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Renewable Feedstocks

Hydrogenolysis Goes Bio: From Carbohydrates and Sugar Alcohols to Platform Chemicals

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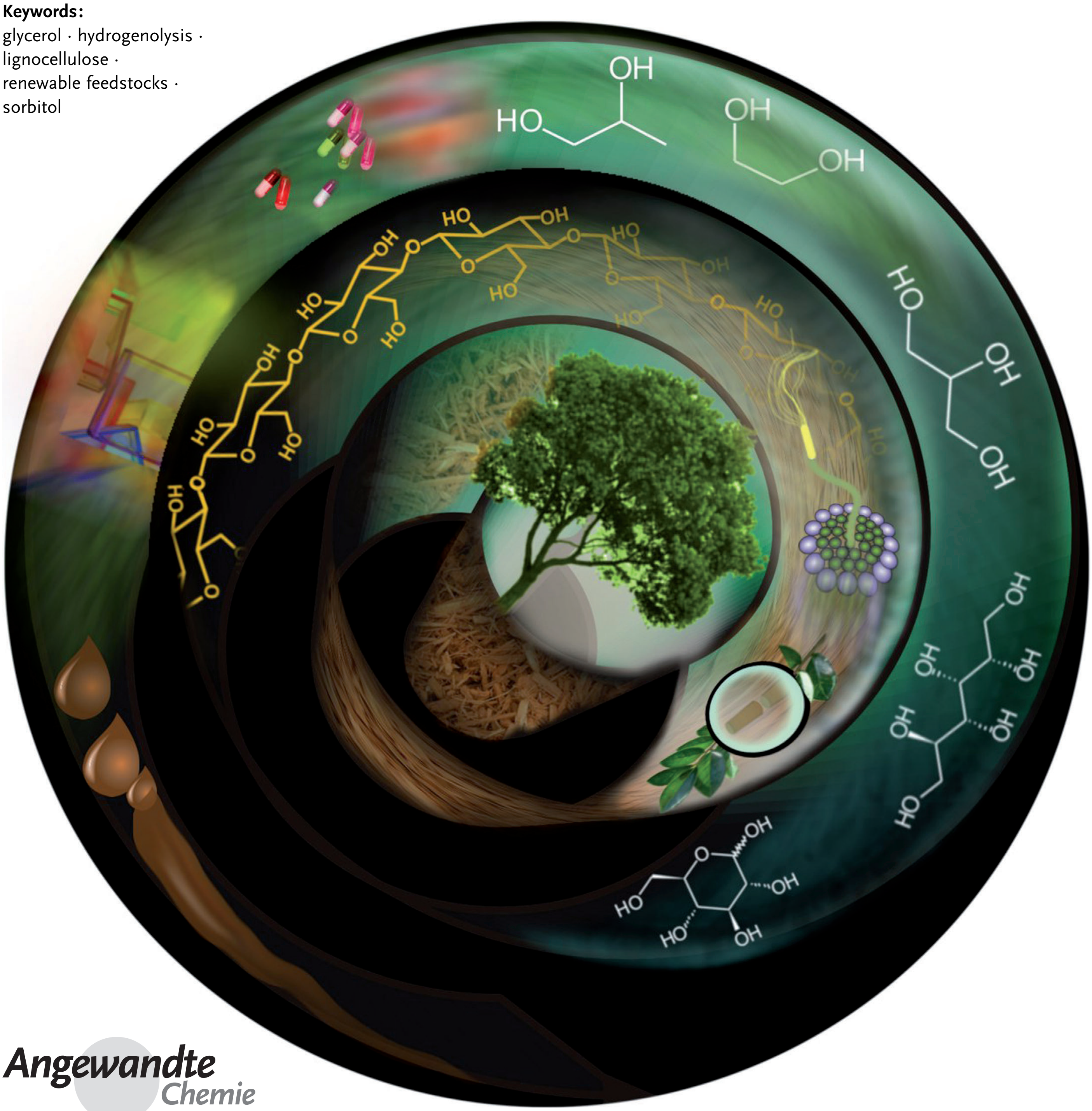

In view of the diminishing oil resources and the ongoing climate change, the use of efficient and environmentally benign technologies for the utilization of renewable resources has become indispensible. Therein, hydrogenolysis reactions offer a promising possibility for future biorefinery concepts. These reactions result in the cleavage of C–C and C–O bonds by hydrogen and allow direct access to valuable platform chemicals already integrated in today's value chains. Thus, hydrogenolysis bears the potential to bridge currently available technologies and future biomass-based refinery concepts. This Review highlights past and present developments in this field, with special emphasis on the direct utilization of cellulosic feedstocks.

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1. Introduction

The depletion of fossil fuel reservoirs, together with the indispensable shift of the feedstock base towards a biorefinery approach, necessitates utilizing renewable resources on a large scale for the production of chemicals and fuel. Thus, the use of efficient and environmentally benign technologies has become an imperative. Hydrogenolysis, which results in the cleavage of C–C and C–O bonds by hydrogen, offers a promising possibility for future biorefinery concepts. This concept is currently intensively discussed in the context of the transformation of glycerol to ethylene and propylene glycol, and has great potential in regard to the conversion of further biomass-derived polyols, such as sugars or sugar alcohols. Moreover, the direct hydrogenolytic conversion of biopolymers, including not only starch but also cellulose and hemicellulose, into valuable platform chemicals has even been demonstrated. The biomolecules can be transformed into various compounds already integrated in today's fossil fuel based value chains; thus, hydrogenolysis bears the potential to bridge the available technologies and future refinery concepts.

This Review documents the past and contemporary advances in the hydrogenolysis of biomass-based substrates, with particular emphasis on promising product ranges and suitable catalyst systems. Where applicable, the hydrolysis of polysaccharides and the hydrogenation of sugars are also described to provide a comprehensive account. The Review will end with future prospects in the area of catalyst and process development, and highlight open questions and future challenges of this concept.

1.1. Motivation

Steadily increasing greenhouse gas emissions and worldwide energy demand, together with limited fossil fuel reserves, are the main social and economic challenges that need to be tackled nowadays. Despite an ongoing discussion about the exact time frame of fossil fuel depletion, the age of fossil fuels is about to end.[1] In terms of future energy supply, renewable energies based on solar, water, or wind energy could account for a major fraction of worldwide energy consumption. In terms of liquid fuels for the transportation sector and the feedstock base for the whole chemical industry, however, alternative resources have to be explored. Biomass appears to be a highly promising alternative carbon source for the production of transportation fuels and chemicals, as, during their growth, plants convert CO_2 and water into sugars and sugar polymers by photosynthesis. By applying biomass as the feedstock, atmospheric CO_2 is technically converted into fuels and chemicals.[2] This significantly improves the CO_2 balance, with the goal being fully CO_2-neutral technologies. With regard to CO_2 neutrality, all energy inputs—including fertilizers or energy to grow and process plants—have to be considered. The direct combustion of biomass and use of biofuels currently are in fact not yet CO_2 neutral. Consequently, efficient conversion technologies for such feedstocks are highly desirable, and possible transformations of such biomolecules have been reported in recent reviews.[3,4] These discuss new value chains for the chemical industry and

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demonstrate the feasibility of a refinery concept based on renewable feedstocks, which will certainly become important in the next few decades. Nevertheless, most routes will require a complete re-design of value chains, not only in terms of the required synthesis strategies, processes, and catalysts, but also in terms of the available product spectrum. Therein, new molecular structures may substitute traditional compounds and necessitate an adaptation of final products, for example, terephthalic acid versus 2,5-furandicarboxylic acid.[5]

These developments will certainly be necessary and valuable on the way to sustainable and CO_2-neutral technologies based on renewable feedstocks. However, a successive transition will be essential as a driving force for the economic integration of renewable feedstocks in the mature technology of today's refineries. Thus, transition technologies that allow the fast integration of alternative feedstocks in existing value chains would be highly desirable. The hydrogenolysis of renewable feedstocks could be such a transition technology and serve as a crossover between value chains in the traditional refinery and renewable feedstocks. Although the hydrogenolytic treatment of biomass may have broader applications, we will limit the feedstocks to carbohydrates and polyols; information on the use of lignin as a feedstock is covered in a recent review.[6,7] Of the polyols, glycerol and sugar alcohols are predominantly discussed, while carbohydrates include mono- and disaccharides, oligosaccharides, and polysaccharides such as starch, hemicellulose, and cellulose. The most frequent target products in all cases are C_1 to C_{6-x} alcohols, together with sorbitol and glycerol, as well as ethylene and propylene glycol.

1.2. Feedstocks

Biomass feedstocks covered in this Review will be briefly introduced in the following. Comprehensive information on their structures and chemical properties may be found elsewhere.[3] In general, plant material consists of lignocelluloses, which can be divided into cellulose (50–70%), a polymer of glucose, hemicellulose (10–40%), a polymer of various sugar monomers including glucose, xylose, mannose, galactose, rhamnose, and arabinose, and lignin (10–30%), an aromatic polymer (Figure 1). Such plant material contains some extracts of terpenes, oils, and various minerals. Additionally, some plants, such as sunflower or rapeseed, produce oil-containing seeds. These vegetable oils can be utilized for the production of biodiesel by transesterification or processed by hydrocracking. Furthermore, certain plants or fruits consist predominantly of starch or sugars, for example, sugarcane, sugar beet, or corn.

Overall, the different substrates can be classified as carbohydrates—which cover sugars, starch, cellulose, and hemicellulose—polyols, or polyhydric alcohols—which include hydrogenated mono- and disaccharides.

1.2.1. Carbohydrates

Carbohydrates have the general formula $C_m(H_2O)_n$ and are usually divided into mono-, di-, oligo-, and polysaccharides, wherein mono- and disaccharides are commonly referred to as sugars. Natural saccharides are generally built of simple carbohydrates called monosaccharides with the general formula $(CH_2O)_n$, where n is three or more. Glucose is the major building block of cellulose, hemicellulose, and starch. Hemicellulose contains a large variety of other monosaccharides, such as xylose and arabinose. Various target products are available from starch, cellulose and hemicellulose. Simple hydrolysis releases the single sugar molecules, which are subsequently hydrogenated to the corresponding sugar alcohols and undergo further dehydration or hydrogenolysis.

1.2.2. Polyols

Hydrogenation of monosaccharides leads to the formation of sugar alcohols, also known as polyols or polyhydric alcohols, with the general formula $H_2(CH_2O)_{n+1}$. Disaccharides can also be hydrogenated to sugar alcohols, for example, maltitol and lactitol, but they contain only one available aldehyde group for reduction. Various sugar alcohols find applications in the food industry as a replacement for conventional sugars and in combination with artificial sweeteners to counter their lower sweetness compared to glucose. Xylitol is one of the most frequently applied sugar substitutes because of its similar appearance and sweetness, but lower energy content compared to sucrose. In regard to applications of other common sugar alcohols, ethylene glycol, the simplest sugar alcohol, is used as an antifreeze and in polymer

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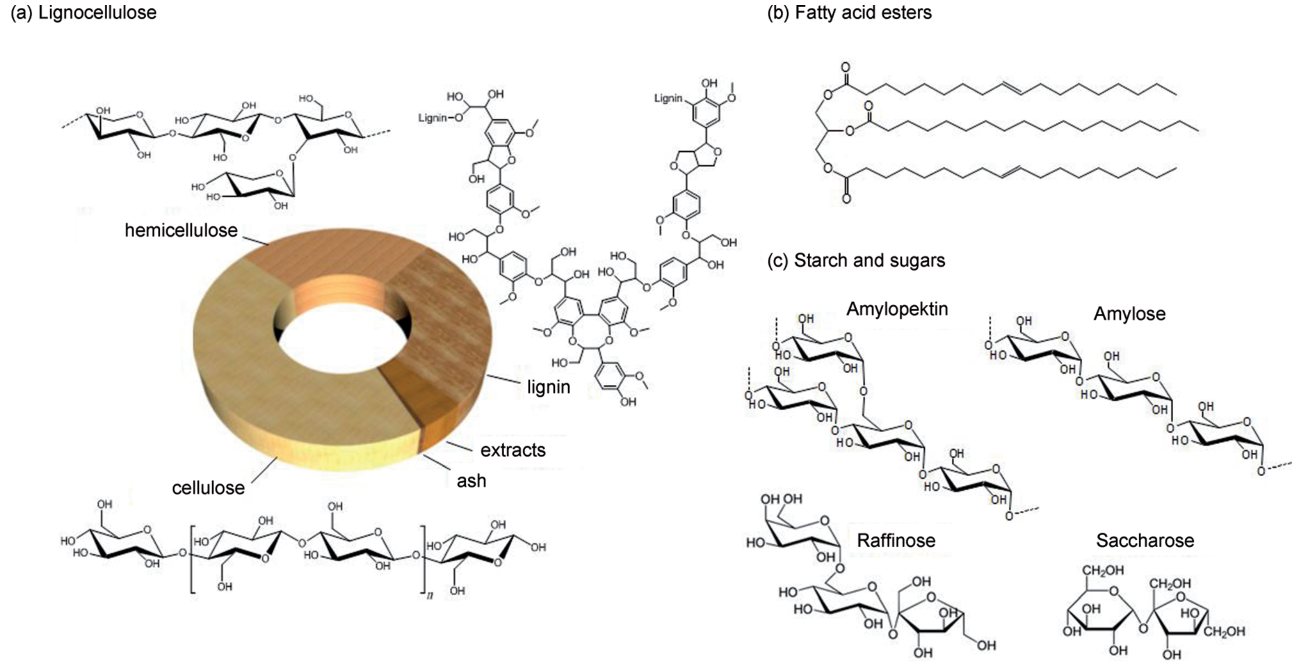

Figure 1. Illustration of the main constituents of renewable feedstocks: a) lignocellulose, b) fatty acid esters and c) starch including amylose and amylopektin and exemplary sugars.

production, while glycerol is used in medicine, pharmaceutics, and personal care, mainly as a lubricant and humectant. Starting from sorbitol, further transformations including dehydration to sorbitan and isosorbide, hydrodeoxygenation, and carbon–carbon bond cleavage by hydrogenolysis are possible, as demonstrated by Li and Huber, and will be discussed comprehensively in Section 3.6 on the hydrogenolysis of sugar alcohols.[8] Scheme 1 gives an overview of the possible transformations of cellulose via glucose to sorbitol and further products.

In regard to the broad product range, one major issue certainly concerns the development and optimization of suitable reaction conditions and catalyst systems to allow high selectivity for the desired target products. Li and Huber demonstrated the controlled hydrodeoxygenation of sorbitol to hexane with up to 50% selectivity.[8] More interestingly, sorbitol, xylitol, and glycerol have been named in a list of 12 potential biomass-based platform chemicals identified by the Department of Energy (DoE).[9] The hydrogenolysis and hydrodeoxygenation of sugar alcohols can yield glycerol, ethylene, propylene glycol, and even methanol. Sugar alcohols present promising intermediates for the production of hydrocarbons for conventional refinery applications and were demonstrated to be efficient feedstocks in reforming for the production of syngas.[10] Sugar alcohols, especially sorbitol, can also be used as dispensing agents and humectants in pharmaceuticals, cosmetics, and textiles, as well as for the further chemical synthesis of surfactants and ascorbic acid or biochemically transformed to bioethanol.

Glycerol, in particular, has the potential to become a primary building block. Technologies for its manufacture already exist and processes for its conversion have recently been investigated intensively, not least because of the growing biodiesel market.[11] Glycerol is converted by catalytic or biocatalytic hydrogenolysis into ethylene and propylene glycols, which are already important platform chemicals for various applications; for example, propylene glycol is a feedstock for the production of acetol and lactic acid. 1,3-Propylene glycol (1,3-propanediol) is also a promising compound for the production of polymers.[5] The dehydration of glycerol also allows access to hydroxypropionaldehyde and acrolein. Acrolein is considered as a future precursor for the production of the bulk chemical acrylic acid. Further applications of glycerol include the synthesis of epichlorohydrin, glycerol ethers, and esters for surfactant and polymer applications. Glycerol carbonate can be used as a nonvolatile solvent and substituent for methyl carbonate in the production of polycarbonate and polyurethan.

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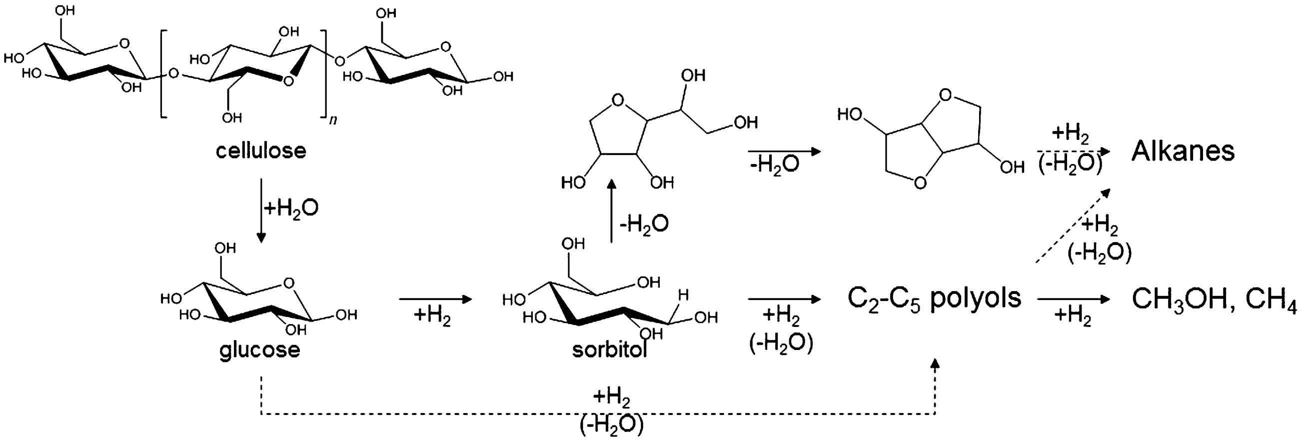


Scheme 1. Possible transformations of polysaccharides to sugars, sugar alcohols and further hydrogenation products.

1.3. Concept of the Reaction

The term hydrogenolysis can be found in several contexts, for example along with hydrocracking in the area of oil refining, for the removal of various heteroatoms in hydrodesulfurizers or hydrotreating, or in combination with oxygen removal by hydrodeoxygenation. In view of this wide field, some effort should be made to discuss appropriate definitions of the various reaction types.

Historically, the term hydrogenolysis goes back to Carleton Ellis, who described the hydrogenolysis of carbon–carbon bonds in organic substances,[12] although Sabatier and Murat had already described the hydrogenolysis of benzyl alcohol to toluene in 1915,[13] and Padoa and Ponti reported the hydrogenolysis of furfuryl alcohol as early as 1906.[14]

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.[15] The definition does not imply any mechanistic considerations, but refers to the stoichiometry of the reaction, which may be summarized as Equation (1),

$$\mathrm{R{-}X + H_2 \rightarrow R{-}H + H{-}X} \qquad (1)$$

where X can represent an alkyl chain or other functional group containing heteroatoms, for example, OH, OR, SH, NH_2, NR, etc.

The hydrogenolysis reactions of hydrodesulfurization and hydrotreating are widely applied in petroleum refineries, wherein sulfur, nitrogen, and oxygen heteroatoms are removed from hydrocarbon feedstocks. Conventional catalyst systems for refinery applications are based on molybdenum sulfide containing small amounts of cobalt or nickel. The term hydrocracking is usually employed for the cleavage of carbon–carbon bonds of hydrocarbons by hydrogen. The reactions take place at rather high temperatures of about 260–425 °C and are catalyzed by difunctional solid acid hydrogenation catalysts. Although several reaction pathways may occur and various mechanisms have been discussed, one may in principle distinguish between:

- noncatalytic thermal cleavage of C–C bonds by hydrocarbon radicals with the addition of hydrogen,
- monofunctional C–C bond cleavage with the addition of hydrogen over hydrogenation catalysts consisting of metals (Pt, Pd, Ni), oxides, or sulfides,
- difunctional C–C bond cleavage with the addition of hydrogen over difunctional catalysts consisting of a hydrogenation component dispersed on a porous, acidic support. Most hydrocracking reactions follow this route in petroleum refining.

Consequently, only the second reaction type describes the classical hydrogenolysis, while the former and the latter proceed by thermal or acid-catalyzed cracking, respectively, followed by hydrogenation, and would strictly speaking not be covered in the present Review, although acidic and basic co-catalysis may take place in the hydrogenolysis of polyols (see Section 4). Nevertheless, simply based on the products, these reaction types are difficult to distinguish and may appear together. Therefore, without knowledge of the exact reaction mechanisms, clear differentiation is not possible.

In regard to the transformation of biomass-derived compounds, a reaction closely associated with hydrogenolysis is hydrogenation, where a pair of hydrogen atoms is usually added to a molecule. In contrast to hydrogenolysis, no bond cleavage occurs. Depending on the reaction conditions and catalyst system, both reactions may take place and sometimes both may even occur in the course of the reaction. Therefore, a combined discussion is often necessary to cover the field fairly.

1.4. Where Can Hydrogen Come from?

The requirement of hydrogen is a major issue in biomass valorization. Today’s production of hydrogen from fossil fuels by gasification and steam reforming is energy-intensive and can not be considered as a sustainable technology either in terms of energy requirements or concerning the feedstock base. Synthesis routes with low hydrogen requirement are preferred in currently discussed biorefinery schemes. Nevertheless, in the long term, alternative production routes for hydrogen will be in place that overcome the lack of a sustainable generation of hydrogen. Such promising technologies for the production of "green hydrogen" have found increasing attention in recent years and are discussed in various comprehensive reviews covering water electrolysis,[16] photocatalytic water splitting,[17] biological systems for hydrogen generation,[18] and reforming of biomass.[19,20]

2. Hydrogenolysis of Glycerol

As a consequence of the recent interest in biofuels, the production of glycerol has increased enormously, and several ways of its valorization have been described. One of those ways is hydrogenolysis to give value-added products, especially propanediols (1,2- and 1,3-PG) and also ethylene glycol (EG). 1,3-PG is copolymerized with terephthalic acid to produce the polyester known as SORONA from DuPont and CORTERRA from Shell. These are used in the manufacture of carpet and textile fibers that exhibit unique properties in terms of chemical resistance, light stability, elastic recovery, and dyeability. Currently, 1,3-PG is produced from petroleum derivatives such as ethylene oxide (Shell route) or acrolein (Degussa-DuPont route) by using chemical catalysts. 1,2-PG is an important commodity chemical derived from propylene oxide. These diols can be produced by an alternative route from glycerol.

Very recently, several reviews and book chapters have been published that meticulously cover the subject of the catalytic hydrogenolysis of glycerol up to 2007–2008.[21–23] This section will thus concentrate on the most recent research on the subject; for the details of previously published literature, the reader is referred to those reviews. The catalysts used in hydrogenolysis of glycerol can be divided into several, sometimes overlapping categories (Table 1). Noble and other metals (Ru, Rh, Re, Ir, Pd, Pt, Au, Cu, Ni, Co, Mn, Mo) have been used as mono- or dimetallic catalysts supported on various materials (C, Al_2O_3, SiO_2, ZnO, Amberlyst, zeolites), in the Raney form (Ni and Cu), and as mixed oxides or salts (Mg, Al, Zn, Ni, Co, and Cu oxides in different combinations, copper chromite). In some cases, homogeneous acidic or basic co-catalysts have been used together with heterogeneous metallic catalysts. The use of homogeneous Rh, Ru, and Pd complexes in the hydrogenolysis of glycerol has also been described.

The general challenge in the hydrogenolysis of glycerol is the selective cleavage of C–O over C–C bonds. Thus, there has been a lot of research to find the right catalytic system that can selectively discriminate between those two bonds. Noble metal catalysts are usually more active than Cu- or Ni-based ones. However, or rather for this reason, their selectivity for propylene glycols is lower, as they are capable of cleaving both bonds. Copper catalysts have, therefore, been used successfully to obtain propanediols, as will be mentioned later in this section. The discrimination between primary and secondary hydroxy groups in the cleavage of C–O bonds is a different problem. For steric reasons, the primary OH group is cleaved more readily. However, several catalyst systems have been described which result in a significant selectivity for 1,3-PG.

2.1. Copper Catalysts

The earliest described study of glycerol hydrogenolysis dates back to 1932, when a copper chromite catalyst was applied for this reaction.[24] Propylene glycols were obtained in 85% yield when the hydrogenolysis was carried out at 250°C and 200 bar of hydrogen. The tendency in later years was to use less-severe reaction conditions. Thus, in the study by Montassier et al. Raney copper gave higher 1,2-PG selectivity compared with Raney nickel, and also no hydrocarbons were formed.[25] A 66% yield of 1,2-PG was achieved at 85% glycerol conversion at 240°C and 30 bar of hydrogen. The same research group also observed a similar behavior with Cu/C, which proved to be very selective towards 1,2-PG.[26] In this case, the selectivity increased with hydrogen pressure, until reaching a maximum (84.5%) at 40 bar. Montassier et al. also found that Raney copper, unlike noble metal catalysts (Ru, Rh and Ir) and Raney Ni, furnished mainly 1,2-PG under drastic conditions (300 bar H_2 and 260°C), while methane was obtained as the main product with the other catalysts.[27] Chaminand et al. achieved nearly 100% selectivity for 1,2-PG on Cu-ZnO under 80 bar of hydrogen, but at the expense of low glycerol conversion (only 20% after an extended reaction time).[28] Wang and Liu showed that smaller copper particles had higher activity.[29] The drawback of copper catalysts is their deactivation through metal sintering and surface oxidation.

Copper catalysts have also been of high interest more recently for the hydrogenolysis of glycerol. Being not as active as noble metals, Cu does not catalyze the C–C bond cleavage and thus increases the selectivity for PG. Guo et al. showed that Cu catalysts supported on γ-Al_2O_3 can be very selective and active even at 36 bar H_2, as a result of the strong metal–support interaction.[30] Another improvement in the performance of copper-based catalysts was reported by Liang et al., who achieved high 1,2-PG selectivity and glycerol conversion (96 and 51%, respectively) by using a Cu-Cr catalyst with a high specific surface area.[31]

Less attention has been given to the selective formation of 1,3-PG in the hydrogenation of glycerol. It is formed with low selectivity in an aqueous environment. To achieve higher selectivity, an organic aprotic polar solvent would be required, which is a major drawback.[28,32] Huang et al. overcame this difficulty by using a difunctional catalyst. They performed the solvent-free hydrogenolysis of glycerol under only 5.4 bar of H_2 and at 210°C in a continuous fixed-bed reactor, and achieved a 1,3-PG selectivity of 32% at 84% glycerol conversion. Their difunctional catalyst was copper with $H_4SiW_{12}O_{40}$ supported on SiO_2.[33] Huang et al. tested a series of CuO/SiO_2 catalysts (effectively Cu/SiO_2 following the prereduction) with different contents of residual sodium (from the use of NaOH in the preparation) in the hydrogenolysis of glycerol.[34] They found that with more residual Na, the catalytic activity generally decreases because of the

Table 1: Overview of catalyst systems and reaction conditions utilized in the hydrogenolysis of glycerol.[a]

Catalyst	Conditions	Main product(s)	Conversion [%]	Selectivity [%]	Ref.
$CuO\text{-}Cr_2O_3$	250 °C; 200 bar	1,2-PG	–	85 (yield)	[24]
Raney Cu	240 °C, 30 bar	1,2-PG	85	78	[25]
Cu/C	260 °C, 40 bar, 65 h	1,2-PG	43	85	[26]
Cu-ZnO, H_2WO_4	180 °C, 80 bar, 90 h	1,2-PG	21	81	[28]
Cu-ZnO	180 °C, 80 bar, 90 h	1,2-PG	19	100	[28]
$Cu/\gamma\text{-}Al_2O_3$	200 °C, 36 bar, 10 h	1,2-PG	34	94	[30]
$Cu\text{-}H_4SiW_{12}O_{40}/SiO_2$	210 °C, 5.4 bar	1,3-PG	84	32	[33]
$Na\text{-}CuO/SiO_2$	180 °C, 90 bar, 12 h	1,2-PG	41	94	[34]
Ru/Al_2O_3 (from $RuCl_3\cdot H_2O$)	240 °C, 80 bar, 5 h	1,2-PG	69	38	[43]
Ru/SiO_2 (from $RuCl_3\cdot H_2O$)	240 °C, 80 bar, 5 h	1,2-PG	25	50	[43]
Ru/ZrO_2 (from $[RuNO(NO_3)_3]$)	240 °C, 80 bar, 5 h	1,2-PG	40	60	[43]
Ru/SiO_2 (from $[RuNO(NO_3)_3]$)	240 °C, 80 bar, 5 h	1,2-PG	22	60	[43]
Ru/hydrotalcite	180 °C, 25 bar	1,2-PG	59	86	[45]
Ru/NaY	180 °C, 50 bar, 12 h	1,2-PG	10	37	[47]
$Ru/\gamma\text{-}Al_2O_3$	180 °C, 50 bar, 12 h	1,2-PG	34	47	[47]
Ru/SiO_2	180 °C, 50 bar, 12 h	1,2-PG	3	55	[47]
Ru/TiO_2	180 °C, 50 bar, 12 h	1,2-PG	66	47	[47]
$Ru/Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$	3–14 bar, no external heating	1,2-PG	21	96	[32]
Ru/C, Nb_2O_5	180 °C, 60 bar, 8 h	1,2-PG	45	61	[50]
Ru/TiO_2	180 °C, 60 bar, 8 h	1,2-PG	46	63	[51]
Ru/C	190 °C, 90 bar, 7 h	1,2-PG	20	22	[52]
Ru/TiO_2	190 °C, 90 bar, 1 h	1,2-PG	20	45	[52]
Ru/C	200 °C, 40 bar, 5 h	EG	40	47	[53]
Ru/C, NaOH	200 °C, 40 bar, 5 h	LA	100	34	[53]
Ru/C, CaO	200 °C, 40 bar, 5 h	LA	85	48	[53]
PtRu/C	200 °C, 40 bar, 5 h	EG	42	49	[54]
PtRu/C, NaOH	200 °C, 40 bar, 5 h	LA	100	37	[54]
$Ru\text{-}Re/SiO_2$	160 °C, 80 bar, 8 h	1,2-PG	51	45	[56]
$Ru/C + Re_2(CO)_{10}$	160 °C, 80 bar, 8 h	1,2-PG	59	57	[57]
Ru-Cu(3:1)/BEN-TMGL	230 °C, 80 bar, 18 h	1,2-PG	100	86	[58]
$Rh\text{-}ReO_x/SiO_2$	120 °C, 80 bar, 5 h	1,2-PG	98	48	[59]
		1,3-PG		20	
$Ir\text{-}ReO_x/SiO_2$	120 °C, 80 bar, 12 h	1,3-PG	100	30	[62]
			20	58	
$Pt/WO_3/ZrO_2$	170 °C, 80 bar, 18 h	1-propanol	88	27	[67]
		1,3-PG		24	
Pd/Fe_2O_3 (transfer hydrogenolysis by ethanol or 2-propanol)	180 °C, 5 bar inert gas, 24 h	1,2-PG	100	94	[68]
$Pt/CaCO_3$, H_3BO_3	200 °C, 40 bar, 18 h	LA	56	60	[69]
Pt/sulfated ZrO_2	170 °C, 73 bar, 24 h	1,3-PG	67	84	[70]
Pt-Re/C	170 °C, 40 bar, 2 h	1,3-PG	20	34	[71]
		1,2-PG		33	
Co/MgO	200 °C, 20 bar, 9 h	1,2-PG	45	42	[73]
Co nanoparticles	220 °C, 30 bar, 7 h	1,2-PG	32	57	[74]
Co nanowires	220 °C, 30 bar, 7 h	1,2-PG	38	54	[74]
Ni/NaX zeolite	200 °C, 60 bar, 10 h	1,2-PG	95	72	[75]
Ni-Ce/C	200 °C, 50 bar, 6 h	1,2-PG	63	77	[76]
$Ni/SiO_2\text{-}Al_2O_3$	200 °C, 25 bar, 8 h	1,2-PG	30	98	[77]
$CuO\text{-}ZnO\text{-}Al_2O_3$	200 °C, 14 bar, 24 h	1,2-PG	52	94	[78]

[a] BEN: bentonite; TMGL: 1,1,3,3,-tetramethylguanidynum lactate; 1,2-PG: 1,2-propylene glycol; 1,3-PG: 1,3-propylene glycol; EG: ethylene glycol; LA: lactic acid.

lowering of the BET surface area, an increasing Cu particle size, and difficulties in CuO reduction. However, a certain amount of sodium proved to be beneficial as it ensures some weak basic promotion of the activity and also prevent leaching of the copper. The tested catalysts reached high 1,2-PG selectivities of 94–99 %, while no formation of 1,3-PG was reported.

One of the most interesting developments in Cu catalysts for this reaction was a recent study by Akiyama and coworkers, who carried out the gas-phase hydrogenolysis of glycerol at an ambient pressure of H_2.[35,36] They used commercial copper catalysts supported on Al_2O_3, Cr_2O_3, ZnO, and SiO_2, as well as nickel on SiO_2. The Cu/Al_2O_3 and Cu/Cr_2O_3 catalysts resulted in quantitative conversion of glycerol and high selectivity for 1,2-PG. A temperature gradient within the catalyst bed was used, as the initial dehydration of glycerol to hydroxyacetone (acetol) requires a higher temperature than the subsequent hydrogenation of the latter. The hydrogenation of hydroxyacetone was also examined separately using Cu/Al_2O_3.

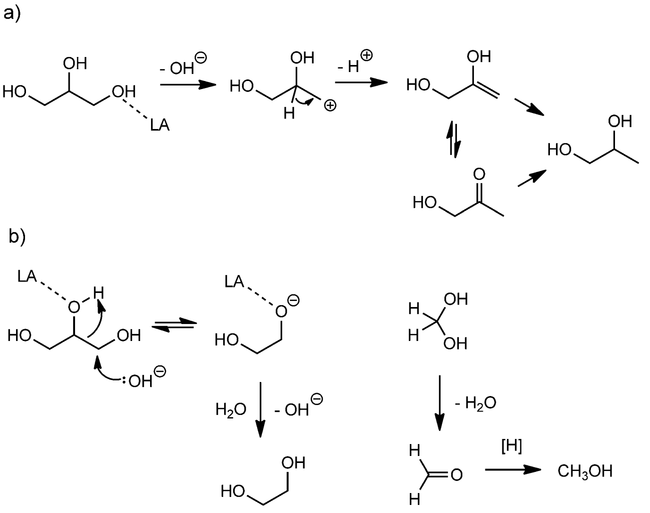
2.2. Ruthenium and Rhodium Catalysts

The earliest applications of rhodium and ruthenium catalyst systems for the hydrogenolysis of glycerol were mainly in the field of homogeneous catalysis. Thus, in 1987 Che patented the use of a [Rh(CO)$_2$(acac)] (acac = acetylacetonate) complex together with tungstenic acid for the hydrogenolysis of glycerol under the somewhat harsh conditions of 300 bar of syngas at 200 °C.[37] Four years later, homogeneous Ru complexes were for the first time used for this purpose by Braca et al.[38] and then, under milder reaction conditions, by Schlaf et al.[39] However, in the meantime, Montassier et al. examined the hydrogenolysis of glycerol over heterogeneous, supported Rh and Ru, as well as other metallic, catalysts, and provided pioneering insights into the reaction mechanism[27] (see Section 4). Chaminand et al. examined different solvents for the hydrogenolysis of glycerol (water, sulfolane, dioxane) with Rh and other supported metal catalysts.[28] The research group of Miyazawa examined carbon-supported noble metal catalysts (Ru, Rh, Pd, and Pt), of which Ru resulted in the highest conversion and also the highest selectivity for hydrocracking products.[40,41] They then showed, however, that Rh/SiO$_2$ is more active than the previously examined Ru/C catalyst.[42] Miyazawa and co-workers also greatly contributed to our understanding of the mechanistic aspects of glycerol hydrogenolysis.

Supported mono- and dimetallic Ru catalysts have recently been used preferentially for this reaction. Vasiliadou et al. used Ru supported on alumina, silica, and zirconia for the selective hydrogenolysis of glycerol to 1,2-PG at 240 °C and 80 bar of H$_2$.[43] The authors noticed the importance of the catalyst to initially dehydrate glycerol to acetol, which is then readily hydrogenated, and suppresses the C–C hydrogenolysis to give ethylene glycol. The zirconia-supported catalyst was found to be the most active; however, Ru on silica showed the highest 1,2-PG selectivity. Of the two Ru precursors used for the Ru/γ-Al$_2$O$_3$ catalyst (Ru nitrate and chloride), the one prepared from the chloride was significantly more active, but had a tendency for excessive hydrogenolysis, thereby leading to the formation of propanols. The authors explained this outcome by the higher acidity of the catalyst because of the presence of chloride ions on its surface, which could create Lewis acid sites on the metal surface.[44] Overall, it was suggested that while the conversion of glycerol increases with the acidity of the catalyst, the presence of moderately acidic sites is sufficient to activate the glycerol dehydration step without leading to excessive hydrogenolysis. The participation of Lewis acid sites in the formation of 1,2-PG is shown in Scheme 2, and will be discussed in more detail in Section 4.

An interesting series of hydrotalcite-like supports was used for ruthenium catalysts for the selective hydrogenolysis of glycerol to 1,2-propylene glycol under mild conditions (180 °C, 25 bar H$_2$).[45] A catalyst containing Ca, Zn, Mg, and Al in the support exhibits the highest conversion (59 %) and 1,2-PG selectivity (86 %).

Noble metal catalysts (Ru, Pd, Pt) supported on carbon, silica, and alumina together with solid acids (ion-exchange resins—Amberlysts or homemade) were tested by van Ryneveld et al.[46] 1,2-PG was obtained as the main product at temperatures up to 200 °C, while condensation products significantly increased at higher temperatures.



Scheme 2. Lewis acid site-assisted glycerol hydrogenolysis towards a) propylene glycols (at the example of 1,2-PG) and b) ethylene glycol (postulated mechanism; leaving of the “nominal” carbanion with concerted proton transfer). The basic species can be the surface OH groups, as it is also suggested in Montassier’s explanation. See also chapter 4.

The hydrogenolysis of glycerol with Ru catalysts on different supports (SiO$_2$, γ-Al$_2$O$_3$, NaY zeolite, C, and TiO$_2$) was also investigated by Feng et al.[47] They noticed that Ru/TiO$_2$ was more active than the other ones, while at the same time less selective for 1,2-PG, producing more ethylene glycol instead. The authors suggested that as titania is not acidic (unlike silica, alumina, and zeolite Y), the reaction on Ru/TiO$_2$ does not proceed through dehydration but by reversible dehydrogenation, according to the mechanism proposed by Montassier et al.[48] The lack of acetol among the detected products is given as supporting evidence. However, it was not mentioned that titania supports in reduced catalysts are known to have oxygen-deficient titanium atoms that can act as Lewis acid sites, which could assist in cleavage of both C–O and C–C bonds, eventually leading to the formation of PG and EG, respectively, as shown in Scheme 2 a,b (see also Section 4). The influence of the Ru/TiO$_2$ prereduction temperature on its properties was also examined. The lower activity of high-temperature-reduced catalysts was attributed to the growth of Ru particles caused by the heat treatment and partial covering of their surface with Ti$_2$O$_3$ species. The latter is known as an SMSI (strong metal-support interaction) effect.[49]

The aforementioned type of difunctional metal-acid catalysts was used by Alhanash et al.[32] Ruthenium-doped acidic heteropoly salts Cs$_{2.5}$H$_{0.5}$[PW$_{12}$O$_{40}$] (TPA) proved to be selective catalysts in the hydrogenolysis of glycerol to 1,2-PG under very mild pressures of 3–14 bar of H$_2$ and without external heating. Typical glycerol hydrogenolysis conditions used with noble metal catalysts involved H$_2$ pressures of 60–90 bar and temperatures between 160 and 190 °C.

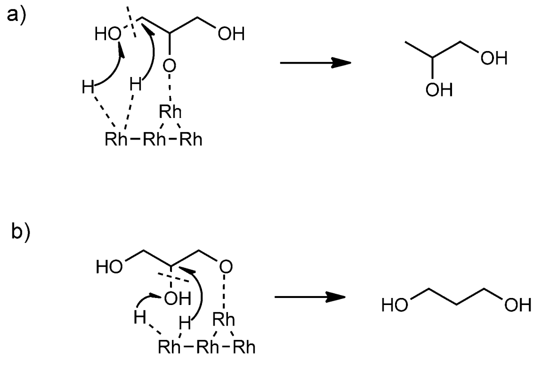
A very recent example of the application of solid acids as co-catalysts has been described by Balaraju et al., who used the Ru/C catalyst together with niobia, TPA supported on zirconia, and the cesium salt of TPA (also supported on zirconia), as co-catalysts.[50] Nb_2O_5 and TPA/ZrO_2 gave the highest glycerol conversion (about 45%), and in all the co-catalyzed reactions 1,2-PG was the main product, with over 60% selectivity. The same research group also described the hydrogenolysis of glycerol over Ru/TiO_2 catalysts prepared by impregnation and deposition/precipitation methods, of which the latter showed significantly higher activity (up to 46% conversion) as a result of its higher dispersion of metal. Their selectivities towards 1,2-PG reached up to 63% and were retained during recycling experiments.[51]

Brandner et al. examined, among other reactions of glycerol valorization, the hydrogenolysis of glycerol over carbon- and titania-supported Ru catalysts.[52] The latter exhibited significantly higher activity and also better 1,2-PG selectivity, as the longer time necessary to reach sufficient conversion over Ru/C resulted in the degradation of 1,2-PG to lower alcohols and gases. Although the authors do not mention it directly, the Lewis acid sites (oxygen vacancies) on the partly reduced titania may be responsible for the higher activity of Ru/TiO_2. The $Cu/ZnO\text{-}Al_2O_3/\gamma\text{-}Al_2O_3$ catalysts, also tested by the authors, turned out to be less active, but their selectivity towards 1,2-PG was higher than that of titania-supported Ru.

The research group of Davis compared Ru/C and Pt/C catalysts in the hydrogenolysis of glycerol, and found that the former was more active, although much less selective for PG—yielding more EG and methane instead.[53] The addition of a base (NaOH or CaO), however, greatly increased the activity of Pt/C compared to that of Ru/C, which suggests that cleavage of the C−C bond on the latter is catalyzed by the metal (by the initial dehydrogenation, according to the authors). The same research group also tested carbon-supported PtRu and AuRu catalysts.[54] Both of them functioned in a similar way as the monometallic Ru catalyst, only AuRu/C was altered by the harsh reaction conditions, with gold migrating off the Ru surface and agglomerating on the support.

Supported dimetallic catalysts with Ru and Re or Cu have also been applied recently for the hydrogenolysis of glycerol. Such RuRe catalysts with SiO_2, ZrO_2, TiO_2, and zeolites (H-β and H-ZSM5) as supports were prepared by Ma and He, and compared with their monometallic Ru counterparts in the hydrogenolysis of glycerol.[55] In all the combinations examined, dimetallic catalysts provided significantly higher (two- to sixfold) glycerol conversions, and in most cases also increased the selectivity for 1,2-PG. Interestingly, all the dimetallic catalysts showed a decreased tendency for C−C hydrogenolysis (EG formation) than the respective monometallic ones. According to the authors' physicochemical examinations of the catalysts, the presence of Re improves the dispersion of rhodium on the surface. The same authors in their next study concentrated more thoroughly on the $RuRe/SiO_2$ system and found that high prereduction temperatures decrease the activity of this catalyst.[56] Before their research on the dimetallic systems, the same research group studied Ru catalysts on alumina, active carbon, and zirconia with $[Re_2(CO)_{10}]$ used as a co-catalyst. This system was also found to increase the glycerol conversion and 1,2-PG selectivity.[57] Jiang et al. used Ru in combination with Cu supported on bentonite (clay) modified with 1,1,3,3-tetramethylguanidinium lactate (ionic liquid) as a glycerol hydrogenation catalyst.[58] The dimetallic catalysts with different Ru/Cu ratios were compared with monometallic ones. They proved to be significantly more active than the monometallic copper catalyst (although less active than Ru), but their selectivity for 1,2-PG was superior to that of monometallic Ru. However, in adjusted reaction conditions (230°C and 80 bar H_2), a catalyst with a Ru/Cu ratio of 3:1 resulted in a quantitative glycerol conversion and a 85% yield of 1,2-PG.

Shinmi et al. demonstrated the application of Rh/SiO_2 catalysts with the addition of a second metal (Re, Mo or W) for the hydrogenolysis of glycerol in water, and also postulated interesting insights into the reaction mechanism.[59] The authors found that the Re in the RhRe catalyst appears to be a partly reduced oxide, thus the catalyst is in fact $RhReO_x/SiO_2$. According to them, glycerol hydrogenolysis on this catalyst proceeds directly and not via the initial dehydration to acetol. Firstly one of the glycerol oxygen atoms is anchored to Re, thereby forming an alkoxide, and its vicinal OH group undergoes direct hydrogenolysis by the H atoms adsorbed on the Rh. The product is either 1,2-PG or 1,3-PG, depending on which OH group is adsorbed and which one is cleaved. Thus, the $RhReO_x$ surface would be the location of the active sites. Some facts not explicitly stated by the authors but implied by this mechanism are worth mentioning. Namely, the electron-deficient Re atoms in ReO_x (neighboring with oxide vacancies) would act as Lewis acid sites, and the relationship between the Rh and ReO_x phases can be compared to the mechanistic aspects typical for a SMSI state,[60] although ReO_x is not a support here. Direct hydrogenolysis of C−O bonds is also postulated (Scheme 3), which is in contrast to the widely accepted mechanism proposed by Montassier et al., which involves a dehydrogenation/dehydration/hydrogenation pathway.[61] The authors refrain from discussing whether such a C−O cleavage involves a hydride and proton transfer, a free-radical reaction, or other mechanisms. In this case, however, another Lewis acid site assisted mechanism is also possible, as



Scheme 3. Glycerol hydrogenolysis to a) 1,2-PG and b) 1,3-PG on the interface between ReO_x and the Rh metal surface over $Rh\text{-}ReO_x/SiO_2$ according to Shinmi et al.[59]

shown in Schemes 2a and 7a,b, and discussed in Section 4. In any case, the relatively favored initial adsorption of mainly primary OH groups on the rhenium atoms would explain the significant (over 20%) 1,3-PG selectivity, as secondary OH groups would then react with hydrogen according to that mechanism.

What was missing in the aforementioned publication is, however, provided in the most recent study by the same research group. Thus, the reaction mechanism is very extensively discussed together with the description of rhenium-doped iridium catalyst for the hydrogenolysis of glycerol, which will be mentioned in Section 2.3.[62]

Similar $RhReO_x$ and $RhMoO_x$ catalysts, but carbon-supported, were examined extensively, both experimentally and theoretically (DFT calculations), by the research group of Dumesic in the hydrogenolysis of cyclic ethers and also polyols (including glycerol).[63] Based on their observations of the selective cleavage of the more hindered C−O bond in cyclic ethers and secondary alcohol group in polyols, they elucidated a mechanism involving the protonation of the less accessible oxygen atom by an acidic OH group of ReO_x (as the departure of a water molecule from the secondary carbon atom is more favored), with a concerted hydride transfer from the neighboring primary alcoholic carbon atom to form an intermediate $RCH_2{-}CH{=}OH^+$ oxocarbenium cation. This mechanism, supported by DFT calculations, plausibly explains the observed selectivity for α,ω-diols, but it differs from the postulations of Tomishige and co-workers in the assisting role of the primary hydroxy group.[62]

Taher et al. studied in recent years the homogeneous hydrogenolysis of glycerol. They used aqueous Ru complexes with bipridine, phenantroline, and terpyridine in sulfolane solution with triflic acid.[64] They demonstrated the possibility of using this system for hydrogenation by successive dehydrations and hydrogenations all the way to propane. Those results suggest that these catalytic systems can be used to deoxygenate higher sugar alcohols and sugars to give value-added products.

2.3. Other Noble Metal Catalysts

Other noble metals that have found applications in the hydrogenolysis of glycerol in recent years are Ir, Pt, and Pd. Iridium was compared with other noble metal catalysts, Raney nickel, and copper by Montassier et al.[27] The first applications of Pd in the hydrogenolysis of glycerol concerned the homogeneous complexes of this metal and were patented by Drent and Jager from Shell.[65,66] Chaminand et al., in their aforementioned work, used Pd among other heterogeneous supported metal catalysts to examine the use of different solvents in the reduction of glycerol.[28]

More recently, Kurosaka et al. obtained 1,3-PG in yields up to 24% (with over 27% *n*PrOH) by using a $Pt/WO_3/ZrO_2$ catalyst.[67] Catalysts with other oxide supports instead of ZrO_2 (TiO_2, HY and AlMCM-41 zeolites, SiO_2-Al_2O_3, and Al_2O_3) exhibited lower activities and selectivities. The use of neither WO_3 nor ZrO_2 alone as supports for Pt resulted in any significant selectivity for 1,3-PG. Thus, the authors suggest that the active sites consist of Pt, WO_3, and ZrO_2. A very interesting example of the use of a Pd catalyst supported on Fe_2O_3 was provided by Musolino et al.[68] They conducted the first selective transfer hydrogenolysis of glycerol to 1,2-PG in the absence of gaseous H_2. The, hydrogen atoms were derived from the solvent (2-propanol or ethanol). The Pd catalyst was used both "as prepared" (in the PdO form) and prereduced with hydrogen. The reaction was carried out in an inert atmosphere at 5 bar and 180°C. In some cases both the glycerol conversion and 1,2-PG selectivity reached close to 100%. In the "as prepared" catalyst, the PdO is reduced to metallic palladium by the solvent (2-propanol is oxidized to acetone). Further acetone is formed by dehydrogenation of the solvent. The resulting hydrogen atoms adsorbed on the Pd are responsible for the hydrogenolysis of glycerol. Unsupported PdO also exhibited some activity, although much lower (32% glycerol conversion), which implies that the Fe_2O_3 support also plays an important role. The authors suggest that the hydrogenolysis of glycerol proceeds mainly by its initial dehydration to hydroxyacetone, although some incidence of direct hydrogenolysis (as on unsupported PdO) cannot be excluded.

A design of $CaCO_3$-supported platinum catalysts is the subject of the most recent study by ten Dam et al.[69] They discovered that the selectivity of the glycerol hydrogenolysis can be shifted from 1,2-propylene glycol to lactic acid by the addition of boric acid. On the other hand, very high selectivity for 1,3-PG (84%) was achieved by Oh et al., who used Pt supported on sulfated zirconia.[70] According to the authors, it is possible to obtain such selectivity because of the strongly acidic support and excess of hydrogen.

In one of their recent publications, the research group of Dumesic described a carbon-supported dimetallic PtRe nanoparticle catalyst which is capable of hydrolyzing glycerol to 1,3-PG in up to 34% yield. The dimetallic system proved to be more active than either the monometallic platinum or rhenium catalyst.[71]

The most recent application of an iridium catalyst for the hydrogenolysis of glycerol was described in the aforementioned work by the research group of Tomishige.[62] Therein, 1,3-PG was formed as the main product with up to 65% selectivity over an $IrReO_x/SiO_2$ catalyst, with the reaction seeming to follow the same mechanism as in their previous studies with the rhenium-doped Rh catalyst. This time the authors provided a whole new reaction mechanism: With the primary OH group initially adsorbed on the Re atom, a hydride transfer is postulated, with the secondary OH^- group as a leaving group. Such a mechanism is strongly supported by experimental results and the products formed. However, with the hydroxy anion being a poor leaving group on its own, the assistance of Bronsted or Lewis acid sites is in our opinion quite probable, but not mentioned by the authors.

2.4. Other Metal Catalysts

Other metal catalysts have also been used for the hydrogenolysis of glycerol. In 1997, Ludwig and Manfred patented a catalyst containing cobalt, copper, manganese, and molybdenum together with an inorganic polyacid.[72] Guo et al. then prepared Co/MgO catalysts calcined at different temperatures.[73] While the low-temperature-calcined material exhibited poor activity, the conversion of glycerol on the sample subjected to high-temperature treatment (calcination at 600 °C) reached 45 %. The 1,2-PG selectivity remained practically independent of the treatment (over 42 %). Higher temperature enhances the interaction between MgO and Co_3O_4, thus promoting the formation of $MgCo_2O_4$ spinel and a Mg-Co-O solid solution, which prevents the aggregation of Co particles under the harsh reaction conditions. Cobalt nanowires and nanoparticles were obtained by Liu et al. by using stearic acid as a surfactant.[74] The materials were tested in the hydrogenolysis of glycerol at 220 °C and 30 bar H_2, and gave moderate glycerol conversion and 1,2-PG selectivity. Zhao et al. studied the hydrogenolysis of glycerol in aqueous solution over nickel catalysts supported on several zeolites, silica, and alumina.[75] Among them, Ni supported on NaX zeolite exhibited the best performance, with 72 % selectivity for 1,2-PG at almost 95 % conversion under 60 bar of H_2. The authors highlight the role of the zeolite acidity in the catalytic activity. The same research group also investigated a Ni-Ce catalyst supported on active carbon, which was treated with KBH_4 following the typical H_2 prereduction or carbothermal reduction.[76] The carbothermal reduction formed the highly dispersed metallic Ni phase, and together with the subsequent KBH_4 treatment generated the phenolic surface groups that increased the acidity. Together, this resulted in the material having a high catalytic activity (over 63 %) and over 77 % selectivity for 1,2-PG. Silica, silica-alumina, and carbon were used as supports for nickel catalysts by Marinoiu et al.[77] Only the Ni/SiO_2-Al_2O_3 catalyst exhibited satisfactory performance in the hydrogenolysis of glycerol, as practically no dehydration of glycerol occurred on the other catalysts. A 1,2-PG selectivity of over 98 % was achieved with the silica-alumina-supported nickel catalyst at 30 % glycerol conversion, under a relatively moderate pressure of 20–25 bar H_2.

Not only typical supported metal catalysts have been recently used for glycerol hydrogenolysis. Meher et al. examined a range of inexpensive, nontoxic, hydrotalcite-derived mixed oxides of Mg, Al, Zn, Ni, Co, and Cu in different combinations.[78] From the evaluated catalysts, the mixed oxides of Cu/Zn/Al proved to be most active, with a propylene glycol selectivity of 93–94 % under only 14 bar of hydrogen. On the basis of the reaction mechanistic pathways proposed and summarized by Miyazawa et al., the authors attribute their good performance to the tailored acidic-basic properties. This pathway includes the possibility of both acid- and base-catalyzed dehydration of glycerol prior to the hydrogenation of the intermediate products.[41]

2.5. Theoretical Investigations

There has also recently been interest in this topic from the point of view of theoretical calculations. The first such investigation of the hydrogenolysis of glycerol to 1,2- or 1,3-PG from first principles was described by the research group of Sautet.[79] The authors found that the role of the catalyst is threefold. Firstly, it makes the glycerol dehydration step more exothermic, and stabilizes the formed isomeric dehydrated intermediate products. The type of adsorption on the catalyst surface determines their relative stability, which has implications on the reaction selectivity, which is the second role of the catalyst. The calculated catalysts also facilitate the hydrogenation step, which leads to propylene glycols. Six intermediates were identified which took part in the reaction (four arising from dehydration at terminal carbon atoms to produce 1,2-PG after hydrogenation, and two resulting from dehydration at the secondary carbon atom to yield 1,3-PG) and this led to the proposed mechanism. As the stability of dehydrated isomers on the metal surface (and therefore the choice of metal) is a crucial factor in the hydrogenation step, the authors compared it to their stability in the gas phase. Acetol and 1,2-aldol were found to be the most stable. Similar observations were made for Ni surfaces, while Rh exhibits a stronger preference for the adsorption of enol structures—although not so strong to completely change the nature of aldol/enol stability, but sufficient to make the formation of 1,2-PG and 1,3-PG competitive. The 1,2-enol becomes the most stable intermediate on Pd surfaces. According to the authors, this difference in the stability of the intermediates as a function of the metal might be a useful descriptor to design new catalysts for the selective formation of 1,3-PG.

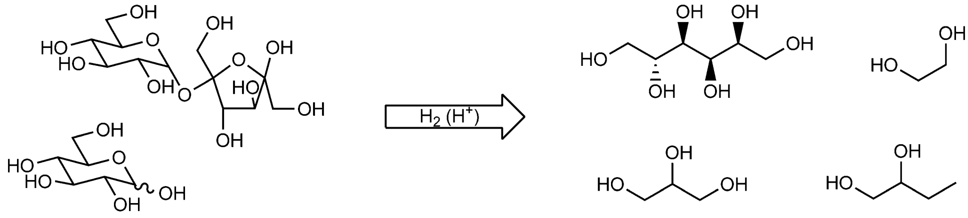
Even more recently, the research group of Dumesic performed DFT calculations on the hydrogenolysis of cyclic ethers and polyols on their ReO_x-doped noble metal catalysts, which they also examined experimentally. They confirmed the preferred formation of an intermediate oxocarbenium cation through protonation by acidic surface OH groups, as a consequence of the presence of oxophilic promoters (ReO_x or MoO_x), which ensures the high selectivity of their catalysts for 1,3-PG.[63]

3. Hydrogenolysis and Hydrogenation of Mono- and Disaccharides

This section concerns the hydrogenative valorization of sugars and in this context deals with two reactions: a) hydrogenation involves the addition of hydrogen to an aldehyde or a ketone (hemiacetal or hemiketal in the ring forms of sugar molecules) to produce a polyol with the corresponding carbon chain length, and b) hydrogenolysis (destructive hydrogenation) is the hydrocracking of the carbon chain and leads to the formation of shorter polyols/alcohols, especially glycerol or glycols. Partial or complete dehydroxylation of polyols (cleavage of OH groups) is also included in the hydrogenolysis reactions. The ultimate product of sugar or sugar alcohol hydrogenolysis is methane. Both reaction types are so mutually intertwined that it would be difficult to review one without the other, especially since many publications concern both of them (Table 2).

In the case of oligosaccharides, the hydrolysis of the glycosidic bond is necessary before (or parallel with) hydrogenation of the the sugar. This is described in more detail in Section 5.

Table 2: Catalyst systems and reaction conditions utilized in the hydrogenation and hydrogenolysis of mono- and disaccharides. Conversions and selectivities are omitted for the sake of brevity, because of the large number of starting materials and formed products.



Catalyst	Conditions		Starting materials	Products	Ref.
	T [°C]	p [bar]			
Heterogeneous					
Pt black, KOH	100–135	84	glucose	mannitol, sorbitol	[81]
$CuO-Cr_2O_3$	250	300	monosaccharides	alcohols, polyols	[82]
$Cu-Al_2O_3$	240	100	crude glucose, molasses	polyols	[84]
$CuO-CeO_2-SiO_2$	225	200	sucrose	glycerol	[86]
Cu/SiO_2	60–80	20–75	glucose fructose	sorbitol sorbitol, mannitol	[90]
CuO-ZnO	90–130	35–65	fructose	mannitol, sorbitol	[92]
$NiCrO_4$	275	200	glucose, sorbitol	1,2-PG	[94]
Ni/SiO_2	125–150	70–100	monosaccharides	sugar alcohols	[95]
Raney Ni	110	20–40	xylose	xylitol	[101]
$Ni-Fe/SiO_2$, $Ni-Cu/SiO_2$	190–230	35	monosaccharides	glycerol	[104]
$Ni-Mo-Cu/SiO_2$	150	50	sucrose	glucose, sorbitol, glycerol, PG, EG	[108]
metallic Ni	250	200–275	monosaccharides	sugar alcohols	[116]
Raney Ni	100–150	140–210	monosaccharides	glycerol, glycols	[117]
Raney Ni, Ni/SiO_2	160	35–135	glucose, oligosaccharides	sugar alcohols	[118]
Ni or Co powder	70	100–500	monosaccharides disaccharides	sugar alcohols glycosyl alditols	[124]
Ru/C pellets	130	50	glucose	sorbitol	[128]
Ru/C, Ru/Al_2O_3, Ru/SiO_2	80–200	10–100	mono- and disaccharides	sugar alcohols	[130]
Ru/C	60–200	25–300	monosaccharides	sugar alcohols	[131]
Ru/Al_2O_3	80–200	10–100	mono- and disaccharides	sugar alcohols	[132]
Ru on zeolites	100–200	10–150	monosaccharides	sugar alcohols	[133]
Ru/TiO_2	100–140	17–130	monosaccharides	sugar alcohols	[136]
Ru/C	100–130	14-55	glucose, fructose	sorbitol, mannitol	[138]
Ru/C, H_3PO_4	80–85	25	sucrose	sorbitol, mannitol	[139]
$Ru/Al_2O_3-TiO_2$, CaO	150–250	250	glucose, fructose	glycerol, 1,2-PG, EG	[141]
sulfide-modified Ru/C	190–250	35-350	monosaccharides	glycols	[142]
Homogeneous					
$[H_2Ru(PPh_3)_4]$	100	20	fructose	glycerol	[145]
Ru complexes	100	20	fructose	glycerol	[146]
Ru and Os phosphine	250	80	monosaccharides	PG, EG	[147]
$Ru-PPh_3$ complex	100–140	3.5	glucose	sorbitol	[149]
Ru-TPPTS complex	100	50	glucose, mannose	sugar alcohols	[150]
Ru-TPPTS complex	90	100	fructose, inulin	sugar alcohols	[154]

The hydrogenation of a sugar to a respective sugar alcohol can proceed at much milder conditions than the hydrogenolysis of C–O and C–C bonds. If both steps are performed in the same process, they can either be carried out in separate reactors, or in one reactor by changing the reaction conditions. The first step (hydrogenation) is carried out at a relatively low temperature and pressure, at neutral pH, and in the presence of a hydrogenation catalyst. For the second step (hydrogenolysis), a base is added, which is usually CaO, and the temperature and H_2 pressure are increased. However, the sugar hydrogenation/hydrogenolysis is also often performed in one step. The role of bases in the reaction mechanism will be discussed in more detail in Section 4.4.

As a consequence of the strong incentives to meet the increasing demand for sorbitol and other sugar polyols, the hydrogenation of sugars has been the subject of numerous patents and research papers. When it comes to the hydrogenolysis of sugars and sugar alcohols, however, the targets and priorities have changed in last decades, as the desired products changed. Previously, glycerol was considered the most desirable product. Nowadays, however, with the abundance of glycerol from biodiesel production, the importance of polyol-related value-added chemicals has shifted towards PG and EG. Since the most commonly used processes for their industrial production are not environmentally neutral, an alternate route for obtaining glycols would be highly desirable that uses renewable and less costly resources. The catalytic hydrogenolysis of carbohydrate-based feedstock provides such an opportunity.

3.1. Earliest Attempts at Sugar Hydrogenation and Hydrogenolysis

The first report on the hydrogenative treatment of sugars and sugar alcohols dates back to 1912, when an attempt was made to obtain sugar alcohols by the reaction of several monosacharides with H_2 at 84 bar and 100–135 °C.[80] Several years later, Cake reported the hydrogenation of glucose to D-mannitol and D-sorbitol on Pt black in aqueous solution in the presence of potassium hydroxide .[81]

3.2. Copper-Based Catalysts

In 1933 Zartman and Adkins reduced several monosaccharides and sugar derivatives (glucose, sorbitol, mannitol, sucrose, lactose, maltose, α-methyl-D-glucoside, pentacetylglucose, gluconic lactone) at 250 °C and 300 bar of hydrogen over a copper-chromium oxide catalyst in anhydrous ethanol.[82] Several hydrogenation products were identified, namely methanol, ethanol, 1,2-PG, C_6 polyols, and a C_6 cyclic ether with a tetrahydrofuran ring and alcohol functionality. The harsh reaction conditions resulted in not only hydrogenation but also hydrogenolytic cleavage of C–C and C–O bonds taking place. Naturally, no attempt was made to formulate the series of involved reactions, or to draw any mechanistic conclusions. A patent from one year earlier also covers the hydrogenation/hydrogenolysis of sugars (and sorbitol), with several catalytic systems mentioned, mainly based on Ni, Cu, and Co, as well as Fe- and Pt-group metals.[83] Another early work concerned the study of the production of polyhydric alcohols by the Cu-Al_2O_3-catalyzed hydrogenolysis of crude sugar materials in a pilot plant.[84] At 240 °C and about 100 bar of H_2, and using a methanol suspension of crude glucose, hydrol, and molasses (sugar by-products), a distillable mixture of polyhydric alcohols was obtained, which contained propylene glycol (main product), glycerol, and higher polyhydric alcohols. At the same time, a process for the hydrogenolysis of sugar and sugar alcohols was disclosed that used a catalyst comprised of copper hydroxide with iron and/or magnesium hydroxide.[85] The authors noticed the beneficial effect of adding magnesium and iron oxide.

The first efforts towards the controlled hydrogenolysis of sugars were made by van Ling et al.[86] in 1967. In the preliminary research, the high-pressure hydrogenation/hydrogenolysis of sucrose over a CuO-CeO_2-SiO_2 catalyst was used as a method to obtain glycerol, glycols, and hexitols. In the next study, the same research group proved that a more than 30 % yield of glycerol could be obtained from sucrose by proper choice of the reactor system and the hydrogenolysis conditions.[87] The glycerol yields were found to be lower in continuous stirred tank reactors (CSTR) than in a batch process.[88] In a CSTR, the stirring results in the reactor mixture being the same as that at the exit. This is a disadvantage for the hydrogenolysis to give glycerol, because the formed lactic acid causes an increased hydrolysis of sucrose to glucose and fructose, while the low exit concentration of $Ca(OH)_2$ (used as a co-catalyst) results in the lower amount of C–C cleavage and the long residence time increases the conversion of glycerol into 1,2-PG, all of which decreases the selectivity for glycerol. The enhancement of C–C cleavage with increasing $Ca(OH)_2$ concentration also proves the role of the base in the mechanism of this reaction, which is broadly discussed in Section 4. On the other hand, to maintain a plug flow, intensive mixing for maximum hydrogen mass transport is impossible in the tubular reactor, which also decreases the selectivity. Two continuous stirred tank reactors in sequence were proposed as a compromise system to achieve the optimum results. On the basis of the earlier findings in the batch reactor experiments, a study on the pilot plant design was subsequently presented for the continuous production of glycerol.[88] Systems of continuous reactors have also been tried for this process, and have resulted in glycerol yields of up to 30 % (with other main products being EG, 1,2-PG, and hexitols).[89] Nowadays, this way of glycerol production is economically less justified since it is a by-product in the generation of biodiesel; however, at that time, the research constituted significant progress, not only from purely scientific considerations but also from a practical point of view.

The hydrogenation of monosaccharides to hexitols under milder conditions has also been performed over copper catalysts. Thus, Makkee et al. reduced fructose and glucose over Cu/SiO_2 as well as other metal catalysts.[90] The hydrogenation of glucose yielded sorbitol, whereas fructose furnished a mixture of sorbitol and mannitol. In the latter case, the copper catalyst proved to be the most selective for the formation of fructose. In agreement with a comparative study by Ruddlesen et al., who also used a Cu/SiO_2 catalyst for the same reaction,[91] the authors suggest that sugars in the furanose form are significantly more reactive towards hydrogenation than the respective pyranoses. They postulated that a furanose or pyranose is coordinated on Cu through its three oxygen atoms, two of which are connected to the anomeric carbon atom. In this way, the sugar becomes ionized, with its anomeric C–O bond partially acquiring double-bond character. The anomeric carbon atom is then attacked by hydrogen adsorbed on another surface copper atom (thus becoming polarized and a hydride-like species). The mechanism of sugar hydrogenation is described in more detail in Section 4.

A much more recent example of a copper-based system was presented by Kuusisto et al., who used a CuO-ZnO catalyst for the kinetic study of fructose hydrogenation.[92] The main products of the reaction were mannitol and sorbitol, and it was found that the initial rates of fructose hydrogenation were second order with respect to hydrogen pressure. As shown above, industrial applications of this reaction have always attracted great interest, which is reflected in the described patents. In fact, the number of patents dealing with this subject since the early days until now has been significantly higher than the number of open literature reports. In addition to the originally used copper-based catalysts, other systems and a large variety of reaction conditions have also been used for the hydrogenation of sugar; furthermore, numerous engineering solutions for the reaction setup have been developed.

3.3. Nickel-Based Catalysts

Of the other catalyst systems used for the hydrogenation/hydrogenolysis of sugars, nickel-based systems are the most common. This tendency was also the case in industrial processes. The system most often used for the hydrogenation of D-glucose in a batch process is a nickel-based catalyst in powder form, particularly Raney nickel promoted by various transition metals.[93]

The first studies on the use of nickel for the hydrogenation/hydrogenolysis of sugars and polyols date back to the 1930s. Although the first patent covers Ni catalysts, it is actually not clear whether they were used,[83] but nickel chromate was applied by Larchar for the hydrogenolysis of glucose and sorbitol.[94] Under quite drastic conditions (275 °C, 200 bar H_2), both C−C and C−O bond cleavage took place, thus leading to the formation of 1,2-PG. The same author applied Ni supported on silica (kieselguhr or silica gel) for the hydrogenation of sugars to their respective polyols.[95] In addition to the hydrogenation of monosaccharides (xylose, glucose), the author also claimed that lactose was reduced to galactitol and sorbitol, as well as sucrose to mannitol and sorbitol, although neither an acid nor any other hydrolyzing agent was mentioned. Kasenhagen[96] claimed Ni on kieselguhr to be an efficient catalyst for the mild hydrogenation of monosaccharides. He first treated the starting sugars with a base to obtain a complex mixture of sugar-like compounds of unknown nature, which was then hydrogenated to yield a mixture of the target polyols. Kieselguhr was also used as a support for Ni catalysts in several later patents concerning the hydrogenation of sugars to polyols.[97–100] The last patent also describes Ni doped with Fe and Cu, as well as kieselguhr-supported nickel phosphate, and covers the hydrogenation of monosaccharides as well as the use of oligo- and polysaccharides (sucrose and starch), which would have to be hydrolyzed simultaneously to hydrogenation. A system of up to five successive autoclaves was employed in the latter case, and sorbitol was always quoted as the primary product, with over 90 % selectivity. More recently, Jiang and Wu used a trickle-bed reactor for the kinetic study of the pseudo-steady-state hydrogenation of xylose to xylitol over Raney nickel catalyst.[101] As partial wetting of the reactor bed is beneficial for conversion—as the hydrogen has better access to catalyst particles—the authors developed a method of modeling the reaction parameters of a partially wetted trickle-bed reactor. The kinetics of the same reaction over the same catalyst were also examined by Mikkola et al., who developed a kinetic model of the xylose and xylitol concentrations that was capable of predicting the behavior of industrial reactors.[102,103]

Nickel doped with iron and copper on kieselguhr has also been used to hydrogenolyze monosaccharides to glycerol, under reaction conditions much more severe than those required for the hydrogenation of sugars to polyols.[104] A series of three or four reactors was found to be the most efficient reaction setup, and a "cracking additive" (calcium oxide, hydroxide, carbonate, gluconate, or acetate) was added to enhance the hydrocracking of the sugar chain. Several years later, kieselguhr-supported Ni with tungsten oxide doped with Fe was used as a catalytic system that did not require a "cracking agent" for the one-step hydrogenation/hydrogenolysis of both mono- and polysaccharides.[105] Under such conditions polysaccharides are hydrolyzed to monosaccharides, which are simultaneously hydrocracked to shorter polyols. In the meantime, the research group of Rozhdestvenskaya and Fadeeva studied both the hydrogenation and hydrogenolysis of glucose over kieselguhr-supported Ni in a more detailed way.[106,107] They found that the rate of hydrogenation can significantly exceed the rate of hydrogenolysis at high temperatures (200–230 °C) and pressures (150–250 bar H_2). Thus, they carried out the reaction under less severe conditions (130 °C, 50 bar H_2) to study the influence of basic additives (NaOH, Na_2CO_3, $Ca(OH)_2$, butylamine) on the hydrogenolysis of glucose. It was found that calcium hydroxide was the most efficient in promoting the hydrogenation of glucose to sorbitol; however, if its concentration was too high it caused alkaline decomposition of glucose. The addition of iron or zinc sulfate was found to increase the conversion of glucose. According to a recent report by Saxena et al., the hydrogenolysis of sucrose was also performed over multi-component catalytic systems of Ni-Mo-Cu supported on kieselguhr.[108] The obtained products include glucose and polyols (sorbitol, glycerol, PG, EG) with the maximum yield of glycerol achieved with a catalyst containing 22 % Ni, which also gave the highest overall yield of polyols (25 %).

Silica-alumina and alumina-based supports for Ni or Ni-Cu catalysts have also been used, for both hydrogenation[109–112] and hydrogenolysis reactions,[113,114] usually in a basic environment. Some of the patent descriptions involve the use of sophisticated multistage reactor cascades for the hydrogenation of glucose to sorbitol and hydrogenolysis to glycerol and glycols.[111,115] Such setups can significantly extend the catalyst lifetime.

The history of catalytic applications of unsupported metallic nickel catalysts in the hydrogenation/hydrogenolysis of sugars also dates back to the 1930s. Rothrock performed the hydrogenolysis of monosaccharides over a metallic nickel catalyst in the presence of alkaline buffers, which he claimed to greatly improve the yields of polyhydric alcohols, the purity of glycerol, and lifetime of the catalysts.[116] Soon afterwards, Raney nickel was used by Hanford for the hydrogenolysis of monosaccharides to glycols and glycerol.[117] He claimed an improvement to the process and the possibility of running it under milder conditions by introducing the step of non-hydrogenolytic "cleavage". This was achieved by autoclaving the aqueous solution of the starting sugar in the presence of a tertiary amine, with Ni already added, for a certain time prior to introducing H_2. Apparently the intermediate "cleavage" products could be "freed from the tertiary amine prior to hydrogenation, but in actual practice this has been found unnecessary". Nowhere is it mentioned what the chemical character of the "cleavage" products is. Apart from glucose, other sugars used included fructose, anhydroglucose, xylose, and sucrose. In the case of sucrose, it was hydrolyzed prior to the hydrogenolysis. Unlike in the previous example, the hydrogenation of sugars over Raney nickel described by Power was carried out in an acidic environment, as the acids were used for the initial in situ hydrolysis of the oligosaccharide starting materials.[118] In the following years, several more applications of Raney nickel for the hydrogenation of carbohydrates to sugar alcohols were patented,[119–122] including an early description of a process with a continuous hydrogen flow.[123]

More recently, unsupported nickel-based catalysts were used in the studies by Darsow. He applied metal powders of Ni or Co, mixtures or alloys thereof, or systems with Fe.[124] Furthermore, those metals with the addition of Cr, Mo, W, Al, Si, Ti, or Mn,[125] and finally Ni, Co, and Fe with added Ti, Zr, or Hf[126] were used for the hydrogenation of mono- and disaccharides to the respective alditols and glycosyl-alditols. Hydrogen pressures of 100–500 bar and relatively mild temperatures (in some cases as low as 70 °C) were applied, and very pure crystalline sugar alcohol products were obtained.

As described above, for a long time nickel in its different forms has been the most popular metal catalyst used in industry for the hydrogenation/hydrogenolysis of sugar compounds. The descriptions of the earliest studies with Ni catalysts contain some ambiguities that might be explained by both the lack of sufficient chemical knowledge at the time they were written, and the unwillingness of the authors to disclose all the details in their patents. In particular, Raney nickel has been used most often for hydrogenation or hydrogenolytic cleavage reactions, but different supported Ni catalysts have also been applied. The application of milder conditions for the process has constituted a general tendency, which is understandable from the economic point of view (both the energy input and the catalyst lifetime). Recent years have also seen the use of unsupported nickel alloyed with other metals, with such materials exhibiting particularly high catalytic performance. However, Ni catalysts have some disadvantages in the hydrogenation/hydrogenolysis of sugars, such as relatively poor stability and leaching to the solution during the reaction in the acidic and chelating reaction medium, which were described, for example, by Gallezot et al.[127]

3.4. Ruthenium-Based Catalysts

Ruthenium catalysts have often been reported to be more active[128,129] and more stable than nickel catalysts,[127] and thus constitute an attractive alternative. In the patent literature, the main trend has been to make the reaction conditions less severe and discover the optimum system by investigation of a large variety of possible Ru supports, for example, C, SiO_2, or zeolites.

The first application of such Ru catalysts (in some examples together with Pd or Pt, supported on C, Al_2O_3, or SiO_2) for the hydrogenation of mono- and disaccharides to the respective hexitols was described in a patent by Gilman Boyers.[130] The disaccharides clearly had to be hydrolyzed to undergo the hydrogenation. In the following years, other Ru catalysts supported on active carbon[97,98,131] and alumina,[132] as well as zeolites,[133,134] crystalline aluminosilicate clay,[135] and titania[136] have also been used for this process. The hydrogenation of xylose over commercial Ru, Rh, and Pd catalysts has also been investigated kinetically, and it was concluded that the reaction is pseudo-first order and is controlled by the surface reaction between atomic hydrogen and unadsorbed sugar.[137] Particularly noteworthy is the report by Gallezot et al. on the hydrogenation of glucose over a very stable and well-dispersed Ru catalyst supported on active charcoal pellets.[128] The selectivity for sorbitol was greater than 99.2 %, but the authors claim that the value could be increased even futher at shorter residence times, as the longer time favors its epimerization to mannitol. Several advantages over kieselguhr-supported nickel, were observed, such as higher stability and higher activity (ca. 50 times). A Ru catalyst was found early on that was more active than either Raney nickel or a rhodium catalyst in the hydrogenation of glucose and fructose.[138] Ru was the only one of the three catalysts that was able to hydrogenate both of those sugars under the conditions used (glucose did not react on Rh and fructose could not be hydrogenated on Raney nickel). Further confirmation of the higher activity of a Ru/Al_2O_3 catalyst than Raney Ni, this time in the hydrolysis/hydrogenation of sucrose to sorbitol and mannitol, was very recently provided by the research of Castold et al.[129] As mentioned above, this so-called hydrolytic hydrogenation requires an acid as a co-catalyst. An interesting example of the latter, together with a kinetic study, was described by Vasyunina and Barysheva[139] They used a Ru/C catalyst with H_3PO_4 to obtain sorbitol and mannitol from sucrose. Quantitative conversion of sucrose was achieved both in an autoclave and a flow reactor (with the products formed in a ratio of 85:15), although the autoclave reaction was faster. Hydrolysis was determined to be the rate-limiting step of the process, as glucose and fructose in this step are already activated and can be readily hydrogenated at the reaction temperature (80–85 °C) instead of the higher temperatures at which those sugars usually react (120–140 °C).

One recent patent by Maas-Brunner et al. describes a two-step hydrogenation of glucose (or starch hydrolyzate as a cheaper material) in which both Ni and Ru catalysts are employed.[140] Raney nickel is used for the initial hydrogenation (preferably at 140–150 °C and 70–90 bar H_2) and then removed (e.g. by filtration) and exchanged for Ru/C to completely hydrogenate the residual glucose (at 100–180 °C and up to 140 bar of hydrogen).

Ruthenium catalysts have also been used for the hydrogenolysis of sugars. Thus, hydrocracking of sugars, including glucose and fructose, to glycerol, EG, and 1,2-PG was described on a Ru catalyst supported on alumina with titania.[141] The reaction was carried out in the presence of alkaline-earth oxides, with CaO suggested to be the optimum co-catalyst; however, more severe conditions were necessary than those typically applied for the hydrogenation of sugars to sugar alcohols (150–250 °C and up to 350 bar of hydrogen). An interesting example is given in a patent, where a sulfide-modified Ru/C catalyst is used.[142] The process comprises a two-stage hydrogenation of monosaccharides, with the second stage being the hydrogenolysis to shorter polyols, mainly glycols. Such modified catalysts give a much higher selectivity for EG and 1,2-PG (90%), thereby avoiding the formation of large amounts of methane, which according to the authors is characteristic of unmodified Ru.

The patent descriptions, by their nature, often cover a very broad scope of applications. Thus, a patent by Arena claims a group of metal-impregnated carbonaceous pyropolymer catalysts as being active for the hydrogenolysis of glucose and sucrose (and also sorbitol), where Cr, Mo, W, Re, Mn, Cu, Cd, and Group VIII metals can be used.[143] A much more recent patent by Werpy et al. also covers the use of supported rhenium-containing catalysts, containing also preferably Ni, Pd, or Ru, but possibly also one of several other metals (Co, Ag, Au, Rh, Ir, Os, or Cu).[144] The preferred supports are carbon, zirconia, and titania. The patent follows the trend of including both sugars and sugar alcohols as the starting materials of hydrogenolysis—hexoses, hexitols, and glycerol—to obtain propylene glycols, ethylene glycol, and glycerol with selectivities adding up to 60–90%.

3.5. Homogeneous Catalysts

Most descriptions of sugar hydrogenation/hydrogenolysis concern the use of heterogeneous catalysts. However, the hydrocracking of a C–C bond on heterogeneous catalysts requires more severe conditions (see examples above). Therefore, there are also some examples in the literature of the applications of homogeneous catalyst systems that can be used in milder environments. Such mild reaction conditions were applied by Andrews and Klären (100°C, 20 bar H_2, *N*-methyl-2-pyrrolidinone as solvent, $[H_2Ru(PPh_3)_4]$ catalyst),[145] who expected hexitols as the main products in their hydrogenation of fructose, but unexpectedly obtained glycerol with 15% selectivity. The selectivity for hydrocracking over simple hydrogenation was dramatically improved (from 1:4 to 5:1) by the addition of KOH as a co-catalyst—the glycerol selectivity was increased to 84%. More details about the role of the basic environment in the hydrocracking mechanism can be found in Section 4.

Another patent describes the hydrocracking of carbohydrates to glycerol and other polyols, catalyzed by Ru complexes under mild conditions (100°C and 20 bar H_2), which resulted in higher selectivity towards the desired products, for example, fructose was converted into glycerol with 38% selectivity at 97% conversion.[146] The most recent applications of homogeneous Ru catalysts are the patents by Crabtree and Tyers, which claim that phosphine compounds of Ru and osmium are capable of catalyzing the hydrogenolysis of both sugars and sugar alcohols (including glycerol) to PG and EG.[147,148] As expected, the conditions are more severe (up to 250°C and 80 bar H_2); however, when a sugar is used as a starting material, the process can be carried out in a two-stage manner, under slightly milder conditions at the start to hydrogenate it to the respective polyol.

Hydrogenation of sugars to their respective sugar alcohols has also been performed with Ru complexes. A representive patent covers the homogeneous catalytic hydrogenation of sugars (glucose to sorbitol in most examples) in the presence of ruthenium-triphenylphosphine complexes in tetrahydrofuran,[149] and in a more recent study, Kolarić and Šunjić applied Ru with the trisulfonated ligand TPPTS (because of its higher solubility in water) for the hydrogenation of glucose and mannose.[150] Several applications of Ru complexes, namely with PPh_3 and chlorides,[151,152] monosulfonated triphenylphosphine (TPPMS),[153] and TPPTS[154] have been described for the hydrogenation of fructose to give a mixture of sorbitol and mannitol. In the latter case, besides fructose, inulin (a polysaccharide containing one glucose and 10–50 fructose units in its molecule) was also used as a starting material for the one-pot hydrolysis/hydrogenation.

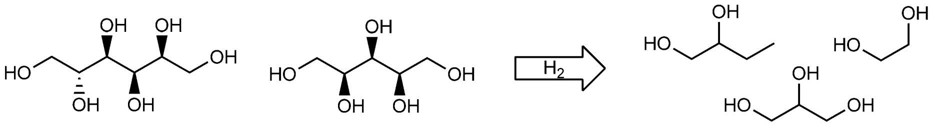
3.6. Hydrogenolysis of Sugar Alcohols

As described above, sugar alcohols themselves can be obtained by the reduction of sugars, namely hexitols, by the hydrogenation of hexoses (e.g. glucose, fructose), and pentitols from pentoses (e.g. xylose; Table 3). However, those polyols can be reduced further by the hydrogenolytic dissociation of C–C or C–O bonds. As the hydrogenation of sugars to their respective sugar alcohols is more facile than the reductive cleavage (hydrogenolysis) of C–C and C–O bonds, the conditions used for the hydrogenolysis of sugar alcohols are basically the same as those described for the hydrogenolysis of sugars. This hydrogenolysis proceeds in the presence of catalysts and inorganic hydroxide bases. The main (desired) products are alcohols, which are either shorter than the starting polyol (mainly glycerol, 1,3-PG, 1,2-PG, and EG, but also tetritols, lactic acid, propanol, ethanol, and methanol), or of the same chain length, but with a lower number of OH groups. The latter case is the subject of, for example, a recent review by Schlaf.[155] As a consequence of the simpler overall reaction pathway, the hydrogenolysis of sugar alcohols can yield the desired products (especially glycerol) with higher selectivities than when sugars are used as the starting material.

As was mentioned above, the first described example,[82] among the hydrogenations of other sugars and sugar derivatives at high temperature and pressure over a copper-chromium oxide catalyst, included the reactions of sorbitol and mannitol. In both cases the main product was assigned as 1,2-PG, as 1,3-glycols were already known to be unstable under the used reaction conditions in the presence of this catalyst.

An early study of the hydrogenolysis of sugar alcohols, with a focus to a large extent on product selectivity, is described in the patent by Bottoms, where most of the examples concern the hydrogenolysis of pentitols and hexitols mainly to glycerol and EG,[156] also in one example when raw cane sugar (sucrose) was used as the starting material (which is initially hydrolyzed in an acidic environment and hydrogenated to the hexitols). An active metallic Ni catalyst was used, although the patent also claims nickel oxide, copper, silver, cobalt, iron, platinum, copper chromite, and nickel chromite as catalysts. Salts of alkaline-earth metals or nitrogen bases were used as co-catalysts ("guidants", as the author

Table 3: Catalyst systems and reaction conditions utilized for the hydrogenolysis of sugar alcohols. Conversions and selectivities are omitted for the sake of brevity, because of the large number of starting materials and formed products.



Catalyst	Conditions T [°C]	p [bar]	Starting materials	Products	Ref.
$CuO\text{-}Cr_2O_3$	250	300	sorbitol, mannitol	1,2-PG	[82]
metallic Ni	235	100	pentitols, hexitols	glycerol, EG	[156]
Ni/SiO_2, Ni/Al_2O_3	200–300	500–1000	sugar alcohols	glycerol, glycols	[157]
Ni, Co and Cu on MgO	200–220	140–160	sorbitol	glycols, glycerol, erythritol	[158]
Ni/SiO_2 with $Ca(OH)_2$	215–245	140–290	sorbitol	xylitol, erythritol, glycerol, EG, methanol	[159]
Ni/SiO_2	200–245	100–250	xylitol	glycerol, glycols, erythritol	[160,161]
$Ni/SiO_2\text{-}Al_2O_3$, base	240–315	140–480	polyols	EG, PG	[162]
$Ru/Al_2O_3\text{-}TiO_2$ with BaO	150–250	35–350	sorbitol	EG, 1,2-PG	[163]
Ru, sulfur-modified Ru	210	60	sorbitol, xylitol	glycerol, 1,2-PG	[48]
Ru/C	220–270	75–150	sugar alcohols	EG, PG, glycerol, butanediol	[164]
Ru/C, Ru/Al_2O_3, Ru/TiO_2	180–250	34–140	sorbitol, xylitol	glycerol, PG, EG	[166]
Ru/C	220	80	sorbitol	glycols	[167]
$Pt/SiO_2\text{-}Al2O_3$	220–245	29	sorbitol	shorter polyols	[8]

calls them). It is claimed that they influence the course of the reaction towards the desired products by assisting the cleavage of long molecules and limiting further destructive hydrogenation (e.g. to PG and hydrocarbons). The reaction conditions are 150–300 °C, 25–300 bar H_2 (most typically 235 °C and 100 bar), and a pH value of about 7 is recommended. In general, high yields of glycerol and glycol (85 %) were obtained. Interestingly, although this is an early study, it is already mentioned that it can be used to convert the waste into valuable chemicals, for example, for the conversion of xylanes present in agricultural waste (corn, cotton, hulls, wheat straw) into xylitols.

Another attempt to achieve the selective hydrogenolysis of polyols to specific products is described in a patent by Conradin,[157] which discloses the hydrogenolysis of sugar alcohols to glycerol and glycols at 200 and 300 °C and at 500 to 1000 bar H_2 over silica- and alumina-supported nickel catalysts. The necessary pH value of 8 to 10 was attained by the addition of calcium hydroxide. It was found that the high pressure helps to achieve a high selectivity for glycerol.

A relatively large amount of research has been dedicated to the hydrogenolysis of sorbitol, the most popular sugar alcohol. Thus, in the patent by Conradin et al., this polyol was the starting material for the hydrogenolysis catalyzed by Ni, Co, and Cu, usually supported on MgO.[158] In one example, copper chromite activated with silver was used as a catalyst. The main product was in most cases 1,3-PG, but also 1,2-PG and glycerol, and sometimes EG or erythritol, were formed. The reaction was preferably carried out at a temperature of 200–220 °C and the H_2 pressure was preferably 140–160 bar. The achieved conversions were moderate to high (up to 92 %) and the highest 1,3-PG selectivity was obtained over the copper chromite/silver catalyst (61 %), although at the cost of lower conversion.

At the same time, a very interesting, in-depth research of the hydrogenolysis of sorbitol, which included a kinetic study, was published by Clark.[159] Nickel supported on kieselguhr together with $Ca(OH)_2$ was used as a catalyst. The reactions were carried out in aqueous solutions at 215, 230, and 245 °C and 140–290 bar H_2. The experiments indicated that the splitting of sorbitol into two glycerol fragments (3,3) is the predominant reaction of the initial cleavage reactions. The 5,1 (xylithol and methanol) and 4,2 (erythritol and EG) cleavages also occur. Propanediols, primary alcohols, hydrocarbons, and water can be formed in the reactions that follow. Hence, the concentrations of glycerol, erythritol, and xylitol start decreasing with time following the initial increase. One of the most interesting results was obtained by running the hydrogenolysis of glycerol alone, in which 1,2-PG and EG were formed in a 2:1 ratio. Thus, under the reaction conditions used, the cleavage of a primary hydroxy group is only about half as difficult as the cleavage of a C−C bond. The kinetics of the hydrogenolysis turned out to be first order in most cases, except at higher pressures when hydrogen apparently occupies most of the active sites of the catalyst and slows the reaction rates. Thus, optimum hydrogen pressures were found to depend on the reaction temperature, for example, about 230–280 bar for 230 °C. The reaction rate and glycerol yield also depended on the amount of $Ca(OH)_2$. Overall, this study provided a very interesting new insight into this reaction, which would soon become increasingly popular. Several years later, the influence of the reaction temperature and pressure[160] as well as basic co-catalysts ($Ca(OH)_2$, $Ba(OH)_2$, and NaOH)[161] was also examined by Vasyunina et al. in the Ni-catalyzed hydrogenolysis of xylitol. While the reaction rate increased with temperature, increasing the temperature too much diminished the yield of glycerol at the expense of 1,2-PG. At lower pressures, the cleavage of terminal OH groups in polyols became more significant. The addition of $Ca(OH)_2$ or $Ba(OH)_2$, and to a lesser extent NaOH, enhanced the cleavage of xylitol to glycerol and EG.

Nickel catalysts were also described in the patent by Tanikella.[162] Ni/SiO_2-Al_2O_3 was applied in the hydrogenolysis of polyols to EG and PG in non-aqueous solvents. Sodium or calcium hydroxide was used preferably as a base, and the preferred conditions were 240–315 °C and about 140–480 bar H_2. EG was obtained as the major product, followed by PG, with only small amounts of glycerol. The author claims that the use of methanol or ethanol as solvents, the presence of a base, and the use of pentitols rather than hexitols as starting materials all contribute to the higher yield of EG. Although it is not mentioned in the patent description, the relatively high H_2 pressure could also be of some significance for the product selectivities.

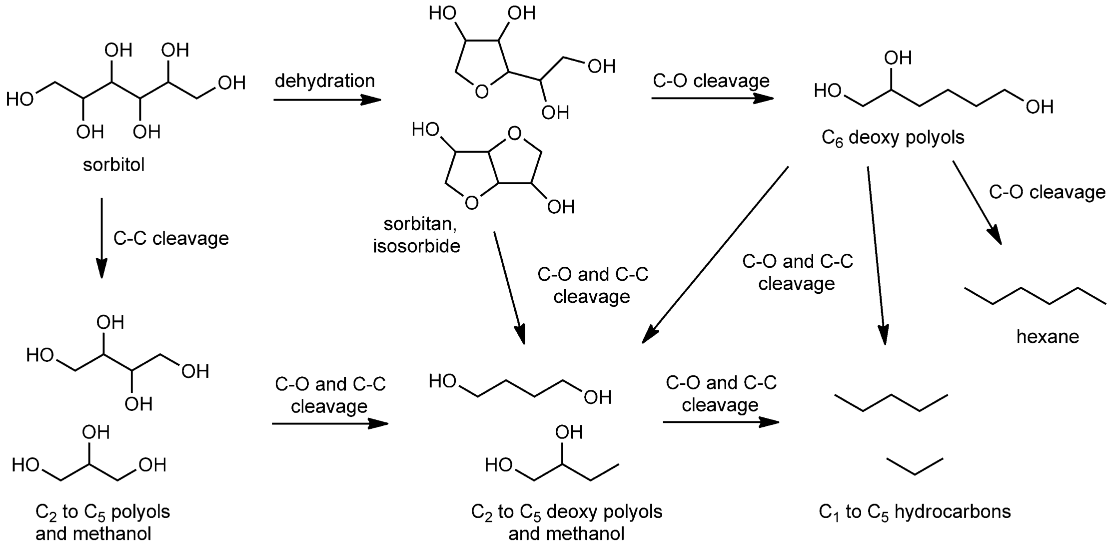
A ruthenium catalyst supported on alumina with titania appeared in a later patent description by Arena, and concerned the hydrocracking of sorbitol to give EG and 1,2-PG.[163] BaO was used as a co-catalyst, unlike in the previous studies, where CaO had been suggested as the best alkaline-earth additive.[141] The choice of the alkaline-earth co-catalyst is, therefore, vital in achieving a high performance of a Ru catalyst.

The mechanism for the hydrogenolysis of sugar alcohols and the competitive hydrogenolysis of C−C and C−O bonds in polyols on Ru and on sulfur-modified Ru catalysts were examined more deeply by Montassier et al.[48] A pathway was postulated, which includes initial dehydrogenation before the final cleavage products are hydrogenated, which may seem controversial considering the excessive partial pressure of hydrogen.

Ruthenium on activated carbon was also used by Gubitosa and Casale for the hydrogenolysis of sorbitol, mannitol, and xylitol to lower alcohols (EG, PG, butanediol and glycerol).[164] Basic promoters (especially NaOH) as well as sulfides as reaction moderators were used, as the authors claim that they prevent the formation of undesirable products, such as methane. The preferred reaction conditions were 220–270 °C and 75–150 bar of H_2. According to the authors, carrying out the hydrogenolysis in a fixed-bed reactor gives an increased selectivity for lower polyhydric alcohols, compared with the same reaction in a batch reactor, which they had described previously.[165] Chopade et al. also used Ru deposited on carbon, as well as on alumina or titania, in the hydrogenation of sugar polyols to shorter ones.[166] Sorbitol and xylitol were reduced this way to glycerol, PG, and EG. In the most recent example, Zhao et al. compared Ru supported on carbon nanofibers with a commercial activated carbon-supported Ru catalyst.[167] In the hydrogenolysis of sorbitol at 220 °C and 80 bar of H_2 (lower than usually used in previous works), the nanofiber catalyst was slightly more active and exhibited significantly higher selectivity for glycols, as a consequence of the Ru particles being more highly dispersed and exposed on the external surface.

Li and Huber investigated the dehydroxylation and hydrogenolysis of sorbitol on Pt/SiO_2-Al_2O_3 and analyzed the rather complex reaction network starting from sorbitol.[8] According to the authors, the main reactions occuring under those conditions are retro-aldol condensation associated with dehydrogenation and hydrogenation, thereby resulting in C−C bond cleavage, hydrodeoxygenation to cleave hydroxy groups, and further dehydration or hydrogenation reactions leading to a rather broad range of possible products. Mechanistic details of those reactions and their possible alternative explanations will be discussed in Section 4. The main reaction pathways and products of sorbitol hydrogenolysis are illustrated in Scheme 4.

The topic of homogeneously catalyzed hydrogenolysis of sugar alcohols has been pursued to a lesser extent. The aforementioned review by Schlaf covers both hetero- and homogeneous hydrogenolysis of C_3–C_6 polyols, with a focus on the methods for the selective cleavage of secondary OH groups that lead to α,ω-diols.[155] It is accepted that the mechanism generally follows the dehydration/hydrogenation



Scheme 4. Major reaction pathways and examples of main products of sorbitol hydrogenolysis. Some minor and intermediate products are omitted and mechanistic pathways are not discussed here. The final product distribution of course depends on reaction conditions.

pathway. As a secondary carbocation is formed more easily, a secondary C–O bond is more reactive in the acidic environment; however, the overall selectivity always depends on the starting material, catalyst, and reaction conditions. Pd, Ru, and Rh complexes are most often used as homogeneous catalysts for the hydrodeoxygenation of polyols. In addition to just describing the homo- and heterogeneous catalytic systems, the author extensively covers the mechanistic aspects of the reaction in question, the advantages and drawbacks of particular catalysts for specific starting materials, and possible applications of the discussed catalysts in other related reactions, for example, the hydrogenolysis of lignin.

Glycerol can also be considered to be a sugar alcohol. However, since it plays a special role in the conversion of biomass, because of its biodiesel-related abundance, its hydrogenolysis deserves to be described separately, and is the subject of Section 2.

4. Kinetics and Mechanism of Monosaccharide Hydrogenation to Sugar Alcohols, and Mechanism of Polyol Hydrogenolysis

4.1. Kinetics of Glucose Hydrogenation

Compared to other monosaccharides, the kinetics of the hydrogenation of glucose has been the most widely studied and described in the largest number of reports.[121,168] It depends mainly on the catalytic system and sometimes on the reaction conditions. Several different conclusions have been drawn and different mechanisms proposed. Those differences may also result from wrong estimations of the kinetic regime and mass transport limitations. The reaction is generally concluded to be first order with respect to the concentration of glucose and hydrogen pressure.[169]

Kinetics were already presented in the early report by Hofmann and Bill,[170] who studied the hydrogenation of D-glucose in a batch reactor at temperatures of 80–130 °C with Raney nickel used as a catalyst. The authors claimed a first order reaction in regard to both glucose and hydrogen. The first order with respect to glucose was also observed by Wisniak and Simon with the same catalytic system.[138] The authors calculated the activation energy to be 18.8 $kJ\,mol^{-1}$ (for 3 % Raney nickel at 41 bar). This value is quite low, which might suggest the presence of diffusion limitations; however, the authors suggest that this was not consistent with the results obtained on variation of the agitation speed and catalyst loading. The same reaction order was found by Pan et al. in the hydrogenation of glucose over Ru supported on carbon nanotubes.[171] A very detailed study was conducted recently by Crezee et al.[172] They studied the hydrogenation of glucose with Ru/C in a semibatch slurry autoclave in the range 40–75 bar H_2 pressure and 100–160 °C. Kinetic experiments were carried out in the absence of mass transport limitations, which were verified by measuring gas–liquid mass-transfer coefficients and estimating the diffusion and liquid–solid mass-transfer coefficients. The activation energy was found to be about 55 $kJ\,mol^{-1}$. A change in the reaction order was observed with respect to glucose: A first order reaction was found for low glucose concentrations (up to ca. 0.3 $mol\,l^{-1}$), while a zero order behavior was observed for higher concentrations. The first order reaction was observed with respect to H_2. Li et al. found that the rate of glucose hydrogenation with Ni-B/SiO_2 at 100 °C increased linearly with the H_2 pressure from 10 to 50 bar and remained unchanged with the glucose concentration.[173] Therefore, they concluded the reaction to be first order with respect to H_2 and zero order with respect to glucose. The same reaction orders were found by Guo et al. in their study with an amorphous Ru catalyst in combination with chromium.[174]

It was also shown for Ni-Pt and Ni-Ru that the hydrogenation of glucose catalyzed by those systems is first order in the H_2 pressure up to 60–80 bar. At higher pressures, zero-order behavior with respect to H_2 was observed.[175] Although most of the tests were performed in batch reactors, the research group of Gallezot also studied the kinetics in a high-pressure trickle-bed reactor with silica-alumina-supported Ni extrudates.[176] The operating conditions ranged from 70 to 130 °C in the pressure range 40–120 bar. The tests were performed on extrudates as such or crushed. For both catalysts, a threefold increase in the amount of catalyst produces only a twofold increase in the initial rate of glucose formation, which indicates that the hydrogenation of glucose is partly limited by external diffusion. Furthermore, for the same catalyst loading, the crushed extrudates provided a strongly increased rate of glucose hydrogenation, which suggests that the reaction rate on the extrudates is limited by internal diffusion. Subsequent kinetic experiments were, therefore, conducted with the crushed catalyst. An activation energy of 67 $kJ\,mol^{-1}$ was calculated from the Arrhenius plot of the initial reaction rates measured at 70 and 130 °C and 80 bar H_2. This value, much larger than the activation energy of diffusion in liquids (12–21 $kJ\,mol^{-1}$), indicates that the reaction rate is controlled by the kinetics on the metal surface.

4.2. Kinetics of Hydrogenation of Other Monosaccharides

As was mentioned before, relatively few kinetic studies on the hydrogenation of other monosugars have been reported. Thus, Wisniak et al. studied the kinetics of the hydrogenation of xylose over Raney nickel (7–55 bar H_2 and 80–140 °C).[177] The authors suggested that the reaction followed a pseudo-first order, with the rate-determinig step being the reaction on the surface between atomically absorbed hydrogen and adsorbed xylose at 100 °C and unadsorbed xylose at higher temperatures. The activation energy was found to be 6.5 $kJ\,mol^{-1}$. The same authors later extended the scope of their research to noble metals, with Ru, Rh, and Pd also used as catalysts.[137] A pseudo-first reaction order was suggested, with the activation energy for 1 % Ru found to be 5 $kcal\,mol^{-1}$ at 14 bar. The rate-determining step involved the surface reaction between chemisorbed hydrogen and unadsorbed xylose.

The hydrogenation of D-fructose on Ru/C catalysts was studied under mild conditions (1 bar H_2, 72 °C) by Heinen et al.[178] The authors suggested that the reaction rate is controlled by product inhibition. Pseudo-first order kinetics were observed, and the Langmuir–Hinshelwood kinetic model was suggested.

4.3. Mechanism of Monosaccharide Hydrogenation to Sugar Alcohols

Several mechanistic explanations have been proposed for the hydrogenation of glucose. The aforementioned research group of Wisniak[138] suggested that the reaction over Raney nickel occurs between unadsorbed D-glucose and atomically chemisorbed hydrogen. No detailed mechanism was postulated, since the reaction at 130 °C and above 41 bar H_2 was found to be too fast for more meticulous observations. Two types of reaction models for the hydrogenation of D-glucose over a Ru catalyst were presented by Crezee et al., depending on the hydrogenation pressure.[172] Below 35 bar, an Eley–Rideal model was suggested, with the surface reaction between atomically chemisorbed hydrogen and unadsorbed glucose as the rate-determining step. At higher pressures, a Langmuir–Hinshelwood model was proposed, in which the surface reaction between atomically chemisorbed hydrogen and adsorbed glucose determines the reaction rate. The Langmuir–Hinshelwood model was also proposed by the research group of Gallezot,[176] where the reaction between glucose and hydrogen, both adsorbed on the surface of Ni, proved to be the rate-determining step. A similar model was postulated by Hoffer et al.[179] in their study with Ru/C and Raney Ni catalysts at 120 °C and 39–79 bar of H_2. Brahme and Doraiswamy[180] performed the kinetic modeling over Raney Ni in the pressure range 4.4–21 bar and below 100 °C. A model was proposed in which the reaction between molecularly adsorbed hydrogen and D-glucose in the liquid phase (Eley–Rideal mechanism), with the desorption of sorbitol, controls the reaction rate.

Crezee et al. assumed the models known from the literature and fitted the data with those models.[172] The possibilities they considered were the following: a) noncompetitive adsorption of hydrogen and glucose at different sites,[181] b) competitive adsorption of molecular hydrogen and glucose,[176] and c) competitive adsorption of dissociatively chemisorbed hydrogen and glucose.[138] Although they were not able to fully exclude any of them, they expressed a preference for the third model (c), additionally noticing that it predicts an entropy loss for the adsorption of glucose, which is thermodynamically expected. Those models are shown in a simplified way in Figure 2.

More detailed mechanistic conclusions on the hydrogenation of monosaccharides are included in the study by Makkee et al., who reduced fructose and glucose over Cu/SiO_2 as well as other metal catalysts.[90] The hydrogenation of glucose yielded sorbitol, whereas fructose furnished a mixture of sorbitol and mannitol. In the latter case, the Cu catalyst proved to be the most selective for the formation of fructose. The authors postulate that a furanose or pyranose is coordinated on Cu through its three oxygen atoms, two of which are connected to the anomeric carbon atom. In this way, the sugar becomes ionized, with its anomeric C–O bond partially acquiring double bond character. The anomeric carbon atom is then attacked by hydrogen adsorbed on another surface Cu atom (thus being polarized and becoming a hydride-like species). It is stated that sugars in the furanose form are significantly more reactive towards hydrogenation than respective pyranoses, although no explanation of this fact is given. Our interpretation of this mechanism is shown in Scheme 5.

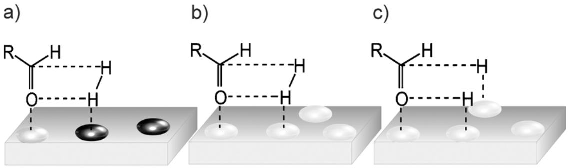
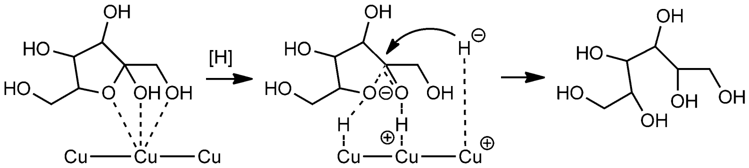


Figure 2. Models of glucose hydrogenation, as summarized by Crezee et al (interpretation by the authors of this review). Non-competitive adsorption of hydrogen and sugar at different active sites (a) or competitive adsorption of hydrogen and sugar at the same type of sites (b and c). Hydrogenation with molecular hydrogen (a and b) or dissociatively chemisorbed hydrogen (c). For simplicity the sugar molecule is shown in the aldehyde form.



Scheme 5. Hydrogenation of sugars on a copper catalyst according to Makkee et al., with fructofuranose as an example (interpretation by the authors of this review).[90]

To gain more insight into the reaction mechanism, Martins Castoldi et al.[182] performed a theoretical study on the interaction of glucose with Pt and Ru surfaces. They adsorbed the most stable monomer of glucose on metal clusters of Ru and Pt. Although experimental results show that Ru is more active than Pt, the results obtained show the adsorption energy on Pt to be larger (18.3 kcal mol^{-1}) than that on Ru (12.4 kcal mol^{-1}), which is contradictory to what could be expected. However, it was suggested that the geometric changes that occur during the adsorption of glucose might have a stronger influence on the reaction profile. Since in the adsorbed state the C–O bond is weaker, the energy necessary to break it is reduced. These results showed that the anomeric carbon atom becomes more susceptible to attack by hydrides. Interestingly, those changes in geometry were smaller on Pt than on Ru. This fact explains that Ru weakens the hemiacetal bond in the glucose molecule, thus facilitating the formation of sorbitol.

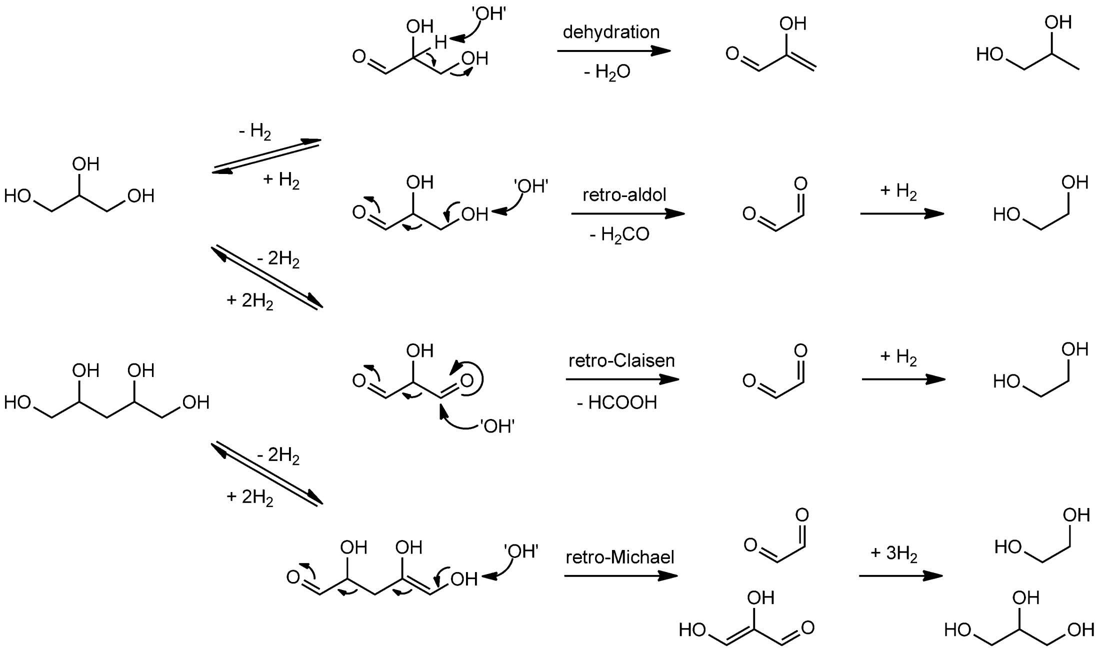
4.4. Mechanism of Polyol Hydrogenolysis

Although the mechanism of the hydrogenation of sugars to sugar alcohols is relatively straightforward, as it involves a simple reduction of an aldehyde/hemiacetal or ketone/hemiketal to an alcohol, many more questions have been raised about the mechanistic aspects of hydrogenolysis, such as, for example, destructive hydrogenation involving the cleavage of C–C and C–O bonds in the sugar or polyol chain. Those reactions take place in the further reductive treatment of hexitols and pentitols as the sugar hydrogenation products, as well as in the degradation of glycerol to diols, both of those processes being the subject of this Review. As the same reactions are involved from a chemical viewpoint in both cases, the hydrogenolysis mechanism will be covered in one section.

While the aforementioned reactions have been explored since the early 20th century, the first thorough mechanistic insight into the hydrogenolytic cleavage of polyols was only carried out in the 1980s by the research group of Montassier[25,27,48,183] They examined the hydrogenolysis of C_3–C_6 polyols over Cu and Ru catalysts, including sulfur-modified ruthenium. In short, they postulated that both C–O and C–C bond cleavage can proceed via the equilibrium step of dehydrogenation/hydrogenation on the catalyst surface, before the final cleavage products are hydrogenated. Thus, the initially formed dehydrogenation product (aldehyde or ketone) would either undergo dehydration to yield a dehydroxylated species, or alternatively react along the retro-Claisen condensation (Cu) or retro-aldolization mechanism (Ru) to furnish the products of C–C bond cleavage. According to the authors, the C–C bond cleavage in the hydrogenolysis of longer sugar alcohol chains could proceed through a retro-Michael condensation mechanism. In all cases these intermediates would be hydrogenated in the last step. A scheme of the reaction pathways with glycerol and xylitol as examples is shown in Scheme 6.

The main controversy in the above explanation is the assumed dehydrogenation step, which is thermodynamically unfavorable due to the excessive partial pressure of hydrogen, even though, in theory, even the formation of trace amounts of a dehydrogenated product would be able to shift the equilibrium by reacting further. The retro-Claisen and retro-Michael pathways have thus been criticized by Wang et al., as they involve double dehydrogenation.[184] They have, however, advocated the dehydrogenation/retro-aldol mechanism, supporting it by their observation of respective reaction products. This explanation has also been accepted by many other authors.[47,53,54,145,185]

Another commonly accepted mechanism, but which is applicable only to the C–O bond cleavage, involves the dehydration/hydrogenation pathway. Dasari et al. discussed it as an alternative to the Montassier mechanism, and suggested the initial formation of acetol by the dehydration of glycerol, and gave the detected presence of trace amounts of acetol as direct evidence.[186] Although no basic species are specifically mentioned in their publication, the presented scheme suggests that the dehydration proceeds through deprotonation. Miyazawa et al. also proposed the possibility of both acid- and base-catalyzed dehydration of glycerol prior to the hydrogenation of the intermediate products.[41] Schlaf, in his review from the same year, supported the same concept, going into more detail about the homogeneous acid-catalyzed selective hydrogenolytic cleavage of secondary OH groups.[155] According to him, as a secondary carbocation is formed more easily, a secondary C–O bond is more reactive in the acidic environment; however, the overall selectivity always depends on the starting material, catalyst, and reaction conditions. In our opinion, the thermodynamically favorable pathway would indeed lead to 1,3-PG, while kinetic control of the reaction

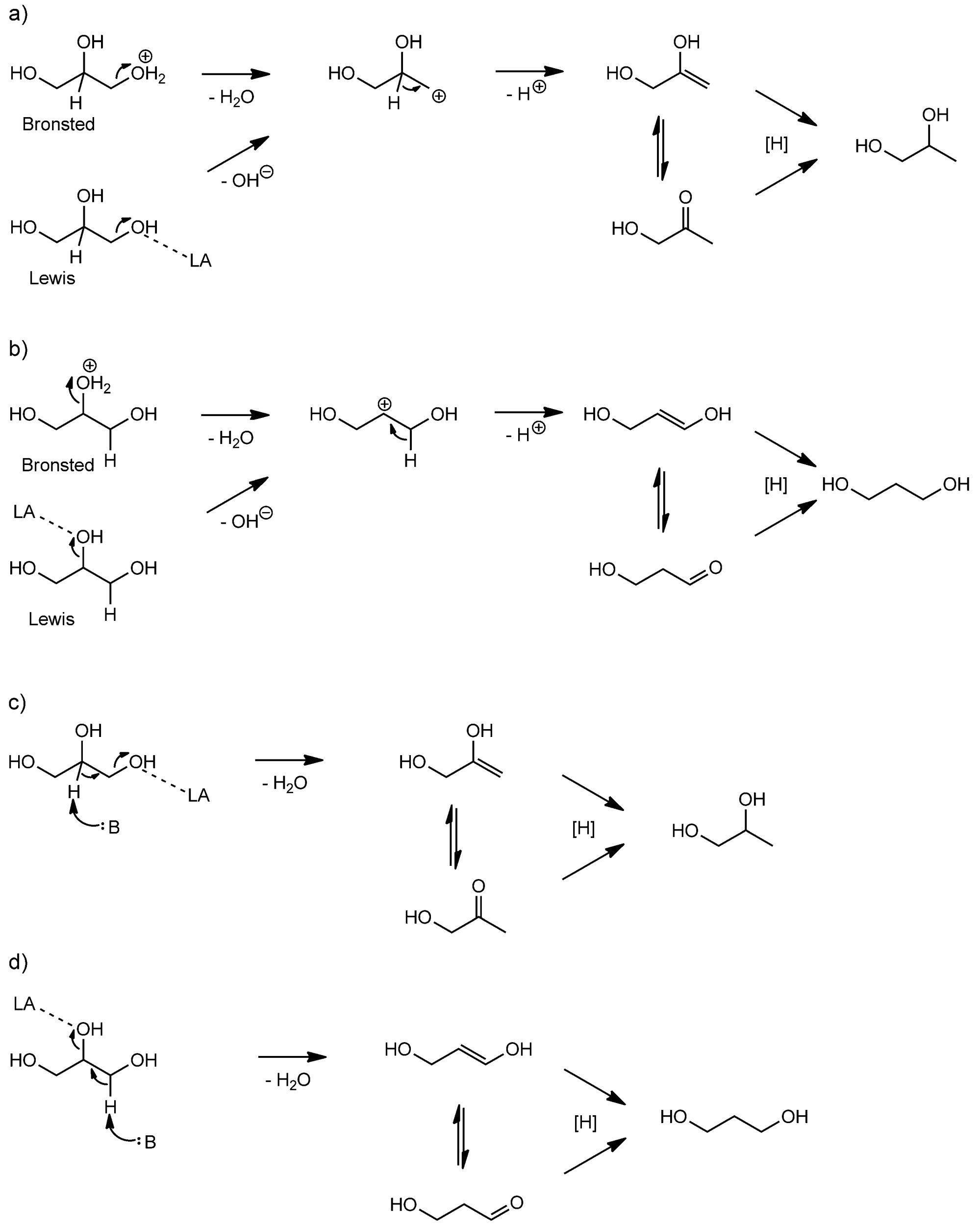


Scheme 6. Glycerol and sugar alcohol hydrogenolysis overview according to Montassier et al.[25,27,48,183] "OH" groups are adsorbed hydroxyl species on the metal catalyst surface.

may furnish 1,2-PG by deprotonation of the more easily accessible terminal carbon atom. Both 1- and 2-propanol would be formed by dehydration/hydrogenation of PG in an analogous way.

The particular cases of acid- and base-catalyzed dehydration followed by hydrogenation are shown in Scheme 7. In a broader context, the role of an acid can be played not only by an acidic catalyst itself but also by acidic sites on the surface of, for example, a supported metal catalyst, whether of the Bronsted or Lewis type. The same can be said about the basic sites/species, where the surface OH groups (as proposed by Tyrlik et al.[187]) or perhaps even water molecules may act as basic catalysts. In the latter case it is perhaps favorable if the leaving of OH^- is assisted by Lewis acid sites. Such a coassistance of basic and Lewis acid sites is also possible in other reactions of glycerol.[188] On the other hand, under certain conditions, the acid-assisted dehydration (Scheme 7a,b) may also proceed, following formation of the carbocation, by hydride transfer and the formation of an oxocarbenium cation,[63] as described in Section 2.2 and below in this section.

Lewis acid sites can also play another role in the hydrogenolysis, namely, by anchoring one of the hydroxy groups of the substrate and thus facilitating the cleavage of the vicinal OH group, as in a mechanism recently postulated by Shinmi et al.[59] Thus, a glycerol molecule is apparently adsorbed on their Rh-ReO_x catalyst through one of its OH groups to an electron-defficient rhenium atom, while atomic hydrogen atoms adsorbed on the rhodium react directly with the vicinal C–O bond (Scheme 3 in Section 2.2). Although the authors refrain from discussing the mechanism in more detail, they provide such a discussion in their following publication on the Ir-ReO_x/SiO_2 catalyst,[62] in a reaction which seems to follow the same pattern. As was mentioned in Section 2.2, they postulate hydride transfer to the secondary carbon atom, with OH^- as a leaving group, and supporting their theory with experimental results and the products formed. However, since the hydroxy anion is a poor leaving group on its own, the asistance of Bronsted or Lewis acid sites is in our opinion quite probable, which the authors do not mention.



Scheme 7. Acid-base co-catalysis of the C–O bond hydrogenolytic cleavage of polyols with glycerol as an example, with dehydration as the initial step. a) Acid-assisted 1,2-PG formation. b) Acid-assisted 1,3-PG formation. c) Base-assisted 1,2-PG formation. d) Base-assisted 1,3-PG formation. In the base-assisted catalysis, Lewis acid sites may play a role as well.

Although the partially reduced rhenium oxide is not a support in this case, the Lewis acid character of Re atoms can be compared to a support oxide in the SMSI state with a metal catalyst.[49,60]

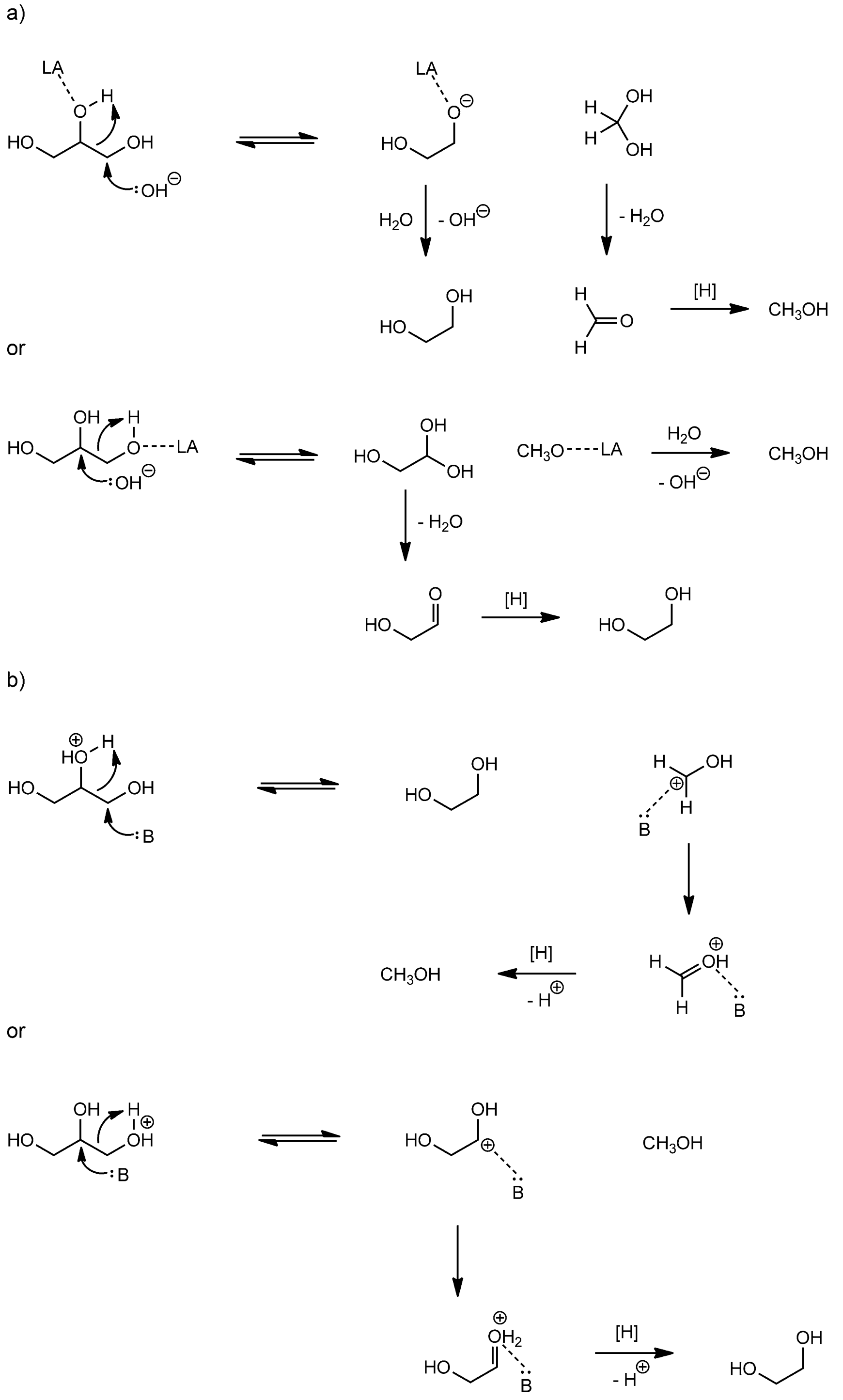
As was also mentioned above, the research group of Dumesic[63] postulated that the presence of an oxophilic promoter (ReO_x or MoO_x) in rhodium catalysts ensures high selectivity for 1,3-PG through a mechanism involving the protonation of the less-accessible oxygen atom by an acidic OH group of the promoter (as the leaving of a water molecule from the secondary carbon atom is more favored), with a concerted hydride transfer from the neighboring primary alcoholic carbon atom to form an intermediate $RCH_2-CH=OH^+$ oxocarbenium cation. This mechanism plausibly explains the reaction selectivity and was also supported by DFT calculations.

In the case of hydrogenolytic C–C bond cleavage, few other mechanistic explanations have been proposed since the aforementioned pioneering research by Montassier et al. and Wang et al. We tentatively postulate a simple alternative mechanism for this reaction that involves the assistance of acidic or basic sites/species or a combination thereof. The possibilities of such pathways are shown in Scheme 8. Glycerol is used as an example, but it can be applied to the hydrogenolytic degradation of polyols in general.

Thus, in the presence of a base and a catalyst with Lewis acid sites (Scheme 8a), the "nominal" carbanion, as a result of the concerted proton transfer from an oxygen to a carbon atom, can be transformed into the Lewis acid stabilized alkoxide anion (glyceroxide or methoxide, depending on the nucleophilic attack direction), thus becoming a plausible leaving group, which is immediately protonated to yield glycerol or methanol, respectively. The other product (aldehyde) undergoes hydrogenation to the respective alcohol.

Following this pathway, the reaction could be even more facile if the alcohol were protonated by a Bronsted acid site and if the assistance of a basic site were possible (Scheme 8b). The leaving group is then a neutral molecule, and the other primary product is an oxocarbenium cation (analogous, in a way, to the Dumesic mechanism of C–O hydrogenolysis),[63] which is then hydrogenated to methanol or glycerol.

The above mechanism is only tentative, and we are aware of its limitations, as it would require quite specific conditions involving difunctional acid/base catalysis. This is, however, often the case in the described reactions of the hydrogenolytic degradation of polyols.



Scheme 8. Our postulated mechanism for the acid-base-assisted C–C bond hydrogenolytic cleavage in polyols, with glycerol as an example.

In this section, the mechanisms have mainly been described for the hydrogenolysis of glycerol, as it has been studied the most extensively in this aspect. They can, however, also be applied to the hydrogenolytic cleavage of C–C and C–O bonds in longer sugar alcohols. To sum up, several explanations of the mechanism of polyol hydrogenolysis have been postulated and it is still not clear how this reaction proceeds. Various possible pathways for the hydrogenolysis of glycerol have been described extensively in the recent excellent review by Zheng et al.,[23] but no opinion in favor of one or the other mechanisms is given here. It is quite likely that different mechanisms take place, depending on the catalyst and reaction conditions.

5. Hydrogenation and Hydrogenolysis of Polysaccharides

The individual sugar units of polysaccharides, including starch, hemicellulose, and cellulose, are connected through ether linkages, which can undergo hydrolysis under acidic conditions and so lead to depolymerization and finally release of the single sugar molecules. The mechanism of the hydrolysis of polysaccharides has been described in detail by various research groups and revisited recently in the frame of biomass valorization. Comprehensive investigations on the exact reaction mechanism and kinetics of the hydrolysis of polysaccharides can be found elsewhere.[189] Different pathways may occur that lead to depolymerization under hydrogenolysis conditions:

1) The reaction may occur by hydrolysis of the polysaccharide to monosaccharides, which are subsequently hydrogenated to the corresponding polyols with the same number of carbon atoms as the corresponding sugars:
   → consecutive hydrolysis and hydrogenation occurs
2) The polyssacharide may be hydrolyzed to monosaccharides, which subsequently undergo further hydrogenolysis to molecules with a lower number of carbon atoms as the starting sugars:
   → consecutive hydrolysis and hydrogenolysis occurs
3) The polysaccharides may directly undergo hydrogenolysis reactions, thereby resulting in C–C and C–O bond cleavage. The depolymerization to smaller units is already catalyzed by metal catalysts in the presence of hydrogen:
   → pure hydrogenolysis occurs

In regard to these pathways, it is not yet clear if hydrogenation occurs first followed by hydrogenolysis or the other way round, or if both reactions can possibly take place simultaneously. Nevertheless, a comprehensive overview of the recent knowledge concerning catalyst systems and reaction pathways is discussed in the following.

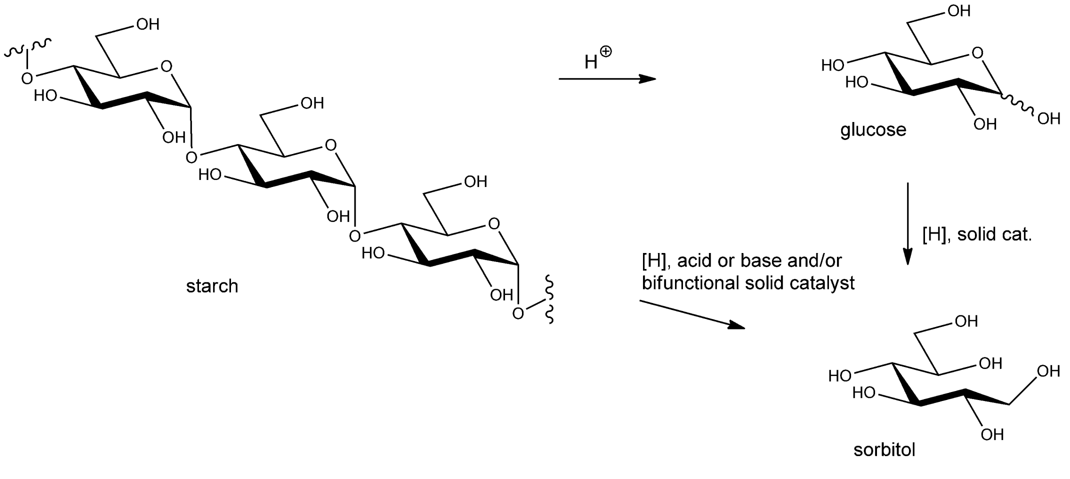
5.1. Starch as a Feedstock

Starch is constituted from α-D-glucose units either connected through α-1,4-glycosidic linkages only in a linear chain with a helical structure (amylose, 20–30%), or as a strongly branched structure from single glucose units connected through α-1,4- or α-1,6-glycosidic linkages (amylopectin, 70–80%). Natural sources used for the commercial extraction of starch include corn, tapioca, wheat, and potatoes and to a lesser extent rice, sweet potato, sago, and mung beans.

Most reports on the hydrolytic hydrogenation of starch are based on the two-step processes (Scheme 9). An apparent procedure for such a process consists of the initial acidic or enzymatic hydrolysis of the polysaccharide to form monosaccharides, which are subsequently subjected to hydrogenation or hydrogenolysis to yield the corresponding polyhydric alcohols. Thus, most of these two-step processes effectively focus on the hydrogenation/hydrogenolysis of monosugars rather then starch, and have been included in Section 3. Accordingly, only a few examples of these stepwise hydrolysis and hydrogenation strategies are discussed here to illustrate the principal concepts.

5.1.1. Two-Step Processes

As a recent example, Abreu et al. presented such a two-step approach, which included the prior hydrolysis of starch in an acidic aqueous solution followed by hydrogenolysis of the resulting mixture over a Ru-based catalyst supported on activated carbon.[190] Interestingly, the authors analyzed the kinetics of C–C versus C–O bond cleavage, and found the former to predominantly occur under their reaction condi-



Scheme 9. Two-step transformation of starch to sorbitol involving hydrolysis and hydrogenation, and one-step hydrolytic hydrogenation of starch to sorbitol.

tions. Methanol was the main reaction product, in a yield of up to 80 wt %. These results are somewhat surprising, as most reports on sugar hydrogenolysis over Ru/C do not describe significant amounts of methanol and may be caused by a rather high reaction temperature of 200 °C. In another example, Blanc et al. reported on starch-derived polyols for polymer technologies, with the main focus on dehydroxyhexitols for the manufacture of polyesters or polyurethanes.[191] The authors recommend the hydrolysis of starch by well known acidic or enzymatic processes to glucose, followed by the hydrogenation to form sorbitol in the second step.[192] Further hydrogenolysis of sorbitol over Ru- and Ni-based catalysts yielded mainly C_1–C_3 products together with a high fraction of volatile hydrocarbons, while Pt and Pd catalysts exhibited very low activity and led to the formation of C_6 cyclic ethers by internal dehydrocyclization. Interestingly, CuO-ZnO (33:65) catalysts, which have rarely been investigated for this purpose, favored dehydroxylation over C–C bond cleavage, and afforded dehydroxyhexitols in a yield of around 63 %.

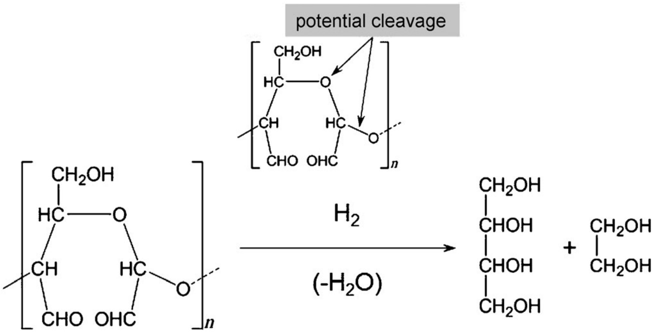
In contrast to the stepwise hydrolysis and hydrogenation, several approaches suggest two-step hydrogenation processes, where one step is usually carried out at a lower temperature and a pH value close to neutral, followed by a second hydrogenation step at elevated temperature and sometimes acidic conditions to facilitate the hydrolysis. Following this line, Lolkema hydrogenated mixtures of mono- and polysaccharides over Ni-based catalysts supported on kieselguhr.[193] The first step at 140 °C led to the hydrogenation of monosaccharides to the corresponding sugar alcohols, and a subsequent temperature increase to above 160 °C allowed the “hydrolytic hydrogenation” of the polysaccharides and led mainly to the formation of sugar alcohols with the same number of carbon atoms as the original monosaccharide, thereby emphasizing the absence of C–C bond cleavage. Kasehagen presented a process under similar conditions for the hydrogenation of carbohydrates, in particular starch hydrolysates, to form hexitols.[194] He described the hydrogenation of monosaccharides at 140 °C and neutral pH over Ni supported on diatomaceous earth followed by the addition of small amounts of phosphoric acid (0.05–1 wt % based on the sugar) and further hydrogenation at a higher temperature to hydrolyze the polysaccharides and reduce the released monomeric species. Interestingly, a patent by Capik and Wright described the combined hydrolysis and hydrogenation of corn starch hydrolyzate over nickel phosphate promoted Ni supported on kieselguhr.[195] Therein, a 50 wt % slurry at pH 6.5 was heated to 160 °C under H_2 pressure, maintained at this temperature for 30 min, and heated to 180 °C for another 30 min to afford sorbitol in a yield of about 95 %, thus emphasizing the commercial potential of such approaches.

5.1.2. *One-Step Processes*

Strategies to achieve the simultaneous hydrolysis of the polysaccharide and hydrogenation or hydrogenolysis of the released monosaccharides include: 1) reactions at high temperatures to provide the activation energy for hydrolysis by water, 2) addition of acidic or basic promoters, and 3) difunctional solid acid/hydrogenation catalysts. In regard to the catalyst systems, the majority of the studies also focused on Ni- and Ru-based systems, with most information reported in patents.

In 1934, Larcher already presented a process for the production of polyhydric alcohols based on mono- and disaccharides at temperatures around 110–150 °C over supported Ni catalysts, with the aim of generating products with the same or half the carbon number as the substrate.[196] Accordingly, selectivity towards target molecules had been identified as the main challenge. Consequently, Hartstra et al. stated that the hydrolysis has to be accelerated to be at the same rate as the subsequent hydrogenation, but they also noticed that suitable acids or bases at the same time promote the formation of by-products.[197] Instead, they suggested adding water-soluble metal or ammonium salts such as $MgCl_2$, $NiSO_4$, or $SbCl_3$ in addition to the Ni catalyst to enhance the rate of hydrolysis. According to the limited information of the patent, full conversion into sugar alcohols with the same number of carbon atoms as the corresponding sugars could be achieved by using such a combined catalyst system. Kool et al. adjusted the pH value during the reaction to 3.5 to facilitate the hydrolysis, and performed a pretreatment with hydrogen peroxide to oxidize impurities in the feedstocks. An influence of the pH value or H_2O_2 on the product distribution cannot be excluded, but is difficult to judge. The products consisted mainly of sorbitol, while the presence of products with fewer carbon atoms such as glycerol and PG or EG was discussed, but not confirmed by experimental data.[198]

In 1957, Sloan et al. already placed a patent application on the combined hydrolysis and hydrogenation of dialdehyde starch over Raney nickel. This feedstock is also termed “periodate oxidized starch” and can be prepared by the oxidation of starch with iodic(VII) acid or the corresponding salts to open the ring structure.[199,200] The particular advantage of this pretreated starch is the unique product mixture that can be obtained from it. Indeed, hydrolytic hydrogenolysis yielded erythritol and EG as the main products, with an up to 62 % yield of erythritol, thus proving a very selective cleavage of the bonds (Scheme 10). Surprisingly, this approach has not been investigated further, as it could open the way towards superior control over the selectivity and may also be applicable for substrates other than starch.



Scheme 10. Hydrolytic hydrogenation of preoxidized starch to erythritol and ethylene glycol.

Jacobs was the first to approach the simultaneous hydrolysis and hydrogenation of water-insoluble polysaccharides in a single step, by using a combination of solid acids and hydrogenation catalysts.[201] His patent description covers supported metals selected from Ru, Cu, Ni, Co, and their mixtures and a solid support with acidic functionality. Therein, Ru supported on ultrastable zeolite Y (HUSY) fulfilled both requirements for a suitable catalyst. The material showed high metal dispersion to allow fast hydrogenation, as well as sufficient acidity to reach comparable rates of hydrolysis and hydrogenation, with the rate constant of hydrolysis being about 70% higher than that of the hydrogenation. In line with this, Heinen et al. described the one-pot hydrolysis and hydrogenation of inulin, a polymer composed of fructose units and typically having a terminal glucose moiety. The fructose units are connected through a β(2→1) glycosidic bond. In their study, the authors aimed to produce D-mannitol, a nonhygroscopic low-calorie sweetener.[202] In their approach, difunctional catalysts based on Ru supported on activated carbon with acidic surface groups were applied and proved to already convert inulin effectively into mannitol at 100 °C. As one of the first examples of a technical application, Lepper et al. proposed a process for the continuous preparation of polyhydric alcohols in a fixed-bed reactor, with Ru supported on activated carbon as the catalyst. The reaction was carried out in an aqueous phase and at neutral pH for monosaccharides or a pH of about 3 to 4 for polysaccharides.[203] Unfortunately, these promising attempts are limited to water-soluble polysaccharides.

In summary, most approaches for the hydrolysis and hydrogenation or hydrogenolysis of starch have concentrated on Ni- and Ru-based catalysts under very similar conditions as those described for sugars, while no real independent directions of research for this feedstock have been developed (Tables 4 and 5). Preoxidation of starch, as well as highly selective CuO/ZnO catalysts and difunctional materials combining solid acid and hydrogenation catalyst properties may provide new promising possibilities to optimize the yields and product distribution.

5.2. Cellulose as a Feedstock

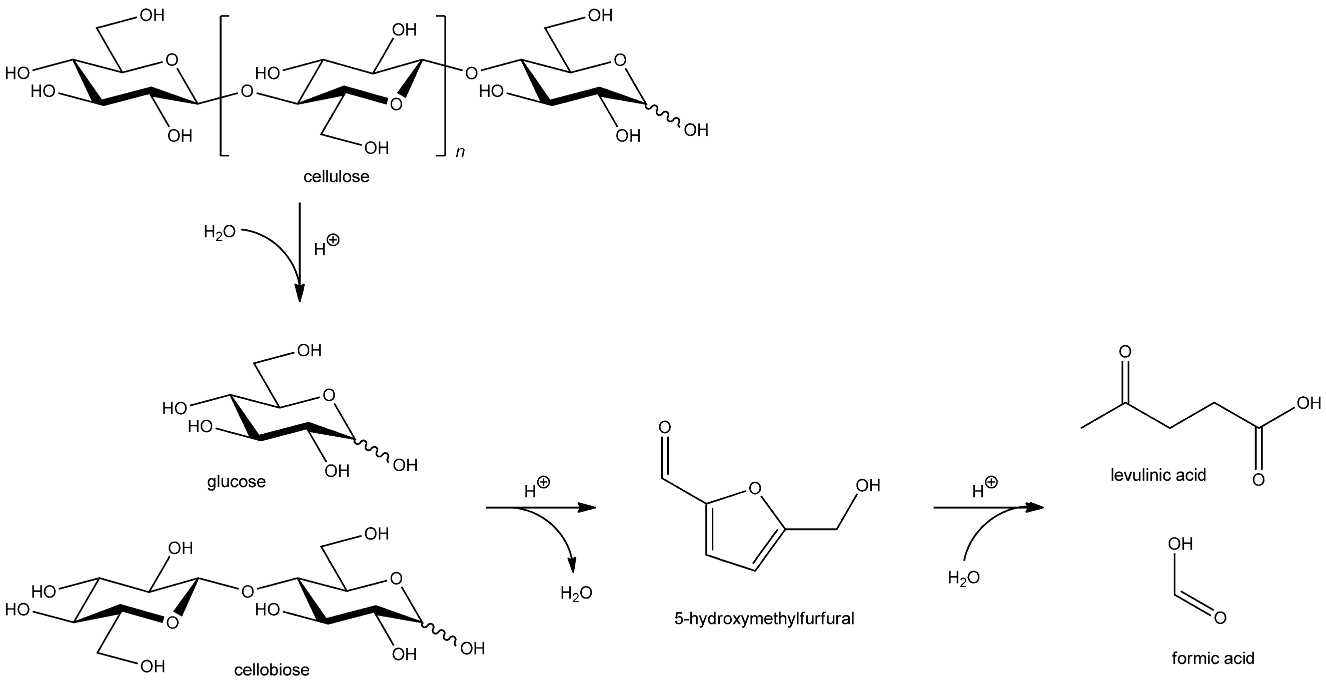
Cellulose is the major part of lignocellulose and the most abundant biopolymer. Consequently, its utilization for the production of chemicals and fuels would be highly desirable. Nevertheless, although a lot of research effort has focused on the degradation of cellulose by applying enzymes or mineral acids and bases, integral progress has not yet been reached. Enzymatic saccharification suffers from rather low reaction rates and consequently low space-time yields, while acid hydrolysis such as in the traditional wood saccharification processes, for example, the Bergius--Rheinau or the Scholler–Tornesch process, suffers from the formation of by-products and it is challenging to recover the acid. Additionally, further acid-catalyzed degradation of glucose to furfural compounds reduces the overall yield of the sugar, and most of the

Table 4: Overview of reaction systems used in the two-step hydrolytic hydrogenation of starch.

Starting material, catalysts and conditions	Products	Catalyst and conditions	Products	Ref.
first step		**second step**		
starch enzymatic or acidic hydrolysis	glucose	H_2, Ru/C	C_1 (methanol)	[190]
		H_2, Ru or Ni	C_1–C_3 incl. volatile HC	[191]
		H_2, CuO-ZnO	dehydroxy hexitols	[191]
		H_2, Pt or Pd	C6 cyclic ethers	[191]
mixtures of mono- and polysaccharides H_2, Ni/SiO_2, 140 °C	C_6 sugar alcohols (only from hydrogenation of monosaccharides)	H_2, Ni/SiO_2, 160 °C	C_6 sugar alcohols (also from hydrogenation of polysaccharides)	[193]
starch H_2, Ni/SiO_2, 140–160 °C	not examined	H_2, Ni/SiO_2, 200 °C, addition of H_3PO_4	sorbitol	[194]
starch H_2, Ni-$Ni_3(PO_4)_2/SiO_2$ or Ni-Fe-$Ni_3(PO_4)_2/SiO_2$	not examined	H_2, Ni-$Ni_3(PO_4)_2/SiO_2$ or Ni-Fe-$Ni_3(PO_4)_2/SiO_2$	sorbitol	[195]

Table 5: Overview of reaction systems used in the one-step hydrolytic hydrogenation of starch and inulin.

Starting material	Catalysts And conditions	Main products	Ref.
starch	Ni/SiO_2, 100 bar H_2, 200 °C, water-soluble metal or ammonium salts (e.g. $MgCl_2$, $NiSO_4$, $SbCl_3$)	sorbitol	[197]
	Ru/zeolite Y, 55 bar H_2, 180 °C	mannitol, sorbitol	[201]
	Ru/C, 250 bar H_2, 150 °C, pH 3–4	polyols	[202]
dialdehyde starch	Raney Ni, H_2, 180 °C, Dowex-50, pH 3–6 (mineral acid for pH adjustment)	erythritol, ethylene glycol	[199,200]
inulin	Ru/C (carbon functionalized with SO_3H groups), 100 bar H_2, 100 °C	mannitol, sorbitol	[202]



Scheme 11. Schematic illustration of hydrolysis of cellulose to glucose followed by further dehydration to 5-hydroxymethylfurfural and rehydration to levulinic acid.

degradation products are potential inhibitors of further enzymatic transformations (Scheme 11).[204]

In terms of controlled chemical transformations, ionic liquids with their ability to dissolve cellulose at the molecular level has attracted increasing attention, and studies on the hydrolysis of cellulose in these solvents have been carried out using either acidic ionic liquids and mineral acids to yield glucose, or metal chlorides with the aim of synthesizing 5-hydroxymethylfurfural.[205] The results were quite promising, but separation of the products from the ionic liquids is tedious and still hampers an application on an industrial scale. By using solid acid catalysts in the ionic liquid butylmethylimidazolium chloride, cellulose could be depolymerized selectively to cello-oligomers, which are interesting as their further enzymatic hydrolysis to glucose could be much faster.[206] The acid catalyst allows a tailored depolymerization to avoid the formation of monosugars and further degradation products. Recycling of the expensive ionic liquids, however, so far remains a challenge. Little progress has been made in regard to the hydrolysis of cellulose in the aqueous phase by using solid acid catalysts, although several studies have demonstrated the hydrolysis of cellulose by functionalized polymers, activated carbon, or silica materials.[207–209] In fact, the heterogeneously catalyzed hydrolysis of cellulose in aqueous media appears to be hampered by the fact that both the substrate and the catalyst are present in the solid state. Consequently, very little contact between the substrate and the active sites results, as reflected by a maximum conversion of even physically pretreated cellulose (ball milling) of only 50%, with 90% selectivity for glucose.[208] Interestingly, the combination of hydrolysis and hydrogenation seems to overcome these challenges, and not only yields sugar alcohols as interesting platform chemicals but also facilitates the depolymerization of cellulose.

5.2.1. *Mechanistic Considerations*

Most studies suggest a stepwise process involving hydrolysis of cellulose to glucose followed by hydrogenation to sorbitol. Starting from sorbitol, dehydration reactions to give sorbitan or isosorbide may take place, or further hydrogenolysis or dehydroxylation can occur to yield various C_1 to C_5 compounds. Li et al.[8] investigated the complex reaction network starting from sorbitol. As already discussed, the main reactions occuring under those conditions are retro-aldol condensations that result in C–C bond cleavage, hydrodeoxygenation to cleave the hydroxy groups, and further dehydration or hydrogenation reactions to give a rather broad range of possible products. The mechanistic details of the aforementioned reactions, as well as the possible alternative explanations of the widely accepted hydrogenolytic C–C cleavage mechanisms, are broadly discussed in Section 4. The main reaction pathways and products from the hydrogenolysis of sorbitol are illustrated in Scheme 4.

It is widely accepted that the hydrolysis of glycosidic bonds in cellulose, just like in other polysaccharides, proceeds via a flat half-chair oxocarbenium cation, which is formed as a result of protonation of the glycosidic oxygen atom and its departure as a good leaving group. The cation then reacts with water to yield a nonglycosylated glucose unit at the end of a chain or a free glucose molecule. If the hydrolytic hydrogenation process is indeed a stepwise sequence, the immediate hydrogenation of the glucose formed by the hydrolysis of cellulose would shift the equilibrium of the latter, thus speeding it up. On the other hand, a possible argument in favor of hydrolysis and hydrogenation occurring at the same time would be that hydrogenated long chains would be more soluble in water and thus would be hydrolyzed more easily. Both of the above possibilities can explain the enhancement of cellulose depolymerization under the hydrogenating conditions, and both can actually take place during the complicated process which is the hydrolytic hydrogenation of cellulose.

As will be shown below, numerous difunctional catalytic systems have been used, including solid hydrogenation catalysts with homogeneous acids, a combination of two solid catalysts, or a single difunctional catalyst. However, applications of metallic hydrogenation catalysts with no apparent acidic functionality have also been reported. Thus, Fukuoka and Dhepe used Pt supported on metal oxides and also included other metal catalysts in a patent on the same topic.[210,211] According to them, hydrogen dissociates on Pt, where the atoms "spill" over onto the oxide surface, where they are ionized as a result of the polarity of the support. Such formed protons can catalyze the hydrolysis of cellulose. Jollet et al. postulate that dissociated hydrogen on the Pt surface can be directly polarized by the reacting substrate.[212] In the case of an oxocarbenium cation, a hydride transfer would take place, thereby resulting in the release of H^+, which would further catalyze the hydrolysis. Such a mechanism (recombination of an oxocarbenium ion with a hydride) would, however, lead to the formation of 1,5-anhydrosorbitol as one of the main products. Since this seems not to be the case, the explanation is not satisfying. These reports will also be discussed further.

5.3. Hydrolytic Hydrogenation of Cellulose

Compared to the literature on sugars or sugar alcohols, there have been significantly fewer investigations addressing the use of cellulose as a feedstock. Nevertheless, some early attempts on the conversion of cellulose by hydrogenolysis, both through two-step processes, including prehydrolysis to sugars followed by hydrogenation/hydrogenolysis, and even one-step processes concerning the direct hydrolytic hydrogenation of cellulose to polyols have been reported (Table 6). Surprisingly, almost none of these findings have found their way into today's literature, being widely ignored in recent studies in this research area.

5.3.1. Historical Aspects of Cellulose Hydrogenation

The early studies of Friedrich Bergius in 1913 on the liquefaction of coal constitute a milestone in the field of both coal and wood chemistry.[213] Special attention should be given to his reports on the liquefaction of carbonaceous residues obtained by the thermal decomposition of cellulose, since this results in a liquid that to some extent resembles crude oil.[214] These investigations may even today present an inspiring piece of work in the direction of the efficient utilization of renewable resources. Interestingly, since then, several attempts have aimed at the reduction of cellulose and lignin to produce liquid fuels or to obtain improved yields of methanol, which was exclusively produced by the distillation of wood in those times. Later on, this motivation gradually lost importance, not least because of the low price of petroleum and the efficient synthesis of methanol from synthesis gas. Nevertheless, several promising approaches for the catalytic hydrogenation of cellulose and wood had already been presented in the first half of the 20th century.

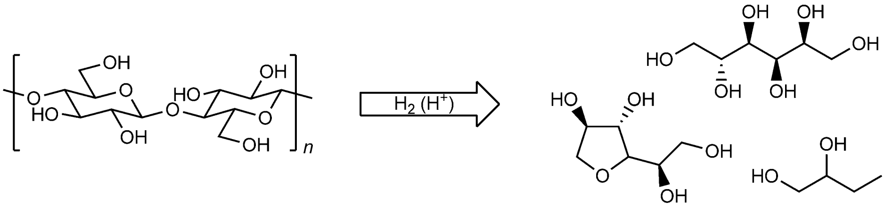
As early as 1925, Fierz-David and Hanning studied the hydrogenation of wood and cellulose with a major focus on wood liquefaction as a tool with which to gain insights into the liquefaction of coal.[215] They distilled cellulose and wood under H_2 pressure and reported a full conversion into liquid and gaseous products in the presence of Ni. In line with this, Bowen et al. reported on a significantly improved conversion of cotton in the presence of nickel oxide, which resulted in coke-like residues, water, CO_2, light oil, and tars.[216] Compared to the hydrogenolysis of sugars, however, these reactions have been carried out at quite high temperatures of over 400 °C. In 1928, Frohlich, Spaulding, and Bacon reported that wood releases methanol under pressure and at temperatures of 280 to 370 °C.[217] Interestingly, a cellulose sample was completely converted into gaseous and liquid products including phenols and hydrocarbons under 200 bar H_2 and in the presence of Ni, while no significant hydrogenation to oils occurred in the absence of any catalyst.

In 1932, Lindblad performed a catalyst screening for the "destructive hydrogenation of wood" at comparable temperatures with cobalt sulfide, cupric hydroxide, molybdic acid, and zinc chloride. In all cases tars and oil were obtained from the biomass, with maximum oil yields as high as 40%.[218] Routala reported in 1930 oil yields of 35% from sawdust by using Cu, Fe, and Co hydroxide, Ni formate, ammonium molybdate, and ammonium chromate as catalysts.[219]

In a stepwise approach, Berl and Biebesheimer, Berl and Schmidt, and later on Henze and Wyatt treated cotton with sodium hydroxide and recovered gases and tarry liquids, which were hydrogenated in the next step.[220–222] In line with their previous research, Berl studied the conversion of sugar cane bagasse into substances which could be further hydrogenated to useful petroleum products.[223] Berl was also the first to discuss the probable shortage of oil and the need for alternative routes for fuel productions, for example, by liquefaction of biomass and coal or Fischer–Tropsch chemistry.

Besides hydrogen, some investigations have addressed other reducing agents. Thus, Willstätter and Kalb examined the reduction of lignin and cellulose with hydrogen iodide and red phosphorus.[224] Despite temperatures around 250 °C, however, only small amounts of liquid and solid hydrocarbons could be obtained. Waterman and Kortlandt addressed the reduction of cellulose dispersed in molten paraffin wax by using a mixture of steam and carbon monoxide at 423 °C and 117 bar, but besides significant carbonization, no evidence of any reduction could be found.[225] In 1935, Boomer, Argue, and Edwards completely converted cotton and sawdust in tetralin into gases and further products (325–350 °C, 182–279 bar). They reported that tetralin may act as a hydrogen carrier and catalyst, and such a system seemed to be a very

Table 6: Catalyst systems and reaction conditions utilized in the hydrolytic hydrogenation of cellulose.



Catalyst	Conditions	Starting materials and products	Ref.
–	thermal decomposition and liquefaction	crude oil-like liquid	[214]
metallic Ni	distillation under H_2 pressure	liquid and gaseous products	[215]
NiO	>400 °C	coke-like residues, water, CO_2, light oil, and tars	[216]
Ni	280–370 °C, <200bar	phenols and hydrocarbons	[217]
–	reduction with HI or P, 250 °C	liquid and solid hydrocarbons (low amounts)	[224]
tetralin (as catalyst and hydrogen carrier)	no H_2, 325–350 °C, 180–280 bar	oil, pitch, CO_2, CO, CH_4, olefins (from cotton)	[226]
Cu nanoparticles (from Schweizer's reagent)	250–320 °C, 50–200 bar, in aqueous methanol	isopropanol, PG, acetol	[228]
Ru/$BaSO_4$ or Ru/C; HCl, H_2SO_4 or H_3PO_4	150–160 °C, 70 bar	sorbitol, sorbitan	[229–232]
Ru/C, H_2SO_4 or H_3PO_4	190 °C, 48 bar	xylitol, sorbitol, sorbitan (from cellulose and hemicellulose)	[234]
Ni	250 °C	liquid hydrocarbons	[236,237]
$Ni(OH)_2$	>400 °C, 70 bar	liquid hydrocarbons (from paper waste)	[238,239]
Raney Ni	350 °C, 100 bar, in water	from poplar wood: gaseous hydrocarbons from cellulose, oils from lignin	[240]
Ru or Cu catalysts	250 °C, 33 bar, in water	fuel oil	[241]
Raney Ni, homogeneous acids (Fe or Ni salts, HI)	250-350 °C, 51 bar, in water	water-soluble products, CO, CO_2	[242]
Pt and Ru on Al_2O_3, SiO_2-Al_2O_3 and zeolites	190 °C, 50 bar, in water	sorbitol, mannitol	[210,211]
Ru/C	245 °C, 60 bar, in water	sorbitol, mannitol, sorbitan, xylitol, erythritol, glycerol, PG, EG, methanol, methane	[247]
W_2C-Ni/C	245 °C, 60 bar, in water	EG	[248]
Ni-W/C, Pd-W/C, Pt-W/C, Ru-W/C, Ir-W/C	245 °C, 60 bar, in water	EG	[249]
W_2C-Ni/C	245 °C, 60 bar, in water	EG, 1,2-PG (from corn stalk)	[250]
Ni_2P	225 °C, 60 bar, in water	sorbitol, mannitol	[251]
Ni/C	230 °C, 20–60 bar, in water	sorbitol, mannitol	[252]
Fe, Co, Ni, Pd, Pt, Rh, Ru, Ir, and Ag on CNTs	185 °C, 50 bar, in water	sorbitol, mannitol	[253,254]
Pt, Pd and Ru on C, with H_2SO_4, H_3PO_4, $H_3PW_{12}O_{40}$, or $H_4SiW_{12}O_{40}$	160 °C, 50 bar, in water	C_4–C_6 sugar alcohols	[255,256]
Ru/C with $H_4SiW_{12}O_{40}$; Ru on zeolites with mineral acids	190 °C, 50 bar, in water	sorbitol, sorbitan	[257,258]
Ru nanoparticles, acidic ionic liquid	80 °C, 10 bar, in BmimCl (ionic liquid)	sorbitol, mannitol	[259]
$[HRuCl(CO)(PPh_3)_3]$, Pt/C, Ru/C	110–150 °C, 35 bar, in BmimCl (ionic liquid)	sorbitol, mannitol	[260]
Ru/C; $CuCl_2$ or $NiCl_2$ for dehydration to isosorbide	100 °C/210–230 °C, 10–200 bar, in molten $ZnCl_2$	sorbitol, isosorbide	[261]

active hydrogenating agent.[226] The products consisted of oil, pitch, CO_2, CO, methane, and olefins. Further insights into the nature of the reactions occuring or the influence of the type of catalysts on the product distribution were not addressed in these studies. The developments in the field were summarized by Weiss in 1972, covering not only the chemistry of cellulose pyrolysis and hydrogenation but also studies concerning the liquefaction of cellulose.[227]

5.3.2. *Application-Driven Approaches*

Most of the studies above were driven by interest in coal liquefaction and aimed for further insight into this issue by using wood as a model system. Nevertheless, several studies in the direction of an industrial application also appeared, mainly driven by the relative availability of petroleum. One of the first accounts on this reaction type was given by Gürkan in 1949.[228] He dissolved cellulose in an ammonia solution of copper sulfate (Schweizer's reagent) followed by heating of the mixture in a hydrogen atmosphere until the cellulose and finely dispersed Cu nanoparticles within the cellulose matrix co-precipitated (Figure 3). The precipitate was subsequently washed, dissolved in aqueous methanol, and subjected to hydrogenolysis at temperatures above 240 °C. Under these conditions a complete conversion of cellulose could be reached to yield liquid and gaseous products, including isopropyl alcohol, PG, hydroxyketones, and acetol together with a CO_2-rich gas phase. Overall, one may conclude that this may have been the first example of cellulose hydrogenolysis using finely dispersed metal nanoparticles.

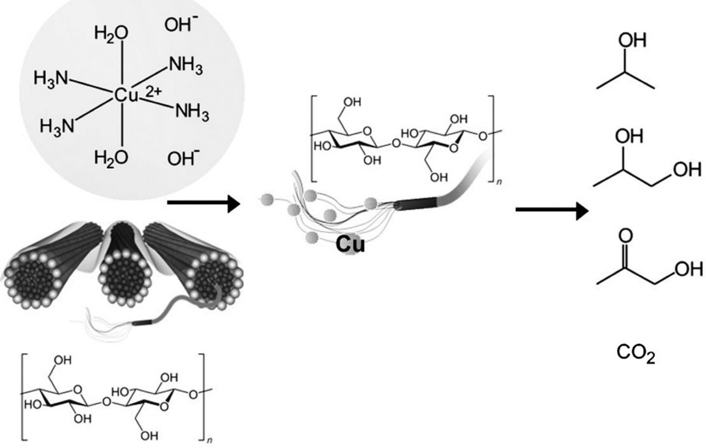


Figure 3. Schematic illustration of the dissolution of cellulose in Schweizer's reagent followed by co-precipitation of cellulose and finely dispersed Cu nanoparticles and subsequent transformation of cellulose into alcohols and ketones.

In 1963, Sharkov reviewed industrially feasible processes that had been developed in the USSR at that time.[229] The investigated procedures covered stepwise hydrolysis and hydrogenation as well as simultaneous approaches to combine these reactions in one step. Various methods for the hydrolysis of polysaccharides by using mineral acids were suggested for the first approach.[230] Accordingly, the produced sugar mixtures were treated with ion-exchange resins and activated charcoal to remove the acid and impurities and subsequently hydrogenated over Ni catalysts.[231] In terms of the simultaneous hydrolysis and hydrogenation of wood polysaccharides, the results of Baladin and Vassiunina need to be highlighted.[232] Therein, complete conversion of cellulose could be reached by combining mineral acids and hydrogenation catalysts. In detail, phosphoric, hydrochloric, and sulfuric acid were used along with Ru supported on barium sulfate or charcoal. The main products were sorbitol or sorbitan, depending on the reaction conditions.[229]

A process for the full utilization of lignocellulose has even been suggested by Balandin and co-workers, wherein cellulose and hemicellulose were converted over phosphoric acid in combination with Ru on charcoal in the first step.[233] The remaining catalyst and lignin could be filtered off, the acid was removed with an ion-exchange resin, and evaporation of the solvent resulted in crystallization of the reaction products, with a 95 % yield of pentitols and hexitols based on the total amount of wood polysaccharides. Thereupon, the lignin could be converted under alkaline conditions over the same catalyst but at an elevated temperature (300 °C instead of 160 °C), and a yield of up to 35 % of phenolic compounds was obtained. Moreover, the catalyst could be recovered, because of its higher density.

Interestingly, in 2004 Robinson et al. revisited these ideas and demonstrated complete conversion of hemicellulose and cellulose into polyols and anhydropolyols.[234] In the study, various real feedstocks were investigated. However, full conversion was rarely achieved and recycling of the catalyst was challenging. In fact, the mineral acids utilized in this study resulted in metal leaching into the reaction solution, which was especially severe in the case of sulfuric acid, but still reasonable for phosphoric acid.

Reese et al. discussed the use of cellulose as a novel energy source and suggested its conversion into synthetic fuels.[235] In this regard, Appell, Wender, and Miller summarized their work at the Bureau of Mines, where they reached over 90 % conversion and an up to 27 % yield of benzene-soluble products in a one-step reaction from cellulose.[236] This process was additionally extended towards municipal refuse, newspapers, and sewage sludge, which could be converted over nickel catalysts at 250 °C, although reactions under carbon monoxide pressure gave slightly higher conversions and yields of oils.[237]

Kaufmann et al. continued the studies on the hydrogenation of newspaper slurries dispersed in mineral oil as a model system of municipal solid waste, and developed a continuous process on a pilot plant scale.[238] Therein, the newspapers were hydrogenated over nickel hydroxide with a yield of up to 45 wt % of liquid hydrocarbon fuels at 85 % conversion. These results illustrated the potential of this technology to satisfy a significant fraction of the fuel demand in the US at that time. Gupta et al. investigated the same system, but suggested hydrogenating cellulose or powdered newspapers at above 400 °C and 70 bar H_2.[239] Under these reaction conditions, which are close to typical water-gas-shift conditions, about 50 % of the H_2 demand in the reaction could be covered by in situ generation of H_2. In terms of the reaction pathway, they suggested the reaction to proceed from cellulose via pyrobitumen to oil and finally gas, with a maximum liquid yield of 45 wt %.

Somewhat in contrast to these findings, Boocock et al. carried out an investigation on the direct aqueous hydrogenation of poplar wood at around 350 °C and 100 bar. They observed complete conversion into oils and gases in the presence of Raney nickel, and suggested that the derived oil results predominantly from lignin, while cellulose is transformed into methane-rich gases.[240] In 1983, Bond and Bird placed a patent on the production of fuel oil from cellulosic materials by using Pt group metals, preferably Ru or Cu catalysts.[241] To achieve full conversion, they autoclaved an aqueous suspension of cellulose along with sodium ruthenate and bicarbonate at 33 bar H_2 and 250 °C for 2 h. They suggested that cellulose is first hydrolyzed and then carbonylated to a keto acid, which decarboxylates to produce an aldehyde and CO_2. The aldehyde polymerizes and is subsequently hydrogenated to produce the final fuel oil.

Interestingly, the addition of CO proved to have a promoting effect on the oil formation. Further insight into this effect was, however, not given.

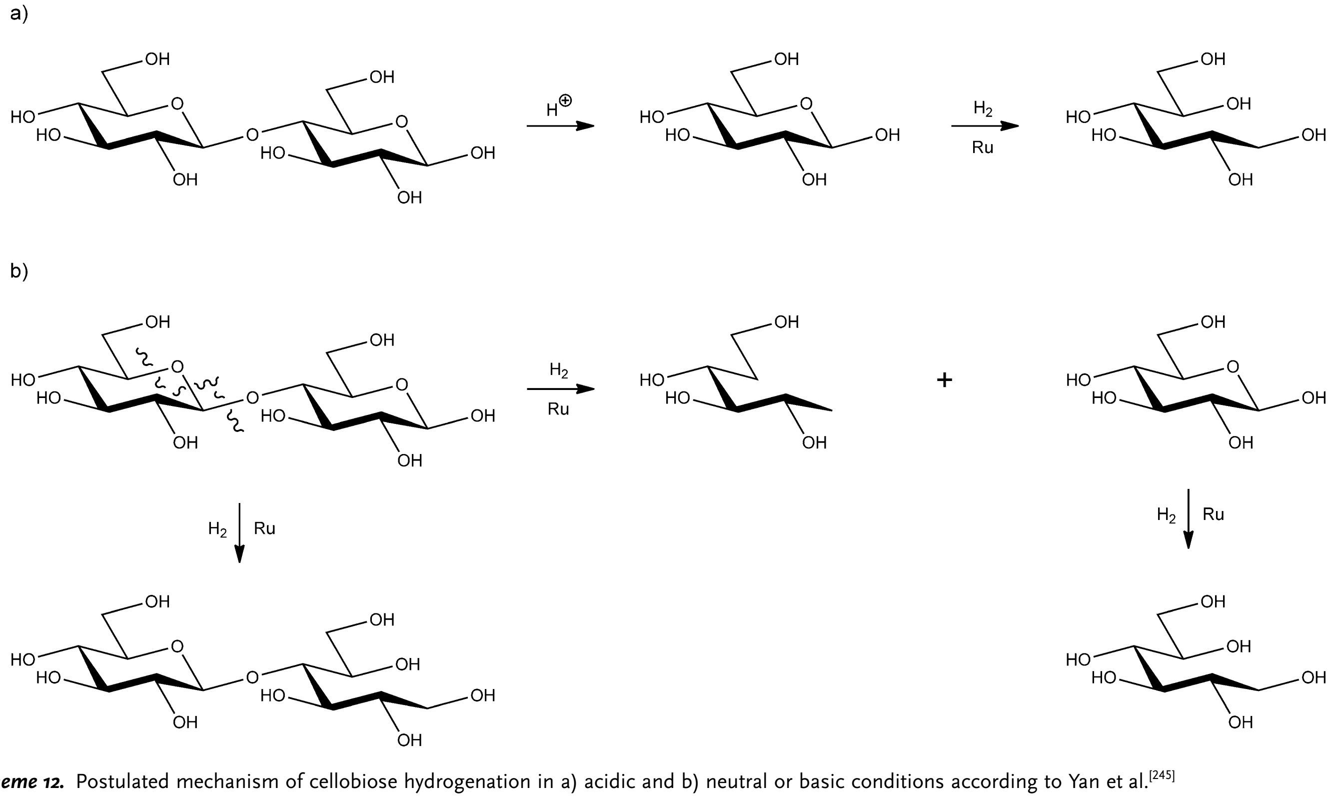
In a slightly different approach, Vasilakos and Barreiros performed the aqueous hydrogenation of cellulose in the presence of various homogeneous acidic catalysts. The conversion of the solid increased in the series $FeSO_4 < NiCl_2 < FeCl_3 < HI$, while the total conversion of carbon increased in the order $NiCl_2 <$ molybdates $< SnCl_2 < FeCl_3$. In the presence of Raney nickel as a heterogeneous co-catalyst, up to 93 % conversion into water-soluble compounds and CO/CO_2-rich gases could be reached, with $FeCl_3$ as the most active and Mo as the most hydrogen-selective catalyst.[242]

Despite these activities, the valorization of cellulose for an industrial application was rarely considered in the last few decades. However, the present energy and climate issues have resulted in the rediscovery of hydrogenolysis as a reaction type for the conversion of cellulose, not least because of the fact that sorbitol and xylitol can be found on the list of the 12 potential biomass-based platform chemicals identified by the DoE.[9] Interestingly, previously described investigations concentrated on Ni- and Cu-based catalysts, while most recent attempts concentrate on noble metal catalysts at temperatures around 190 to 250 °C.[243] Van de Vyver et al. have summarized recent developments in the field.[244]

5.3.3. *Application of Noble Metal Catalysts in the Aqueous Phase*

A first mechanistic investigation on the hydrogenation of cellobiose to form sorbitol was presented by Yan et al., who reported on the one-step conversion of cellobiose into C_6 alcohols over PVP-stabilized Pd, Pt, Rh, and Ru nanoclusters in the aqueous phase.[245] Pd, Rh, and Pt allowed 100 % conversion of cellobiose, but the major product was in all cases glucose. As the reaction was carried out at pH 2, one may assume that it most likely occurred through acid hydrolysis, while the catalysts exhibit only minor activity for the further hydrogenation of glucose to sorbitol. In contrast, around 88 % conversion could be reached by using Ru nanoparticles at neutral pH, with β-D-glucopyranosyl-D-sorbitol formed as the main product together with sorbitol, small amounts of glucose, and other polyols including dideoxyhexitols. Interestingly, at pH 2 the conversion reached 100 % and the product distribution shifted completely to sorbitol, while a pH value of 10 led to only 75.6 % conversion and 3-α-D-glucopyranosyl-D-sorbitol as the main product along with sorbitol, glucose, and dideoxyhexitol. On the basis of these results, the authors discuss two possible reaction mechanisms. The authors suggest the initial hydrolysis of cellobiose under acidic reaction conditions forms glucose, which is subsequently hydrogenated to sorbitol (Scheme 12 a). In contrast, under neutral or basic conditions the cellobiose may be hydrogenated directly to 3-α-D-glucopyranosyl-D-sorbitol or may even undergo hydrogenolysis of a C−O bond at position 1, as indicated in Scheme 12 b.

In regard to supported noble metal catalysts, Fukuoka and Dhepe demonstrated the direct hydrogenolysis of cellulose to



Scheme 12. Postulated mechanism of cellobiose hydrogenation in a) acidic and b) neutral or basic conditions according to Yan et al.[245]

sugar alcohols over Pt on various supports, including γ-Al_2O_3, SiO_2-Al_2O_3, and HUSY.[210] These findings were also covered in a recent patent application.[211] Besides the described systems, Ru on HUSY was also tested, and in all cases a yield of around 30 % of the sugar alcohols after 24 h at 190 °C was obtained. Although no further information regarding the conversion of cellulose was given, our previous experience suggests there is reasonable carbon utilization under such reaction conditions.[210,211] Somewhat puzzling, the yield of glucose was only up to 3 % over the pure supports. Other products resulting from further dehydration reactions were, however, not reported, and information on the overall conversion of cellulose was not reported so as to allow determination of a correlation between the acidity of the material, activity in the hydrolysis, and selectivity for certain products. Furthermore, the authors' conclusion of the metal having a promoting effect on the hydrolysis of cellulose is difficult to follow without information on the conversion of cellulose with and without metal being present. In terms of the mechanism, spill-over was suggested to explain the claimed cooperative effect. Therein, acid sites for the hydrolysis of cellulose would form in situ from H_2 in addition to the acidic surface sites intrinsic in the support.[246] In their mechanism, hydrogen is proposed to spill over on to the surface of the support, undergo heterolytic dissociation on the metal surface, migrate to Lewis acid sites, and release an electron to form protonic acid sites, which could act as active sites for the acid-catalyzed hydrolysis of cellulose. Jollet et al., in their report on cellulose conversion over Pt/γ-Al_2O_3, went one step further by postulating an analogous mechanism involving the heterolytic dissociation of hydrogen on the Pt surface, where a H atom can react further as a proton or hydride depending on the reacting substrate.[212] Those mechanisms were discussed in more detail at the beginning of this section.

Based on their previous studies on the hydrogenolysis of cellobiose, Luo et al. accomplished the hydrogenolysis of cellulose at 245 °C within 5 or 30 min.[247] They used ruthenium supported on carbon as the catalyst, with water as the solvent. Clearly, the high temperature allowed fast hydrolysis of cellulose followed by a subsequent hydrogenation to form sorbitol and mannitol. Further hydrogenolysis reactions also occurred, and resulted in various other C_1–C_5 products, including sorbitan, xylitol, erythritol, glycerol, PG, EG, methanol, and methane. Interestingly, water proved to be essential for the reaction. While dioxane or ethanol solvents gave no cellulose conversion, a mixture of H_2O and ethanol resulted in the conversion of cellulose, but a conversion of only up to 10 % was reached. The authors suggest that in situ formed acid sites in H_2O, arising from a shift in the autoprotolysis equilibrium of H_2O, are essential for this behavior and that, consequently, a high dielectric constant is essential. Interestingly, a 40 % yield of the sugar alcohols could be reached in pure water. This result, however, was at the expense of the full conversion of cellulose, which means, in fact, that a rather low carbon utilization to the desired products was achieved.

The influence of pretreatments of both cellulose and carbon nanotubes (CNTs) has also been studied. Therein, the degree of crystallinity of the cellulose substrate was varied from 85 to 33 % by using a phosphoric acid treatment step. The surface properties of the CNT support were modified by oxidation with nitric acid under different conditions, thereby resulting in different kinds and concentrations of acidic surface groups. They found that Ru supported on strongly modified carbon nanotubes were the most effective catalysts for the formation of sorbitol, with a yield of up to 40 % of hexitols for microcrystalline cellulose (85 % crystallinity) and even up to 73 % for pretreated cellulose. The impact of the support was investigated by carrying out comparative experiments with Ru supported on silica, ceria, MgO, alumina, and CNTs (185 °C, 50 bar, 3 h); the results support the proposal that acidic surface groups are advantageous for the hydrolysis reaction.

Some recent studies have been presented by the research groups of Palkovits and Sels on the hydrolytic hydrogenation of cellulose by using a combination of molecular acids and hydrogenation catalysts. Therein, Palkovits et al. investigated the use of Pt, Pd, and Ru supported on activated carbon with mineral acids such as phosphoric and sulfuric acid at temperatures as low as 160 °C.[248] Close to full conversion of cellulose and yields of C_4 to C_6 sugar alcohols of up to 60 % could be reached by combining Ru/C with sulfuric acid. Interestingly, heteropoly acids such as $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ in combination with Ru/C allowed even better results, with a greater than 80 % yield of C_4 to C_6 sugar alcohols within only 7 h.[249] Additionally, this system could be directly applied for the conversion of a real biomass feedstock, namely spruce. Full conversion of the cellulose and hemicellulose fraction contained in the wood and an up to 67 % yield of polyols was achieved. In line with this, Geboers et al. demonstrated the efficient conversion of concentrated cellulose feedstocks with $H_4SiW_{12}O_{40}$ and Ru/C. Optimization of the reaction conditions and the acid to metal catalyst ratio led to up to 100 % selectivity for hexitols (85 % sorbitol, 15 % sorbitan) at full conversion of ball-milled cellulose (190 °C, 1 h).[250] Interestingly, ion exchange with caesium not only led to higher activites, but also facilitated recycling of the heteropoly acids. Subsequent studies revealed that even trace amounts of mineral acids (35–177 ppm) in combination with Ru-loaded zeolites such as USY and MOR allow fast conversion of ball-milled cellulose to give hexitol in yields of up to 90 %.[251]

5.3.4. *Application of Nickel Catalysts in the Aqueous Phase*

Recently, Zhang et al. presented an interesting approach in which Ni-promoted tungsten carbide supported on activated carbon was used. Such noble metal free catalysts could be low-cost alternatives to Pt and Ru systems, and under similar reaction conditions allowed full conversion of cellulose within 30 min.[252] Interestingly, the main product proved to be EG, and a maximum 61 % yield of liquid-phase products could be obtained. The addition of Ni stabilized the W_2C, which was suggested to be more active. Later, they showed that tungsten carbide is not essential to the reaction. Instead, dimetallic catalysts of tungsten with metals of Groups 8, 9, and 10, for example, Ni-W, Pd-W, Pt-W, Ru-W, and Ir-W, supported on activated carbon gave promising yields and selectivity for EG. Tungsten in combination with Ni gave the best selectivity for EG, reaching up to 75.4 % yield at full cellulose conversion.[253] Recently, Pang et al. reported the application of such Ni-promoted tungsten carbide catalysts in the catalytic hydrogenation of corn stalk to EG and 1,2-PG.[254] In further investigations, Ni_2P catalysts were presented that allowed selective transformation of cellulose into sorbitol, with yields as high as 48.4 %. The catalytic activity was assigned to a cooperative effect between the acidic and metallic sites present on the support.[255] The stability of the catalyst after recycling has not been investigated.

Interestingly, Van de Vyver et al. presented a study wherein carbon nanofibers instead of porous solids were used to support Ni at the tip of the carbon filaments to facilitate contact between the cellulose and the catalyst.[256] This approach enabled an up to 92 % conversion of cellulose and 50 % yield of sorbitol (56.5 % hexitols) to be achieved. The high yield of hexitols was assigned to a synthesis-induced reshaping of the crystal structure of the supported Ni particles that suppressed undesired C–C and C–O bond cleavage. Similarly, Deng et al. investigated various metals supported on carbon nanotubes including Fe, Co, Ni, Pd, Pt, Rh, Ru, Ir, and Ag for the one-step conversion of cellulose into sorbitol.[257,258]

5.3.5. *Recent Developments Using Ionic Liquids*

Despite the promising results, reactions in the aqueous phase are certainly hampered by the limited contact between the solid cellulose and the solid catalysts. Consequently, a suitable solvent to dissolve the cellulose during the hydrogenolysis would be desirable. Besides the well-known Schweizer reagent, which is, however, not stable under hydrogenolysis conditions, ionic liquids have gained increasing attention in recent years, not least because of their ability to dissolve cellulose and even wood at the molecular level. Zhu et al. have reported the conversion of cellulose into hexitols catalyzed by ionic liquid stabilized ruthenium nanoparticles and a reversible binding agent.[259] They prepared a boronic acid functionalized ionic liquid which may act as an acid catalyst for the hydrolysis of cellulose in the ionic liquid 1-butyl-3-methylimidazolium chloride (BmimCl), while the Ru nanoparticles allow further hydrogenation to sorbitol and mannitol. The dissolution of cellulose at the molecular level resulted in temperatures of around 80 °C being sufficient to achieve close to complete conversion into glucose after 5 h. In the combined hydrolysis and hydrogenation, not only pure hydrogen but even sodium formate or formic acid could serve as the hydrogen donors, and allowed yields of sorbitol and mannitol far greater than 85 %. Consequently, one may suggest that the ruthenium nanoparticles are not only active in the hydrogenation of glucose but also for the release of hydrogen from the hydrogen transfer agents.

Ignatyev et al. reported on the reductive splitting of cellulose dissolved in BmimCl.[260] They investigated the activity of $[HRuCl(CO)(PPh_3)_3]$ as a molecular catalyst in combination with bases, but only its combination with Pt/C or Ru/C allowed full conversion of cellulose. Interestingly, the main product in most cases proved to be glucose rather than sorbitol, in up to 76 % yield. Besides, dimers, other C_6 sugars, sorbitol, mannitol, levoglucosan, as well as small amounts of shorter sugars and alcohols together with hydroxymethylfurfural could be detected. Product distribution, especially in terms of the fraction of hydrogenated products, was mainly dependent on the ratio of the molecular and the solid catalyst. The combination with Ru/C resulted in a yield of up to 74 % sorbitol. Nevertheless, the hydrogenation reaction appeared to proceed rather slowly under these reaction conditions when compared to hydrolysis.

An important aspect of this certainly promising approach is the separation of the very polar products from the ionic liquid. This challenge was recently addressed by the research group of Moulijn, and is also the topic of a recent patent by the same group.[261] They dissolved cellulose in $ZnCl_2$, which also facilitates the hydrolysis to glucose. The addition of small amounts of HCl allowed full conversion into glucose, while no significant amounts of by-products were formed. Interestingly, even acid-free reactions appear feasible at temperatures around 100 °C instead of 85 °C. Subsequently, HCl may be removed with the gas phase, and glucose is hydrogenated over Ru/C to yield sorbitol in close to maximum yield. Interestingly, no mannitol from the isomerization of glucose to fructose was observed. Therefore, catalysts such as $CuCl_2$ or $NiCl_2$ were added to catalyze the subsequent dehydration to isosorbide via formation of 1,4-, 3,6-, and 2,5-anhydrosorbitols, known as sorbitans. Indeed, 2,5-anhydro intermediates do not undergo further dehydration, thus their presence would reduce the selectivity to isosorbide. Surprisingly, in the described system, rather clean dehydration to isosorbide occurred even without the addition of a co-catalyst, but at the somewhat elevated temperatures of 210–230 °C. An explanation for the selective dehydration of sorbitol to isosorbide is based on an interaction of the hydroxy groups with $ZnCl_2$ salt hydride species, as has been reported for the dehydration of sorbitol in pyridinium chloride.[262]

5.3.6. *Recent Trends and Future Challenges*

Overall, several metals have been used as catalysts, although recent research has focused on supported noble metals and nickel-based systems. Nevertheless, earlier studies indicate that other base metals, such as Cu, are potential catalysts in the reaction. In regard to potential reaction systems and conditions, aqueous systems at rather high reaction temperatures above 190 °C have been described in which supported metal catalysts were utilized, while reactions at 190 °C or even lower require acidic supports or the addition of a molecular acid to facilitate the hydrolysis of cellulose. In the case of supported noble metal catalysts, the balance between the acid functionality and the metal had a strong impact on the product distribution and selectivity. Ni-doped supported tungsten catalysts, although less-well understood but highly promising, exhibit high selectivity for the formation of ethylene or propylene glycol, although the stability of the catalyst certainly needs to be optimized. Thus, investigations into the involved reaction mechanism and the origin of these selectivities would be necessary. Highly promising systems based on ionic liquids and molten salts could be demonstrated for the efficient conversion of cellulose. However, the separation of sugar alcohols from such solvents as well as the recycling of the catalysts and solvents remains a challenge. Consequently, further developments in the field and the potential of a technical implementation of the two systems will intrinsically depend on the development of new catalysts as well as the efficient recovery and separation of the products.

6. Outlook

Feedstocks: Various catalysts and reaction systems have been employed in the valorization of sugars, sugar alcohols, and polysaccharides. The major feedstock base covered monosaccharides such as glucose and fructose as well as their hydrogenation product sorbitol. Recently, glycerol has been the subject of growing attention as a result of the increasing supply of glycerol through the production of biodiesel. Although some early studies were aimed at a direct transformation of polysaccharides, including starch, inulin, hemicellulose, and cellulose, only a few systematic studies exist. Further investigations are certainly mandatory, considering the shift of the feedstock base towards a broad utilization of renewable resources in the chemical industry. Compounds such as xylose, arabinose, and erytrose will become available and could broaden the potential product scope. Further investigations concerning the one-pot transformation of cellulose or even lignocllulose are also essential to gain insight into the reaction mechanism and the impact of catalysts and reaction conditions. An industrial application of the discussed transformations will strongly depend on highly selective and robust catalysts, which would allow the synthesis of desired products in good yields and withstand potential impurities in the natural feedstocks. Moreover, efficient separation techniques need to be established to separate the polar products from aqueous or otherwise polar reaction media.

Products: Although glycerol has been a product of major interest in the past, the attention has nowadays shifted towards propylene and ethylene glycol. They are already valuable feedstocks, but novel transformations, for example, to ethylene and propylene for the production of biopolymers, additionally increase the interest in such compounds. Furthermore, C_4–C_6 sugar alcohols such as sorbitol, xylitol, and erythritol are promising intermediate products which can be further dehydrated to yield tetrahydrofuran derivatives, for example, for application in biofuels, surfactants, or biopolymers. In addition, C_5–C_6 alkanes can be produced starting from sorbitol or xylitol. Overall, the synthesis of target products with high selectivity will be mandatory to reach economic transformations of renewable feedstocks. Thereby, the controlled hydrodeoxygenation and the combined hydrogenation/hydrogenolysis and dehydration wil gain in importance as they allow access to compounds with fewer oxygen functional groups.

Catalysts: Various catalyst systems have been investigated for the hydrogenolysis and hydrogenation of sugars and sugar alcohols, with a major emphasis on ruthenium-based systems, while other noble metals have received little attention. Of the other metals, nickel and copper catalysts were mainly studied. Copper-based dimetallic catalysts demonstrated superior selectivity and productivity with glycerol. Surprisingly, only a few investigations have concerned the development of dimetallic catalysts based on copper for the transformation of other feedstocks such as sorbitol, starch, or even cellulose. Dimetallic systems based on non-noble metals may also exhibit superior properties for the transformation of other feedstocks. The first examples of nickel-doped tungsten and supported CuO have already been applied in the transformation of cellulose, but further experimental and theoretical studies are necessary to elucidate the influence of doping metals and set the base for the knowledge-driven development of new catalysts.

7. Conclusions

The hydrogenation and hydrogenolysis of renewable feedstocks could be a promising transition technology to serve as a crossover between value chains in the traditional refinery and renewable feedstocks. The reaction has already proven its potential in the transformation of glycerol to ethylene and propylene glycol, and is also a valuable tool in the conversion of biomass-derived polyols, such as sugars or sugar alcohols. Moreover, even the direct conversion of biopolymers, including starch, cellulose, hemicellulose, and even lignin into valuable platform chemicals has been demonstrated and give access to various compounds already integrated in today's fossil fuel based value chains. Consequently, hydrogenolysis bears the potential to bridge available technologies and future refinery concepts.

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