cleaved in the presence of added hydrogen [23, 35]. Even if the stoichiometry of the reactions is identical ($R\text{-}X + H_2 \rightarrow R\text{-}H + H\text{-}X$ with X = O or C), from a thermodynamic point of view, the cleavage of C-O bond is generally highly exothermic while hydrogenolysis of C-C bond are almost energetically neutral (e.g. in the hydrogenolysis of the internal C–C bonds of sorbitol, the $\Delta H°$ value is of about -5 kcal/mol) [27]. In polyols reactions, the hydrogenolysis of C-O bonds generally involves a prior dehydration (acid- or base-catalyzed) followed by a hydrogenation process (metal-catalyzed) while the cleavage of C-C bonds occurs via dehydrogenation/decarbonylation or retro-aldol reactions allowing the production of alcohols and glycols with a shorter carbon chains (such as glycerol, 1,2-propanediol and ethanol in the case of sorbitol) [23].

Due to the low solubility of molecular hydrogen in aqueous/alcoholic media, the cleavage of C-C and C-O bonds in polyols can be promoted by an indirect H-source in the so called "catalytic transfer hydrogenolysis" (CTH) reactions (generally 2-propanol, ethanol, methanol or formic acid are used) that allow, at the same time, the reduction of problems related to purchase, transport, storage and handling of the high H_2 pressure [36-39]. These kind of reactions are getting more and more attention since most of the H-donor sources are now obtainable from renewable resources and represent a key component in the biomass valorization *via* the "lignin first" approach [40]

2.2 Aqueous reforming processes

At present, hydrogen (one of the most promising energy carrier) is mainly produced from fossil fuels such as natural gas, naphtha or coal. From a general point of view, polyols are surely between the most suitable substrates for the production of molecular hydrogen or syngas (H_2 and CO) that can be further used as building blocks for the production of methanol and other chemicals, including liquid hydrocarbons through the Fisher-Tropsch technology [41,42]. The production of CO and H_2 from polyols are conducted under vapour phase conditions and follows the general reaction:

$$C_nH_{2y}O_n \rightarrow nCO + yH_2$$

By using water, CO can be further converted *via* water gas shift reaction (WGS) into H_2 and CO_2. The overall reaction process, known as Aqueous Phase Reforming (APR) [43-45], can be summarized as follows:

$$C_nH_{2y}O_n \rightarrow nCO + yH_2 \qquad \text{(Reforming)}$$

$$nCO + nH_2O \rightarrow nCO_2 + nH_2 \qquad \text{(Water Gas Shift)}$$

$$C_nH_{2y}O_n + nH_2O \rightarrow nCO_2 + (n+y)H_2 \qquad \text{Aqueous Phase Reforming}$$

APR reactions are conducted under relative mild reaction conditions generating gas products with very low level of CO concentration (≈ 100 ppm) since the pressure employed shifts the equilibrium conversion of CO and H_2O toward the production of CO_2. However, using temperatures and pressures adopted for APR reactions, the CO_2 methanation is a competitive process that lowers the overall H_2 yield [46, 47]

Moreover, if APR reactions are carried out both in presence of H_2 and a bifunctional catalyst (metal+acid sites), the conversion of polyols can be oriented towards the production of alkanes in the so called "Aqueous Phase Dehydration/Hydrogenation" (APD/H) process:

$$C_nH_{2y}O_n + nH_2 \rightarrow C_nH_{2y} + nH_2O$$

3. Energy, fuels and chemicals from polyols

3.1 Reductive upgrading into added value chemicals

The reductive upgrading of sorbitol and xylitol allows the production of linear hydrocarbons as fuel compounds as well as other high value chemicals including C3-C2 polyols and alchols. In the past two decades, starting from the pioneering studies of Montessier and co-workers [48], research efforts have been targeted mainly towards polyols conversion into GLY, 1,2-PDO, EG and lactic acid under hydrodeoxygenative conditions with Cu, Ni and Ru being the most adopted metals for the preparation of heterogeneous catalysts.

Table 1. Overview of deoxygenative conversion of xylitol (XYL) and sorbitol (SORB) into added value chemicals promoted by heterogeneous Ni-based catalysts.

Substrate	Catalyst	Additive	Temperature [°C]	H_2 Pressure [bar]	Time [hours]	Conversion [%]	Main Products	Ref.
XYL	Ni/C	$Ca(OH)_2$	200	40	3	100	1,2-PDO, EG, LA	49
SORB	Ni/C	$La(OH)_3$	220	50	1	100	1,2-PDO, EG, GLY, LA	50
SORB	$Ni/Mg_{1.29}Al_{0.06}O_{1.38}$	-	200	20	2h	97	1,2-PDO, EG, GLY	51
SORB	$Ni/Mg_{2.4}Al_2O_{5.4}$	-	180	20	2	78	1,2-PDO, EG, GLY	52
SORB	Ni/FA	$Ca(OH)_2$	200	60	6	50	1,2-PDO	53
SORB	Ni/SrHAP-R	$Ca(OH)_2$	200	60	6	68	1,2-PDO, EG	54
XYL	Ni_2P/AC	-	200	40	0,75	99	EG, 1,2-PDO	55
SORB	Ni_2P/AC	-	200	40	0,75	99	EG, 1,2-PDO	55
SORB	2%Ce–20% Ni/Al_2O_3	$Ca(OH)_2$	220	70	2	100	1,2-PDO, EG, GLY	56
XYL	8% Ni/meso-Ce–TiO_2	-	245	50	4	88	EG	57
SORB	Ni/MgO	$Ca(OH)_2$	200	60	4	86	EG, 1,2-PDO	58

SORB: sorbitol; XYL: xylitol; 1,2-PDO: 1,2-propandiol; EG: ethylene glycol; GLY: glycerol; LA: lactic acid.

From a general point of view, polyols hydrogenolysis are carried out in the presence of high pressure molecular H_2 and hydroxides as additive in order to drive the product selectivity. To this regard, it has been proved that in presence of an alkaline base, the C−C bond breaking of aldehydes and ketones via retro-aldol condensation is favored, thus allowing the production of 1,2-PDO and EG.

Surely, nickel-based catalysts have been the most investigated systems for their intrinsic high activity in the C-C and C-O bond breaking (Table 1). For example, in the hydrogenolysis of xylitol, Ni/C was found to be more selective to 1,2-PDO and EG if compared with the analogous Ru/C system as a result of its higher ability in the C-C cleavage of xylose [49].

The presence a solid base prevents also leaching and sintering phenomena thus increasing the catalyst stability and reusability with $Ca(OH)_2$ being the most adopted. To this regard, it has been proved that the addition of $La(OH)_3$ positively promotes the hydrogenolysis of sorbitol decreasing the selectivity towards lactic acid and other C3 products [50].

The role of the support is another key factor in the improving polyols conversion and in driving the selectivity towards desired products. The increase of the catalytic activity of Ni nanoparticles, as a consequence of the metal dispersion on the support, was demonstrated in plate-like Ni–Mg–Al layered double hydroxide systems where more accessible solid basic sites can positively promote the hydrogenolysis of sorbitol [51].

In general, if EG and 1,2-PDO are the desired reaction products, the use of a basic support favors dehydrogenation, retro-aldol and hydrogenation processes. For example, C2 and C3 polyols can be obtained, under mild conditions (200°C, 20 bar of H_2, 2 hours), in the hydrogenolysis of D-sorbitol over Ni/MgxAlyOx based catalysts with different Mg/Al molar ratio [52]. Accordingly, when inert fly ashes were used as support of Ni-based catalysts for sorbitol hydrogenolysis, very low conversions were registered at 200°C and 60 bar of H_2 [53]. Hydroxyapatite (HAP) was found to be a valid support for Ni based catalysts with rod-shape (HAP-R) more active with respect to needle (HAP-N) and sphere (HAP-

S) shapes [42]. Moreover, the addition of Sr (up to 6%) in the hydroxyapatite structure increases the catalyst activity as a result of the increase of the support basicity [54].

The superior activity of nickel as active metal was also confirmed in M-phosphides (Ni_2P, CoP, Cu_3P, Fe_2P, WP) supported on carbon systems in the hydrogenolysis of sorbitol and xylitol [55]. Likewise, the addition of cerium into Ni/Al_2O_3 catalysts afforded a promoting effect in the conversion of sorbitol into C3-C2 polyols [56] as well as a stabilizing effect of the nichel nanoparticles on the mesoporous metal-oxide support (TiO_2) for the hydrogenolysis of xylitol [57]. Accordingly, with respect to the analogous Ni-MgO system, Co-MgO catalyst promotes the formation of 1,2-PDO more than EG even if a lower conversion of sorbitol was registered [58].

From a general point of view, platinum-group metals (PGMs) were found, by far, less efficient than nickel in the hydrogenolysis of polyols. Even the addition of nickel on Pt/NaY catalysts had only a marginal effect in promoting sorbitol conversion into 1,2-PDO and EG [59]. Over the Pt/C catalyst, the major reaction product observed was lactic acid in presence of NaOH that efficiently promotes the C−C bond breaking of aldehydes and ketones via the retro-aldol condensation. The process is self-sustainable with the hydrogen necessary for the hydrogenolysis process generated in-situ *via* dehydrogenation of polyols [60]. Palladium was surely the less investigated metal of the PGMs group. In a recent report, Mauriello and co-workers investigated the hydrogenolysis of several polyols at low molecular hydrogen pressure (5 bar) [61]. The heterogeneous Pd/Fe_3O_4 catalyst was found to be much more active than the commercial Pd/C system in the production of C2-C3 alcohols (ethanol in particular) as a result of bimetallic Pd-Fe species on the catalyst surface. Moreover, the Pd/Fe_3O_4 catalyst shows excellent performance in promoting the water-gas-shift (WGS) reaction as revealed by the total absence of CO in gas phase products.

Heterogeneous copper systems represent one of the most attention-grabbing alternatives to nickel-based catalysts in promoting the conversion of polyols in presence of H_2 (Table 2) [62-69].

Table 2. Overview of deoxygenative conversion of xylitol and sorbitol into added value chemicals promoted by heterogeneous Cu-based catalysts.

Substrate	**Catalyst**	**Additive**	**Temperature [°C]**	**H_2 Pressure [bar]**	**Time [hours]**	**Conversion [%]**	**Main Products**	**Ref.**
SORB	25%Cu/C	$Ca(OH)_2$	160	50	2	42	1,2-PDO, EG, GLY	62
XYL	Cu/SiO_2	$Ca(OH)_2$	200	40	2	58	1,2-PDO, EG, LA	63
XYL	10%Ni-80%Cu/SiO_2	$Ca(OH)_2$	200	60	2	95	1,2-PDO, EG	64
XYL	Cu–Ni/ZrO_2	-	245	40	3	97	EG, 1,2-PDO	65
XYL	Cu-Pd/rGO	NaOH	200	14 (N_2)	6	88	LA	66
SORB	Cu-Pd/rGO	NaOH	200	15 (N_2)	6	97	LA	66
SORB	1Pd-3Cu/ZrO_2	-	200	50	4h	81	EG, 1,2-PDO	67
XYL	Cu/CaO-Al_2O_3	-	230	80	10	98	1,2-PDO, EG, GLY, LA	68
SORB	Cu/CaO-Al_2O_3	-	230	80	10	100	1,2-PDO, EG, GLY, LA	68
XYL	CuO/ZnO/Al_2O_3	-	245	50	1	31	1,2-PDO, EG	69
SORB	CuO/ZnO/Al_2O_3	-	245	50	1	59	1,2-PDO, EG	69

SORB: sorbitol; XYL: xylitol; 1,2-PDO: 1,2-propandiol; EG: ethylene glycol; GLY: glycerol; LA: lactic acid.

In presence of Cu/C, sorbitol can be transformed, under mild reaction conditions (160°C, 50 bar H_2, 2 hours reaction time), into 1,2-PDO and EG in a good conversion (42%) [62]. The variation of the copper nanoparticle size has no significant effect on the product selectivity that, in contrast, is strongly influenced by the amount of the added $Ca(OH)_2$. Lactic acid and glycerol, formed during the hydrogenolysis reaction, can be in-situ converted, over the copper surface, into the desired 1,2-PDO. In contrast, by using SiO_2 as support in the xylitol hydrogenolysis, a strong dependence of the catalytic activity and of the products selectivity on the Cu particle size was registered [63].

Bimetallic Ni-Cu/SiO_2 and Ni-Cu/ZnO catalysts were efficiently adopted in the hydrogenolysis of xylitol showing a better activity and selectivity towards C3-C2 glycols than analogous monometallic Cu-systems [64, 65]. Together with nickel, also palladium was efficiently used as co-metal in Cu-based catalysts [66, 67]. Addition of Pd to Cu-based nanocatalysts supported on graphene allows to achieve a remarkable enhancement of the catalytic systems activity and stability in the production of lactic acid at 200°C from sorbitol and xylitol [66].

Accordingly, bimetallic Pd-Cu/ZrO_2 systems shows superior activities in sorbitol hydrogenolysis as well as a higher selectivity to the two target glycols (EG and 1,2-PDO) if compared with analogous monometallic Cu/ZrO_2 and Pd/ZrO_2 catalysts [67]. Moreover, addition of palladium prevents agglomeration of Cu nanoparticles leading to a high catalyst stability and recyclability [67].

On using bimetallic Cu/CaO-Al_2O_3 catalysts can also avoid addition of base promoters in the aqueous-phase hydrogenolysis of sorbitol. The direct interaction between metallic Cu and Ca^{2+} cations in the catalytic system facilitates, in fact, the C−C and C−O bond breaking allowing the production of EG, 1,2-PDO and 1,2-BDO [68].

Table 3. Overview of deoxygenative conversion of xylitol and sorbitol into added value chemicals promoted by heterogeneous Ru-based catalysts.

Substrate	**Catalyst**	**Additive**	**Temperature [°C]**	**H_2 Pressure [bar]**	**Time [hours]**	**Conversion [%]**	**Main Products**	**Ref.**
Xylitol	Ru/C	silicotungstic acid	150	60	3h	70	C3-C5 polyols, EG	70
Sorbitol	Ru/NbO	-	220	50	4	97	1,4-sorbitan, isorbide	73
Xylitol	Ru/C	$Ca(OH)_2$	200	40	1	184 (h^{-1})	1,2-PDO, EG, GLY, LA	74
Xylitol	Ru/C	$Ca(OH)_2$	200	60	24	100	EG, 1,2-PDO	75
Sorbitol	Ru/C	$Ca(OH)_2$	200	40	2h	23	EG, 1,2-PDO	76
Sorbitol	Ru/CNTs	CaO	220	80	4	59	1,2-PDO, EG, GLY	77
Sorbitol	Ru/C	-	200	100	4	88	AR, XYL, GLY	78
Sorbitol	Ru/CNTs	$Ca(OH)_2$	205	50	2h	99	1,2-PDO, EG, GLY	80
Sorbitol	Ru/NMCN	NaOH	210	60	2h	27	EG, 1,2-PDO, GLY	81
Sorbitol	NiRuCa-HT	$Ca(OH)_2$	220	40	4h	94	EG, 1,2-PDO, GLY	82
Sorbitol	RuRe/C	$Ca(OH)_2$	250	35	1	68	1,2-PDO, EG, GLY, LA	83
Xylitol	Ru/MnO/C	-	200	60	30	100	1,2-PDO, EG, GLY	84

SORB: sorbitol; AR: Arabitol; XYL: xylitol; 1,2-PDO: 1,2-propandiol; EG: ethylene glycol; GLY: glycerol; LA: lactic acid.

From a mechanistic point of view, a lot of research efforts has been done by the research group of Prof. Palkovitz in order to elucidate the complex reactions that occur in the hydrogenolysis of C6-C5 polyols. A schematic representation of the reaction pathways in the conversion of sorbitol into EG,1,2-PDO and other added value chemicals is presented in Figure 4.

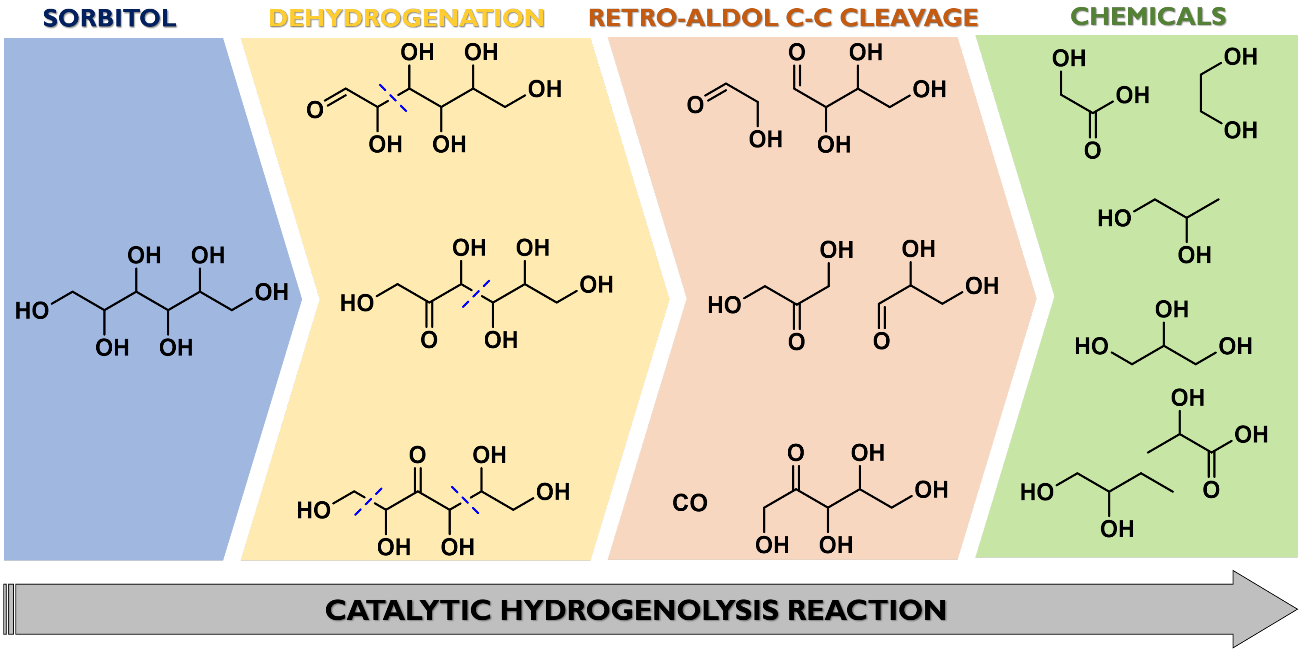

Figure 4. Conversion pathways of sorbitol into EG,1,2-PDO and other added value chemicals (adapted from Ref. 62)

By using the $CuO/ZnO/Al_2O_3$ catalyst, at 245°C and 50 bar of H_2, the composition of liquid-phase products allowed to propose a unified reaction mechanism ruled by elementary transformations that include dehydrogenation/hydrogenation, dehydration, isomerization and retro-aldol cleavage [69].

The same authors elucidated the complete product spectrum (as well as reactions kinetics) of the aqueous Ru/C-catalyzed hydrogenolysis of sorbitol, erythritol, xylitol, sorbitol both in presence and in absence of acidic additives [70, 71]. Under neutral conditions, the decarbonylation of terminal groups is favoured while, by adding silicotungstic acid in the reaction medium, deoxygenative products are formed [70].

The research attention on ruthenium systems as heterogeneous catalysts, for production of chemicals and fuel from biomass derived polyols, has been progressively increased since they were found to show high performance both in conversion and selectivity as well as relatively low market price.

The hydrogenolysis of sorbitol over Ru based catalysts shows a dependence on pH and temperature [72]. In a basic medium, independently from the temperature adopted, the main reaction is a reverse aldolization while under neutral conditions, the hydrogenolysis of C-C bonds in the middle of the carbon chain is generally observed. Interestingly, by using an acidic niobium phosphate support, Ru nanoparticles can promote dehydration of sorbitol into sorbitan avoiding its hydrogenolysis into glycols [73].

Surely carbon (C), active carbon (AC) or carbon nanotubes (CNTs) were the most adopted support for ruthenium nanoparticles [74-83]. In one of the first report, Sun and Liu, presented the superior activity of the Ru/C catalyst than analogous Ru/TiO_2, Ru/ZrO_2, Ru/Al_2O_3 and Ru/Mg_2AlO_x systems in the hydrogenolysis of xylitol [74] demonstrating that the dehydrogenation of xylitol to xylose on the ruthenium surfaces, and the base-catalyzed retro-aldol condensation are the key step in the production of 1,2-PDO and EG. The presence of a base is, in fact, crucial for the production of C3-C2 glycols since, without its presence, epimerization and cascade decarbonylation were the predominant reactions thus allowing production of C5-C4 alditols and light alkanes [75].

Also in the hydrogenolysis of sorbitol, the best results were obtained by using carbon-based supports containing Ru nanoparticle (Ru/MgO, Ru/Al_2O_3, Ru/ZrO_2 and Ru/TiO_2 were found to be less efficient) with $Ca(OH)_2$ or CaO being the best base additive for the production of 1,2-PDO and EG [76, 7]. The kinetic isotopic effect studies highlight that the dehydrogenation is the kinetically-relevant step in the hydrogenolysis reaction. It was also demonstrated that the presence of sulphur reduces the ruthenium activity, in the hydrogenolysis of sorbitol, minimizing, at the same time, formation of straight chain hydrocarbons. Under semi-continuous conditions, the Ru/C catalyst allows the production of arabitol, xylitol and glycerol as the main reaction products while, upon increasing the reaction temperature, a higher selectivity to methane and ethane was also registered [78]. On the other hand, if xylitol hydrogenolysis is carried out in alkaline aqueous solutions, by using a trickle-bed reactor EG and 1,2-PDO can be obtained under relative mild conditions (200°C, 60 bar H_2) [79].

On the other hand, using activated carbon or carbon nanotubes as support, the catalytic properties of Ru strongly depend on the location of ruthenium nanoparticles. In particular, an excellent performance can be observed in the hydrogenolysis of sorbitol as a result of the altered metal-support interaction and the electronic state of ruthenium nanoparticles located outside CNTs [80]. Moreover, CNTs can be functionalized with NH_2, COOH, OH and nitrogen-doping groups with the aim to further increase the activity of Ru/CNTs in the hydrogenolysis of sorbitol [81].

When ruthenium is directly impregnated with $Ca(OH)_2$, a higher yield of glycols can be obtained than with analogous systems where the alkali promoter is added separately to the reaction medium [82]. At the same time, incorporation of nickel into the calcium hydroxide supported ruthenium catalyst permits a positive effect both on sorbitol conversion and a glycols selectivity as well as on catalyst stability. Interestingly, analogous results were also obtained by adding Re on the Ru/C catalyst [83].

The bifunctional Ru/MnO/C catalyst was tested in the hydrogenolysis of xylitol in different water/organic solvent mixtures showing that an increasing the organic fraction (methanol) produces a higher selectivity to glycols with a concurrent catalyst deactivation caused by the alcoholic solvent dehydrogenation affording light alkanes and coke on the Ru surface [84].

Ru-Pt based catalysts supported on SiO_2-Al_2O_3 were tested in the hydrogenolysis of sorbitol carried out in an aqueous medium in a batch reactor at 240°C under 60 bar H_2 pressure with oxygenated compounds in liquid phase and hydrocarbons in gaseous phase being the main observed products [85].

3.2 Conversion of sorbitol and xylitol into hydrocarbon fuels

In the case of C6-C5 polyols, the production of linear hydrocarbons follows the general stoichiometry:

$$C_6H_{14}O_6 \text{ (sorbitol)} + 6H_2 \rightarrow C_6H_{14} \text{ (hexane)} + 6H_2O$$

$$C_5H_{12}O_5 \text{ (xylitol)} + 5H_2 \rightarrow C_5H_{12} \text{ (pentane)} + 5H_2O$$

It is well established that the production of alkanes from polyols involves (i) a dehydration step, on a solid support, and (ii) a following hydrogenation process ensured by the hydrogen formed over the metal sites of the catalyst [26]. To this regard, in one of the first contributions, Dumesic and co-workers demonstrated that C2-C6 alkanes can be formed starting form sorbitol over bifunctional catalyst systems ($Pt/SiO_2–Al_2O_3$ and $Pd/SiO_2–Al_2O_3$) in which sorbitol is primarly dehydrated on $SiO_2–Al_2O_3$ support and then hydrogenated on Pt or Pd metal species with the hydrogen produced in-situ by APR process [86]. However, it is worth to underline that, under the reaction conditions, generally adopted, many other catalytic processes can take place, including methanation, alkylation, hydrocracking and cyclization reactions.

Whereas deoxygenative processes of polyols can be promoted by a wide range of active metals, the conversion of sorbitol and xylitol into C6-C5 alkanes, in high yield, have been carried out mostly on heterogeneous Pt, Ru and Re catalysts (Table 4).

The catalytic activity of Ni/HZSM-5 in the hydrogenation of sorbitol into liquid alkanes can be improved by adding MCM-41 allowing a liquid alkanes selectivity of 98.7% [87, 88].

The superior activity of Pt-based catalysts was confirmed in the continuous flow hydrodeoxygenation of sorbitol into gasoline-range hydrocarbons investigated over Pt, Pd, Rh, Ru, Ni metals supported on tungstated alumina (WA) [89].

At 250°C and 40 bar of H_2, the $Pt/NbOPO_4$ catalyst is able to convert sorbitol to C6 and C5 alkanes (60% overall yield) with isosorbide being the key intermediate in the Aqueous Phase Dehydration/Hydrogenation (APD/H) process which undergoes ring opening followed by C-O bond cleavage [90].

The addition of a second metal (Re, Ir, Rh and Pd) was proved to increase the activity of the Pt/SiO_2-Al_2O_3 catalyst in the conversion of sorbitol into hexane with Re being the most active [91, 92].

The addition of ruthenium on MoO_{3-x}/C catalysts positively promote the production of C6-C5 alkanes from sorbitol in a continuous flow reactor. $RuMoO_{3-x}/C$ catalysts shows high performance in sorbitol aqueous phase dehydration/hydrogenation without a significant decrease of activity after 200 h of time on stream [93].

The research group of Prof. Tomishige deeply investigated the ReOx-modified Ir metal catalyst (Ir-ReOx) as an effective catalytic system able to convert C5-C3 polyols, sugars and cellulose into linear alkanes [94-97]. A model structure of the Ir-ReOx catalytic system is presented in Figure 5.

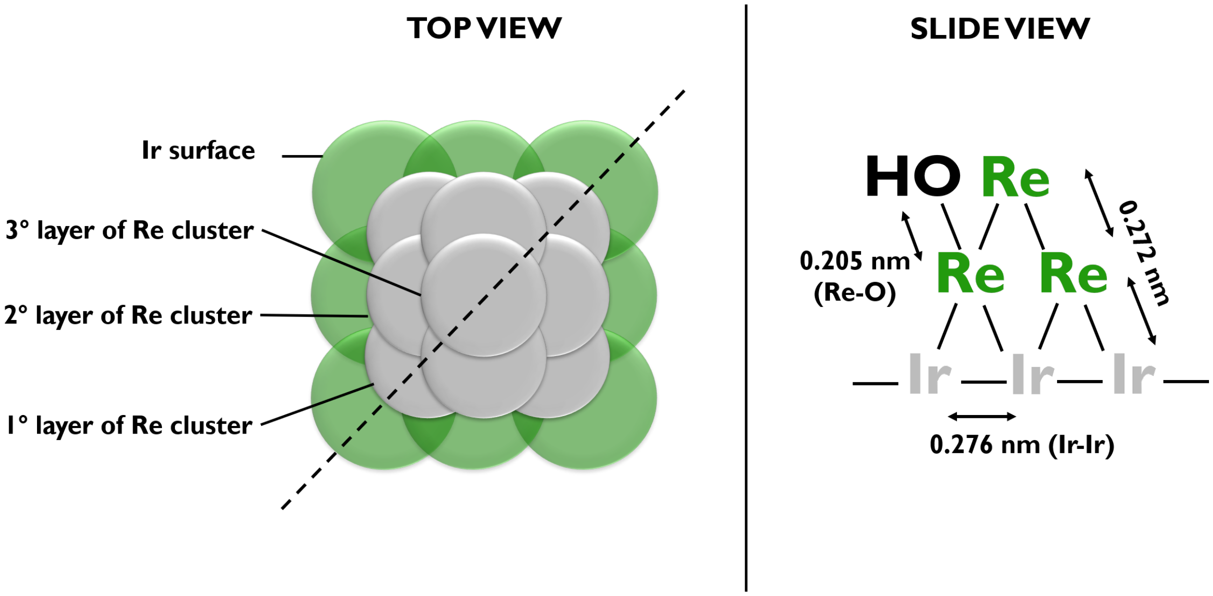

Figure 5. Model structure of the Ir-ReOx catalytic system (adapted from Ref. 94).

By using the Ir-ReOx/SiO_2 catalyst combined with H-ZSM-5, n-hexane and n-pentane can be obtained, in high yield, at very low reaction temperatures (170-140°C) [95]. On the other hand, addition of Pt as co-metal in the Ir-ReOx/SiO_2 system improves the C-C cracking activity of the catalyst allowing to obtain gasoline-ranged products in high yield.

Table 4. Overview of xylitol and sorbitol conversion into linear alkanes promoted by heterogeneous Ni-, Pt- and Ir-based catalysts.

Substrate	**Catalyst**	**Temperature [°C]**	**H_2 Pressure [bar]**	**Time [hours]**	**Conversion [%]**	**Main Products**	**Ref.**
Sorbitol	2 % Ni/HZSM-5 + MCM-41	240	40	1h	67	hexane, pentane	87
Sorbitol	0.5%Pt/WA	380	40	1h	100	C6 and C5 hydrocarbons	89
Sorbitol	4wt%Pt/$NbOPO_4$	250	40	12	100	Hexane, pentane	90
Sorbitol	Ru-Pt/SiO2-Al_2O_3	240	60	3	100	C6 hydrocarbons	91
Sorbitol	1%Ru-50%Mo/C	280	40	1	100	alkanes	93
Sorbitol	Ir-ReO_x/SiO_2 + H-ZSM-5	140	80	72	100	hexane	94
Xylitol	Ir-ReO_x/SiO_2 + H-ZSM-5	140	80	72	100	pentane	94

3.3 Hydrogen production via Aqueous Phase Reforming (APR)

Hydrogen production *via* Aqueous Phase Reforming (APR) was introduced, for the first time in 2002, by Dumesic and co-workers [98] and appears as research area of great interest since:

- with respect to "classic" reforming processes that are highly endothermic, APR reactions require a little energy supply to be carried out;

- catalytic APR processes can be achieved by using a mixture of various lignocellulosic-derived compounds as feedstock;

- H_2 can be produced in high purity and, theoretically, directly useable for energy production in fuel cells;

- H_2 production by APR could be generated from sorbitol at a very competitive price if polyols can be directly obtainable from lignocellulosic biomass (instead of sugars) [99, 100].

In APR reactions, the crucial step is the terminal C-C bond breaking by combined dehydrogenation/decarbonylation processes that produce H_2 and CO, shortening, step by step, the polyol carbon skeleton as represented in Figure 6. As already mentioned, carbon monoxide can further undergo WGS reaction allowing the additional production of H_2 and CO_2.

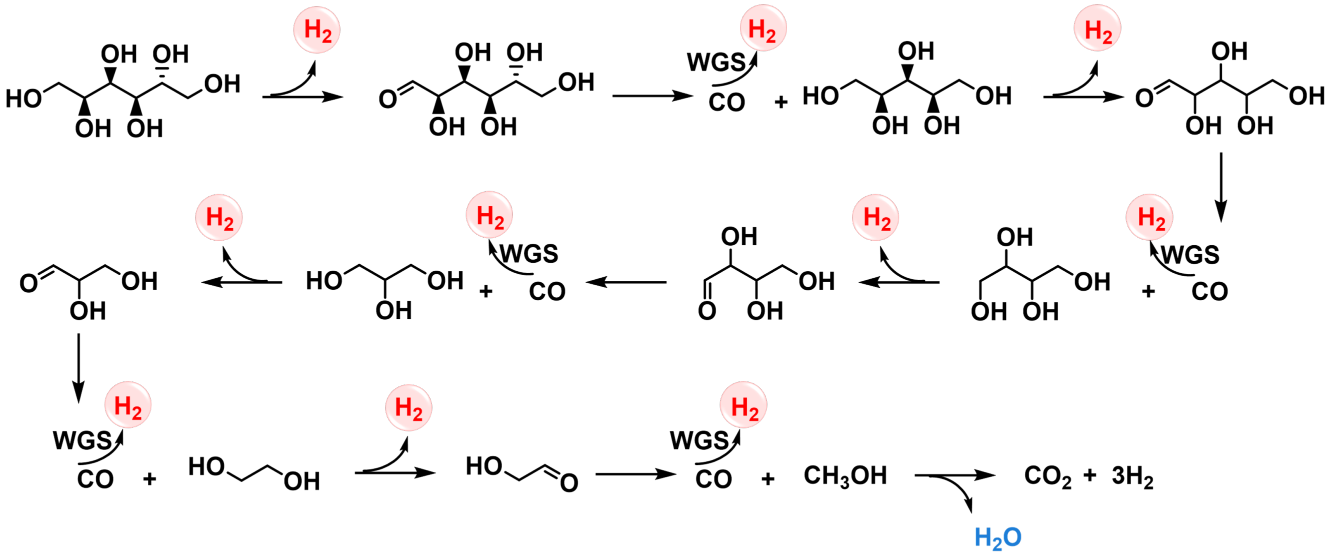

Figure 6. Hydrogen production from sorbitol (C6) and xylitol (C5) *via* aqueous phase reforming (APR) reactions.

In a recent contribution, an in-situ ATR-IR study of the surface reactions occurring during the APR of sorbitol over the Pt/Al_2O_3 catalyst confirms that the key intermediate is the CO formed from the dehydrogenation process [101]. The dehydrogenation of sorbitol, strongly anchored on the the Lewis acid sites of the alumina support with adsorbed alkoxy species, in fact, may allow the formation of an aldehyde or a ketone with the first easily decarbonylated whereas latter cannot undergo the same reaction and contribute to poison platinum sites.

Surely, platinum-based catalysts are the most adopted systems under both batch and continuous flow apparatus with the latter being the largely used conditions (Table 5). APR of sorbitol can be carried out also in carbon-coated ceramic (Al_2O_3) tubular membrane reactor where the hydrogen produced can be continuously removed from the reaction medium by permeation to the shell side whilst the liquid remains into the tube side [102].

Since its pioneering use as efficient heterogeneous catalyst for the aqueous phase reforming of sorbitol, glycerol, ethylene glycol and methanol, Pt/Al_2O_3 is the most studied catalytic system in the production of H_2 from polyols [103-109]. Both kinetics modelling [103] and mechanism investigations [104] have been presented showing that over 260 reaction intermediates are involved in the transformation of sorbitol into H_2 *via* APR. In general, under the same reaction conditions, C5 and C6 polyols show similar APR behaviour even if higher H_2 selectivity can be obtained in the case of xylitol [105]. In a very elegant contribution, it was also demonstrated that the chirality of the initial feedstocks does not affect the reaction rate and selectivity to the final products in the APR of C6 polyols [106].

Apesteguía and co-workers investigated the effect of Pt loading and reaction conditions on H_2 production from several C6-C2 polyols, including sorbitol and xylitol [107-109]. H_2 yield and productivity increase on increasing the platinum surface and by using shorter-chain polyols [107]. By using sorbitol as feedstock, at a given space velocity, it was demonstrated that the production of H_2 does not depend on the feed-concentration [108] in contrast with xylitol where H_2 selectivity and productivity decrease on increasing the xylitol concentration [109].

Table 5. Overview of the conversion of xylitol and sorbitol into H_2 via aqueous phase reforming (APR) processes.

Substrate	Catalyst	Temperature [°C]	Conversion [%]	H_2 Selectivity [%]	Reaction conditions	Ref.
Xylitol	Pt/Al_2O_3	225	79	81	Continuous flow (WHSV=1.2 h^{-1})	109
Sorbitol	Pt/Al_2O_3	225	61	75	Continuous flow (WHSV=1.2 h^{-1})	109
Pt/C	Pt/C	225	80	80	Continuous flow (WHSV=2.0 h^{-1})	110
Sorbitol	$Pt\text{-}Ni/Al_2O_3$	225	42	36	Continuous flow (WHSV=2.5 h^{-1})	115
Xylitol	$Pt\text{-}Re/TiO_2$	225	91	28	Continuous flow (WHSV=3.6 h^{-1})	117
Sorbitol	Raney-$Ni_{14}Sn$	225	13	93	Continuous flow (LHSV=3.6 h^{-1})	120

Platinum was also efficiently supported on several carbon materials (e.g. activated carbons, sibunit carbon type, three dimensional bimodal and mesoporous carbons) for the preparation of heterogeneous catalysts active in the conversion of polyols into H_2 [110-113]. Carbon-supported mono- and bimetallic-systems based on VIII group metals (Pt, Ni, Re, Ru, Pt-Ni, Pt-Re, Pt-Ru and Pt-Co) were prepared and tested in the APR of xylitol in a fixed-bed reactor at 225°C [110]. Monometallic Pt/C was found to be an optimum carbon-supported system since Ni/C, Ru/C and Re/C catalysts notably exhibit lower activity. Moreover, in this case, addition of a second metal to Pt/C was not found to be beneficial for hydrogen production with the exception of the Pt-Fe/CMK-9 (3-D cubic ordered mesoporous carbon) catalyst where the presence of Fe considerably enhances the catalytic performance, showing the optimum activity at the Pt:Fe ratio of 1:3 [114].

Nevertheless, heterogeneous bimetallic systems represent an important field of research also in the APR of biomass derived polyols [115-123]. $PtNi/Al_2O_3$ and $PtCo/Al_2O_3$ catalysts allow a higher H_2 yield, as well as a better stability during the on-stream experiments, if compared with the monometallic Pt/Al_2O_3 [115]. In particular, on using the $PtNi/Al_2O_3$ a higher hydrogen production can be boosted even at long reaction times while addition of Co ensures to keep low levels of methane and coke formation. Also Re was adopted as co-metal in the aqueous phase reforming of sorbitol [116] and xylitol [117], although bimetallic Pt-Re systems were also found very active in alkane formation but, by far, less efficient than monometallic Pt/TiO_2 and Pd/Al_2O_3 catalyst in the production of hydrogen that, anyway, can be enhanced by its continuous stripping from the reaction medium.

Beyond traditional APR methods carried out under batch and continuous flow conditions, Colmenares and co-workers proposed, for the first time, a photocatalytic reforming process that allows to produce H_2 from a glucose aqueous solution in the presence of Pt/TiO_2 as heterogeneous catalyst. High-thermal redox treatment of the system at 850 °C allows a greater SMSI effect and a better catalytic performance of the Pt/TiO_2 system together with an increase in the hydrogen molar production [118].

It is also worth to mention that Ni-Pt and Ni-Pd species supported on alumina nano-fibers have been successfully used as bimetallic heterogeneous systems in the APR of sorbitol [119, 120] with a rate of H_2 formation 3 to 5 times higher than that obtained with the analogous monometallic Ni-based catalyst.

Furthermore, Raney-Ni and Raney-NiSn catalysts show good activity and stability in the continuous aqueous-phase reforming of oxygenated hydrocarbons with a concomitant low formation of methane with analogous Al_2O_3-supported Ni and Ni-Sn systems exhibiting a significant catalyst deactivation as a consequence of sintering processes [121]. The excellent performance of this non–precious metal catalysts in the H_2 production of hydrogen from ethylene glycol, glycerol, and sorbitol is surely a milestone in the study of APR processes [122].

4. Concluding remarks

The use of biomass and their derived molecules for production of energy, biofuels and chemicals cannot longer wait. To this regard, it is out of the question that in the near future biomass derived C6 and C5 polyols, already included in the list of the most promising bio-derived platform molecules, will be among the key renewable feedstocks for greener future biorefinery processes.

Deoxygenation processes can be the key to convert sorbitol and xylitol, C6 and C5 polyols respectively, into important chemicals such as 1,2-propandiol and ethylene glycol with heterogeneous Cu-, Ni- and Ru-based catalysts that can efficiently promote the C-O and C-C cleavage in the presence of a solid base, generally calcium hydroxide or sodium hydroxide, that avoids the phenomena of catalyst leaching and sintering and drives the selectivity into desired reaction products (glycols). Addition of a co-metal improves the activity, selectivity and stability of the catalytic systems allowing, at the same time, the use of milder reaction conditions (180-200°C and 5-20 bar of H_2).

Heterogeneous bimetallic systems are also the most adopted heterogeneous catalysts in the production of linear hydrocarbons from polyols. These processes are conducted, if compared with deoxygenation reactions, at harsh reactions conditions (250-300°C and 40-80 bar of H_2) and suffer the concurrent presence of several competing reactions that lower the selectivity into C6 and C5 alkanes.

Production of renewable H_2 from biomass derived polyols can be successfully accomplished *via* aqueous phase reforming (APR) reactions that represent a sustainable, low energy demanding catalytic process that allows formation of hydrogen in high yield with a low carbon monoxide content. APR processes are generally conducted under continuous flow conditions at relative mild temperatures (220-250 °C) and high pressures (20-50 bar) and are promoted by Pt- and Ni-based catalysts. Surely the monometallic Pt/Al_2O_3 is the most adopted heterogeneous catalyst, however, comparable results can be obtained also by using bimetallic Ni systems.

Even though catalytic hydrogenolysis, deoxygenation and aqueous phase reforming are very well known processes, it is more necessary now than ever to develop more efficient and non-precious heterogeneous catalysts able to produce chemicals, fuels and H_2 from biobased sorbitol and xylitol. Moreover, with respect to dehydrogenation/hydrogenation processes, new catalytic systems with base functionalities should be tracked in order to avoid the use of inorganic additives that cannot be recovered from the reaction medium. On the other hand, the design of new catalytic systems able to promote the conversion of polyols into linear alkanes in presence of lower H_2 pressure as well as the preparation of stable and reusable heterogeneous catalysts operating for long for long time-on-stream APR processes are absolutely among the future targets to be achieved.

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Abbreviations

1,2-BDO: 1,2-Butanediol

1,2-PDO: 1,2-Propandiol

1,3-PDO: 1,3-Propandiol

1,4-BDO: 1,4-Butanediol

AC: Active Carbon

APD/H: Aqueous Phase Dehydration/Hydrogenation

APR: Aqueous Phase Reforming

AR: Arabitol

C: Carbon

CNTs: Carbon NanoTubes

DEH: Dehydration

EG: Ethylene Glycol

GLY: Glycerol

HAP: Hydroxyapatite

HAP-N: Needle-Shape Hydroxyapatite

HAP-R: Rod-Shaped Hydroxyapatite

HAP-S: Sphere-Shape Hydroxyapatite

HYDRO: Hydrogenation/Hydrogenolysis

LA: Lactic Acid

PET: Polyethylene Terephthalate

PGMs: Platinum-Group Metals

SORB: Sorbitol

VPR: Vapour-Phase Reforming

WA: Tungstated Alumina

WGS: Water Gas Shift

XYL: Xylitol