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Copper catalyzed hydrogenation reactions of saccharides in aqueous phase

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Abstract

Introduction

Saccharides represent precious and versatile chemical structures to be shaped for a wide variety of purposes through several transformations. The possibility to derive them from biomass, due to their presence as the main constituents of cellulose, hemicellulose, chitin and many other natural polymers, makes them a gold mine for the preparation of biobased products and materials [1] (Figure 1). Naturally occurring polysaccharides vary from their origin and can be mainly divided into homopolymers, formed by a single repeating unit, as it is the case of cellulose or starch, and heteropolymers comprising more than one type of elementary unit as for example hyaluronic acid.

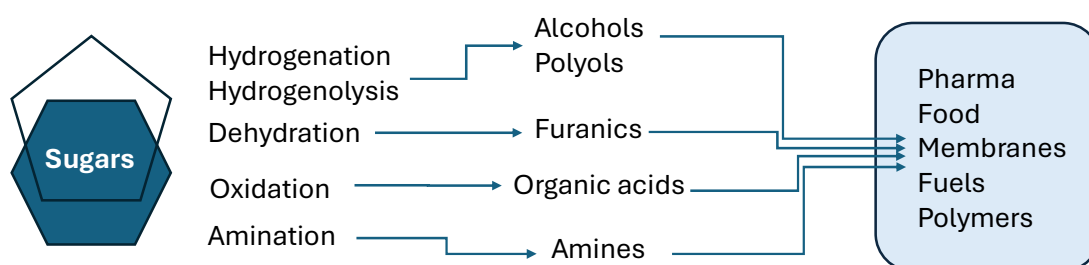


Figure 1. From carbohydrates to chemicals

Glucose is the almost ubiquitous monomer in natural polysaccharides, being the repeating unit of cellulose and starch, and present in many disaccharides such as maltose, lactose, and sucrose. Huge amounts of these starting materials can be derived from lignocellulosic deconstruction streams, such as glucose, and from agro-industrial residues and wastes. This is the case of lactose, one of the main constituents of milk whey[2], and of maltose, that can be derived through fermentative processes from starch, and therefore from cereals residues and bakery wastes[3].

Their production starting from the parent natural polymers or biomass source has seen an enormous research activity exploiting chemical, bio-chemical and physical-chemical approaches, as well as their transformation into platform and building blocks for the chemical industry.

Within these processes the reduction of saccharides into the corresponding reduced sugars is an important field, due to their use in both pharma and food industry and as starting materials to produce monomers [4][5].

A particular case is represented by sorbitol, one of the more promising biobased building blocks for the chemical industry of the future. Thus, besides its traditional applications in the food, toiletries, pharma and surfactants industry [6] it is the precursor of the bicyclic ether isosorbide. This is a monomer for the bioplastic industry with a market size around 600 Million € in 2023 and supposed to grow with a 7,5% rate during the 2024-2032 period. This significant growth is mainly due to the increasing demand for non- fossil based and non-toxic additives in the polymer industry.

Several isosorbide-based chemicals have already been introduced into the market, such as polyethylene isosorbide terephthalate (PEIT), renowned for its superior thermal resistance and mechanical strength. Isosorbide is also widely used as a feedstock in the production of polycarbonate isosorbide (PC), which finds numerous applications in manufacturing automotive components, electronic devices, and optical lenses due to improved stiffness and heat resistance, compared to polymethylmetacrylate (PMMA) and poly(bisphenol-A) carbonate, and of isosorbide diesters with fatty acids of natural origin able to substitute phthalates as plasticizers in the production of PVC due to their outstanding compatibility and processability with PVC resins[7].

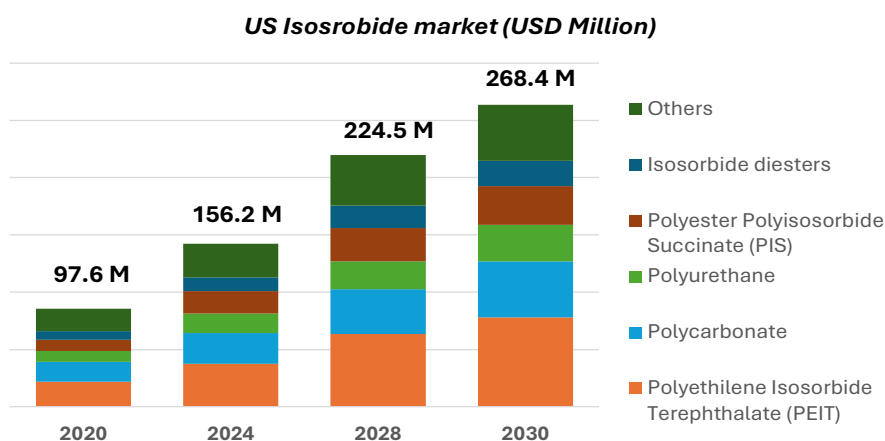


Figure 1. US Isosorbide market for materials (adapted from www.grandviewresearch.com)

However, most of sorbitol is produced through hydrogenation of corn starch-based glucose therefore competing in some way with the food supply chain, therefore there is a need to use more sustainable raw materials. Sidestreams of the agrifood industry such as maltose and lactose are very good candidates and also the direct conversion of cellulose to sorbitol is attracting a lot of interest [8].

The heterogeneously catalyzed processes for the carbohydrates hydrogenation mainly rely on the use of noble metals or Nickel based systems. Ni Raney has traditionally been employed as the primary

sugar alcohols manufacturing method [9] but although convenient from the economic point of view, it is quite easily poisoned and deactivated [10].

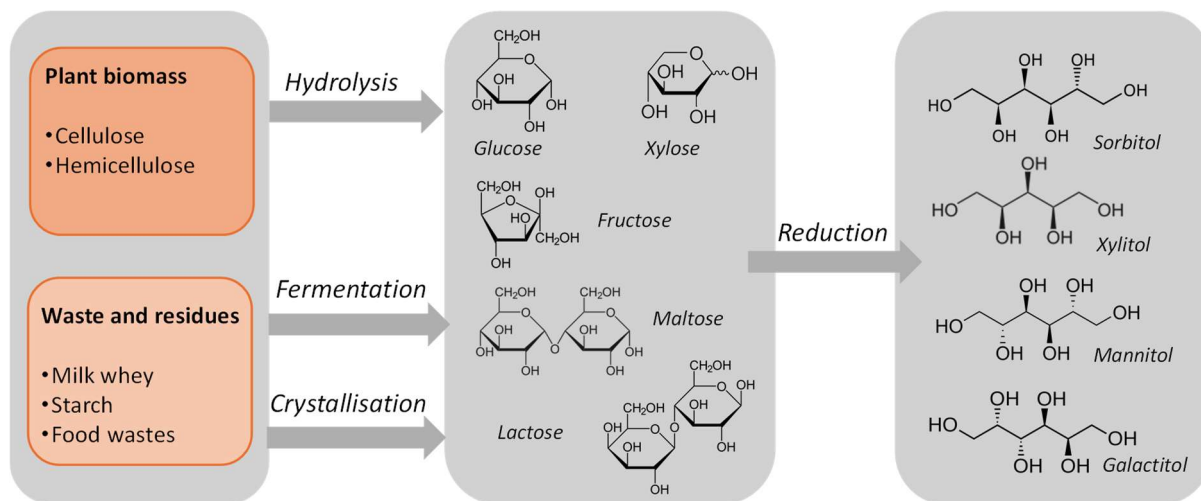


Figure 2. Main streams from biomass to sugar alcohols

For this reason, a lot of studies have been carried out to design noble-metal catalysts [11], mainly Pt and Ru ones, the latter generally revealing to be the most performant.

In this scenario not negligible aspects are the high polarity and the high oxygen content of carbohydrates, that put a major issue related to their poor or any solubility in organic solvents. This aspect, although irrelevant when using an enzymatic approach, represents a challenge in the case of chemo-catalytic strategies. The search for catalytic systems stable and active in water becomes mandatory and this is not trivial considering the common stability concerns related with the use of metal-based systems in aqueous environment related with sintering, oxidation, leaching and nanoparticles collapse problems.[12]

On the other hand, the use of water as solvent is highly desirable also from the process sustainability point of view. Besides being the best medium to solubilize the typically biomass-derived substrates, water is a green solution and can moreover play an important role in the chemical reaction. Thus, the hydrogen bonds formed with water molecules could act as either reaction promoters or reaction inhibitors.

Several aspects have been envisaged to design efficient Ruthenium systems. In particular, the particle size is a critical point to obtain high selectivity in the hydrogenation of glucose into sorbitol; a series of Ru/C catalysts tested allowed to obtain a maximum of conversion and selectivity with metal

nanoparticles ranging from 2 to 4 nm. [13] The very high performances in terms of activity and stability were also obtained with a commercial Ru/Al₂O₃ were also mainly ascribed to the particle sizes of Ru around 2 nm and to the control of secondary reactions [14]. The morphological distribution of Ru is also invoked as the main reason for the high stability of a (RuO₂)(SiO₂) nanomaterial prepared by a one-pot sol-gel route [15].

The preparation technique generates a multimodal size distribution of the metal nanoparticles, stabilized by the interaction with both the support and the reaction environment. The Ru valence regulation strategy has been exploited on multiwalled carbon nanotubes (Ru/MWCNTs) catalysts for the selective sugar hydrogenation with high selectivity and yield [16]. The simultaneous presence of Ru⁰ and Ru³⁺ sites on the surface respectively activates hydrogen and coordinates the C=O group of the sugar aldehyde.

In some cases, the combination with the use of Ni allows to design a trade-off system able to face with both economic and efficiency needs [17] [18]. The activity of Ru catalyst on a NiO modified TiO₂ has been proposed in the liquid phase catalytic hydrogenation of xylose to xylitol [19].

The direct transformation of lignocellulosic biomass into sugar alcohols has been also reported.[20] [21]For example, xylitol was produced directly from biomass. In another work, polyols production was used as a mean to purify sugar streams after biomass hydrolysis.

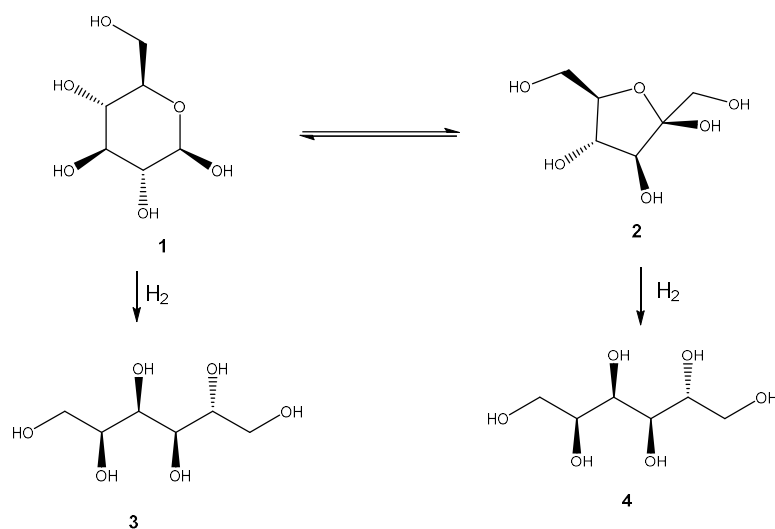
A potential alternative to noble metals and to Nickel is represented by copper. Supported Cu catalysts are somehow overlooked in the hydrogenation of carbohydrates due to their usually lower activity not only with respect to noble metal systems, but also with respect to commercial Ni materials. Nonetheless their capacity in the hydrogenation of carbonyl groups in organic solvents is well known and appealing in the increasing shift from precious to nonprecious metals in catalytic use [22]. Mainly Cu/SiO₂ and Cu/Al₂O₃ have been explored in the hydrogenation of aliphatic and aromatic ketones under mild conditions [23][24][25], the most important feature for the high activity observed emerging from these applications being the high dispersion of the copper phase. Selectivity issues have been also faced in the hydrogenation of cinnamaldehyde [26][27].

More recently the pool of platform molecules made available from lignocellulosic deconstruction processes, i.e. levulinic acid, γ -valerolactone and furanics, has offered new carbonyl group as reduction target. Cu/MgO has been proposed for the hydrogenation of furfural[28], Cu/SiO₂ for γ -butyrolactone[29] and γ -valerolactone [30].

In this review we will sum up the main examples reported in the use of heterogeneous copper catalysts in aqueous phase for the hydrogenation of saccharides, besides some unpublished results from our group on the reduction of xylose and galactose.

Reduction of Monosaccharides

Glucose **1** and fructose **2** are two hexoses that can interconvert by isomerisation. Their corresponding reduced sugars are respectively sorbitol **3** and mannitol **4** (Scheme 1), both products of great industrial interest.



Scheme 1 – the hydrogenation products from glucose and fructose

Sorbitol is listed by the US National Renewable Laboratory (NREL) among the top value-added chemicals from biomass [31].

Glucose hydrogenation into sorbitol is mainly performed with noble metal-based catalysts, namely Pt and Ru [11]. It is worth underlining that even when using noble metals this kind of reductions need harsh conditions in terms of temperature and specially of hydrogen pressure, usually ranging from 15 to 40 atm. This means that considering the missing advantage of the milder conditions usually related with the use of noble metals, the search for non-noble alternatives is a desirable route. In this scenario the great part of the studies on monosaccharides hydrogenation relies on Nickel catalysts [32]. On the other hand, the activity of copper as both active reductive metal and/or as co-catalyst is known although less studied.

A pioneering work by the group of van Bekkum relies on the use of Ni, Cu, Ru, Rh, Pd, Os, Ir and Pt catalysts for the hydrogenation of fructose and fructose/glucose mixture [33]. The authors put in light the high performances of Cu/SiO₂, particularly in the reduction of fructose.

The valorisation of copper in terms of activity when using silica as the support has been also recently highlighted in a comparative study of glucose hydrogenation with Cu and Ni by using SiO₂ or Al₂O₃ [34]. By means of a high throughput approach the authors studied the activity of a wide set of catalysts based on nickel with different loading and prepared over silica or alumina. From data reported, relying on the results of 36 experiments carried out over two days The Cu/SiO₂ catalysts exhibited higher activity in glucose hydrogenation compared to Ni/SiO₂ whereas, Ni/Al₂O₃ showed higher activity compared to Cu/ Al₂O₃.

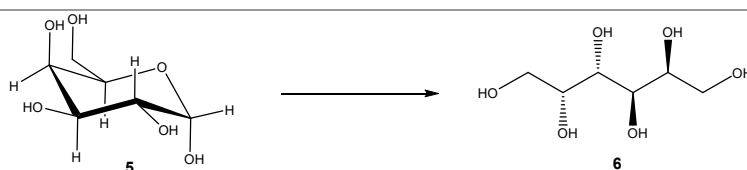
Nonetheless, the synergistic effect of copper with transition metal and metal oxides can be exploited to obtain hydrogenolysis products instead of hydrogenation ones [35]. In particular, the contribution of acid/basic sites from the support promotes isomerisation and retro-aldol condensation leading to the formation of C₂, C₃ and C₄ polyols. A comparison between Cu/Al₂O₃, Cu/MgO, Cu/ZrO₂ and Cu/TiO₂ shows that the support non only influences the Cu properties, but also affect the activity of C-C and C-O bond cleavage: Cu/Al₂O₃ favours the formation of glycol with 66.6% selectivity by virtue of Lewis acid sites, and Cu/MgO possessing a large number of basic sites accelerates the retro-aldol condensation and isomerisation giving C₂, C₃ and C₄ polyols.

Some of us also reported on the use of Cu/SiO₂ prepared with a chemisorption-hydrolysis technique in the hydrogenation of glucose obtaining 90% conversion and 82% selectivity in sorbitol [36].

Very high activity and selectivity was obtained with the same catalytic system also in the hydrogenation of galactose **5** into galactitol **6**. In this case the comparison with two other supports, namely alumina and an acidic mixed oxide such as SiO₂-ZrO₂ with a 5% by wt of ZrO₂, clearly show the critical effect in selectivity obtained by using silica, that gave 62.2% yield in galactitol vs the 22.4% and only 10% respectively obtained with the alumina and silica zirconia-based catalysts (Table 1).

Table 1- Hydrogenation of galactose over Cu/SiO₂, Cu/Al₂O₃ and Cu/SiO₂-ZrO₂

Entry	Catalyst	T °C	P atm	Conv %	Yield %	Sel %
1	Cu8/SiO ₂	180	30	98.0	62.2	63.4
2	Cu8/Al ₂ O ₃	180	30	99.4	22.4	22.5



3	Cu8/SiO ₂ -ZrO ₂	180	30	96.95	9.96	10.3
5	Cu8/SiO ₂	160	40	100	68.6	71.2
6	Cu16/SiO ₂	160	30	95.2	61.6	64.7
7	Cu16/SiO ₂	160	40	100	76,4	76,4
8	Cu16/SiO ₂	160	50	100	75.7	75.7

The yield can be further improved up to 76% by increasing the copper loading and adjusting the reaction conditions at 160°C and 40 atm of H₂.

A very interesting trend in galactitol yield was observed with the variation of galactose concentration in the starting reaction mixture (Figure 3). A yield of 80% can be reached for a starting concentration of 50 mg/mL.

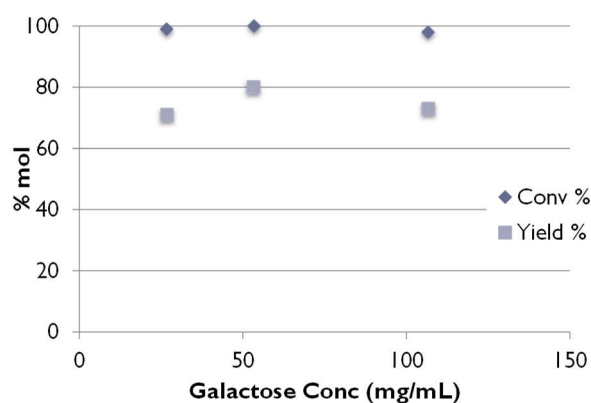
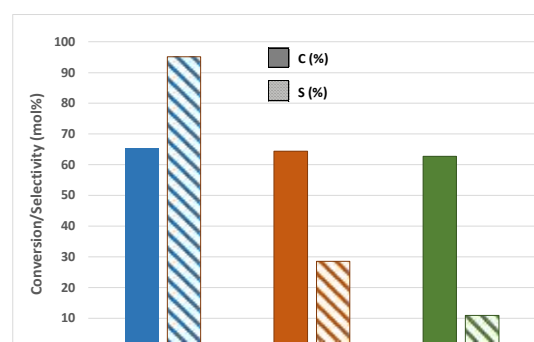


Figure 3. Effect of galactose concentration on conversion and yield

The very great influence of the support used and the potentialities of copper catalysts as interesting substitutes to noble metal-based systems have been investigated also in the reduction of xylose **7**, that is the main component of xylan derived from hemicellulose. By virtue of this it is considered a key platform to produce furan dicarboxylic acid (FDCA), furfural, glycols and xylitol **8** [37]. The latter polyol is widely used in food and pharmaceutical industry as low calorie sweetener and as additive with a market size of US\$ 976.7 Million in 2023 [38]. Main studies rely on the use of ruthenium solid catalysts for the transformation of xylose into xylitol [39].

Some new results obtained with Cu/SiO₂ in the hydrogenation of xylose revealed the reduction of xylose at 120°C and 40 atm leads to the formation of xylitol with excellent selectivity into xylitol (Figure 4).



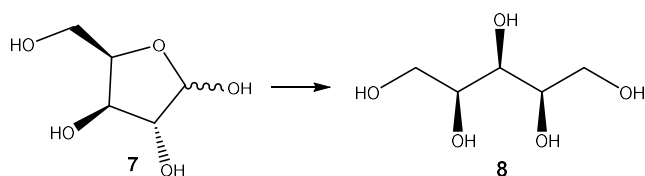


Figure 4. Hydrogenation of xylose with three heterogeneous catalysts (120°C, 40 bar H₂)

The comparison with Cu/ZrO₂-SiO₂ and Cu/TiO₂ clearly show the outstanding effect in terms of selectivity obtained by using silica as the support. In particular, by-products corresponding to lyxose and xylulose, derived from isomerization processes are formed (Figure XXX) and then hydrogenated to polyols, arabitol and ribitol. Cu/ZrO₂-SiO₂ yielded a higher final content in xylitol, followed by arabitol and ribitol, accounting for 30.5% of total polyols at 60% xylose conversion. On the other hand, Cu/TiO₂ gave only 15% yield in polyols at the same conversion, thus suggesting that ZrO₂ based supported catalysts favours the isomerisation processes (Figure 5). To have a deeper insight into the effect of the support the same reaction with the bare ZrO₂-SiO₂ was carried out under the same conditions. As expected, polyols were not detected, whereas lyxose and xylulose were formed in high yields just from the beginning reaching a maximum 28-30% yield not increasing with conversion, suggesting the existence of a thermodynamic equilibrium between xylose and its isomers. On the other hand, furfural was produced continuously during reaction with a final 13% yield, conversely to its absence when working with the corresponding copper catalyst.

The poor selectivity of Cu/ZrO₂ prepared by incipient wetness technique has been also reported in the reduction of glucose to sorbitol when compared to noble-metal catalysts supported over the same oxide [40]. The authors report a catalyst selectivity for sorbitol decreasing in the order PdFe/ZrO₂ > Pd/ZrO₂ > Fe/ZrO₂ > PdCu/ZrO₂ > Cu/ZrO₂, mainly ascribing the different products distribution to the catalyst acidity.

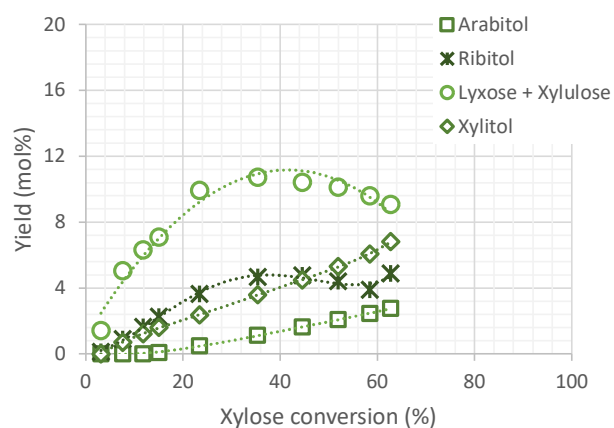
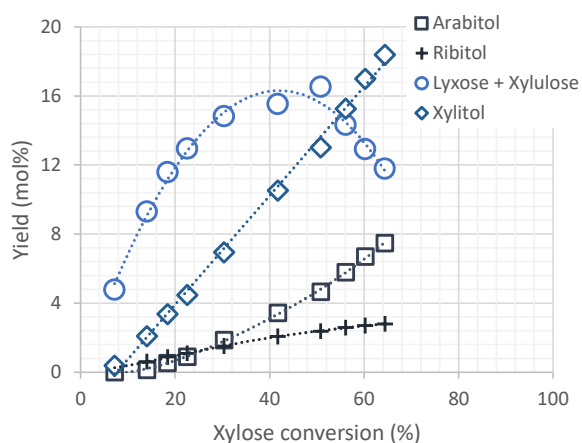
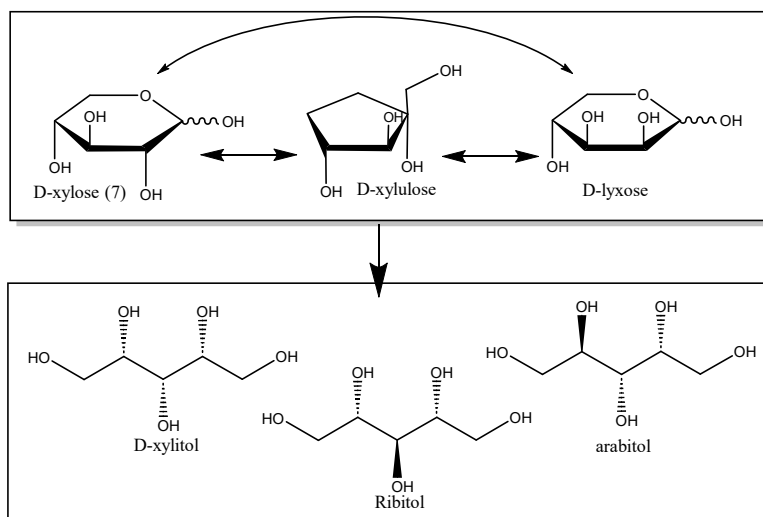


Figure 5 – by-products yield during xylose hydrogenation over Cu/ZrO₂-SiO₂ (left) and Cu/TiO₂ (right) (120°C, 40 bar)

Some more insights into the use of copper for the hydrogenation of saccharides have been reported in the reduction of fructose **2**. As shown in Scheme 1, mannitol is the polyol derived from fructose hydrogenation and its widespread industrial use in pharma and food sectors make its production highly appealing. As already pointed out, the use of Cu catalysts results more selective in the hydrogenation of fructose with respect to Nickel systems [33]. A CuO-ZnO catalyst containing 61% of CuO and 39% of ZnO gave 60-68% selectivity in mannitol [41]. A different approach has been explored with a magnetic Ni/Cu/Al/Fe hydrotalcite-like compound prepared by a co-precipitation method that allowed to obtain 56,9% yield in mannitol [42]. The catalyst is recyclable, and the authors underline the importance of the complete reduction of Cu²⁺ to Cu⁰.

Fructose conversion up to 98% with selectivity of 78% in mannitol have been reported with a monometallic Cu/SiO₂ prepared by a precipitation-deposition technique at controlled pH, showing much higher performances with respect to the catalyst prepared over Al₂O₃ [43]. The high activity and selectivity can be ascribed to the metallic copper nanoparticles present on the surface and interacting with a support with low acidity and basicity such as silica. The use of Mg-Al and Zn-Al mixed oxides with a spinel-like crystalline structure also depress activity and selectivity. On one hand the strong adsorption of fructose blocks copper active sites, on the other the support basic sites promote the isomerisation of fructose into glucose, thus lowering mannitol selectivity.

The same group reports an improvement in activity by using a bi-metallic CuNi/SiO₂ system prepared with the same technique [44]. The bimetallic catalysts gave 95% conversion of fructose *versus* 50-55% obtained with the mono-metallic systems, both the Cu and the Ni based ones. It is interesting to note that the Nickel catalyst besides being less active it is less selective and poorly stable. On the other hand, the monometallic Cu/SiO₂ is less active than the bimetallic CuNi/SiO₂, but equally selective. The higher activity is ascribed to a high interaction between Cu and Ni leading to monocrystalline nanoparticles of Cu-Ni alloy able to dilute the strong interaction of polyols with catalytic sites, thus lowering the deactivation and therefore increasing the activity.

The optimal interaction between copper and Nickel has been also invoked as the successful feature imparting to a hydrotalcite deriving Cu-Ni-Al catalyst used as hydrogen transfer system [45]. The reduction is performed under flow conditions by feeding a solution of different monosaccharides in water/donor alcohol in 20:80 ratio by weight. The choice of hydrogen transfer condition with respect to molecular hydrogen is aimed to more industrial viability of the reduction process to avoid storage and handling issues related with the use of hydrogen under high pressures. The reduction of glucose, fructose, mannose, xylose and arabinose in the presence of 1,4-butandiol as hydrogen donor is reported, obtaining yields in the corresponding reduced sugars ranging from 60 % (mannitol and xylitol), to 61% (sorbitol) and 66% arabinitol. The use of 1,4-butandiol as hydrogen source has the advantage of giving 2 moles of H₂ while forming γ -valerolactone as by-product.

Vale la pena fare una tabella riassuntiva anche per i monosaccaridi?

Reduction of disaccharides

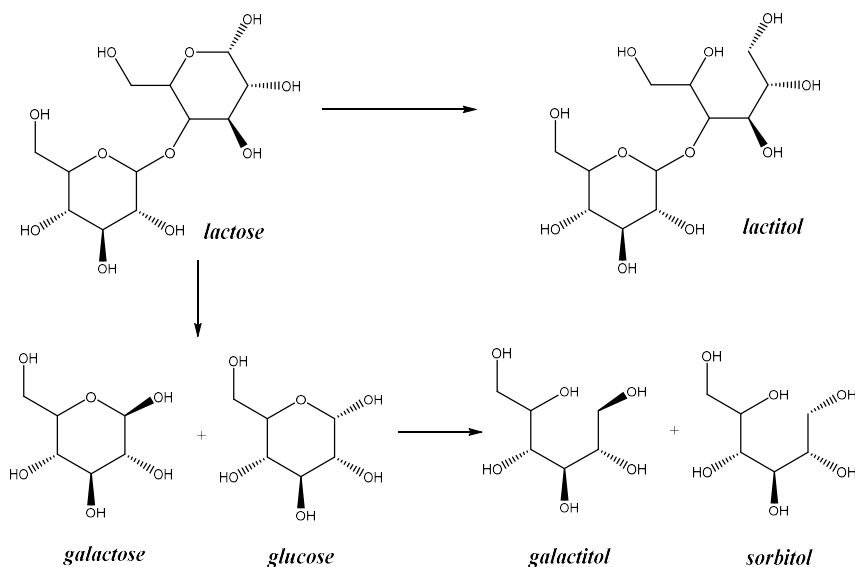
Among disaccharides, *lactose* deserves attention as it is a main constituent of the milk whey. It is worth noting that the use of milk whey as starting material represents entails a double advantage. In

fact, it is an abundant source of proteins and carbohydrates, and its exploitation allows to avoid the disposal of a high pollutant biomass.

Whey accounts for about 85–95% of the milk volume and retains 55% of milk nutrients, namely lactose (4.5–5% w/v), soluble proteins (0.6–0.8% w/v), lipids (0.4–0.5%w/v) and mineral salts (8–10% of dried extract)[46]. On the other hand, it represents an important environmental problem just because of its high organic matter content. The world whey production is over 160 million tons per year and its biochemical oxygen demand (BOD) is 30–50 g L⁻¹ and the chemical oxygen demand (COD) 60–80 g L⁻¹.

Moreover, as the utilization of whey protein as food ingredients increases, so does the volume of the primary by-product stream, that is lactose, whose demand is generally static. This prompts to find solutions to manage its surplus and to convert it into valuable products [47].

The reduction of disaccharides can take two main pathways that are the hydrogenation of one of the two saccharides into the corresponding reduced dimer on one hand, and the hydrogenation of the hydrolyzed monosaccharides on the other. In the case of lactose, the reduction can therefore lead to lactitol or to the mixture of sorbitol and galactitol, according to the scheme reported (Scheme 2).



Scheme 2 – Reduction of lactose

The reduction to lactitol, that is the reduced disaccharide, has been extensively studied over the last years due to its importance in the development of sugar-free, reduced calorie and low glycemic index products [48]. Nickel and Ruthenium based catalysts play a major role in this transformation [49] [50], with main improvements focused on increasing stability and activity. Nanocatalysts based on ruthenium-containing nanoparticles (NPs) formed in the pores of hypercrosslinked polystyrene (HPS) modified with amino groups have been proposed for example for the reduction to lactitol with excellent conversion and selectivity [51]. Ru–Ni bimetallic nanohybrids catalyst were found to exhibit a remarkably high selectivity if compared to monometallic Ru/TiO₂ one.

On the contrary the one-pot hydrolysis and reduction into the mixture of galactitol and sorbitol has been scarcely studied. In this case the use of heterogeneous copper catalysts in aqueous phase allows one to obtain in one-pot the mixture of the two reduced sugars with high conversion and selectivity [36]. The use of Cu/SiO₂ for this application put in light the difference obtained just by changing the solvent from MeOH to water. As shown in Table 2 the use of water allows to address the reaction towards the one-pot hydrolysis and reduction process, thus allowing to obtain a mixture of galactitol and sorbitol, differently to what observed with Ru and Ni catalysts.

It is interesting to note that even when operating at lower temperatures (150-160°C), therefore less favorable for the hydrolysis step, with Cu/SiO₂ the reduced monosaccharides mixture represents the main product.

Table 2 – Hydrogenation of disaccharides over different solid systems compared to copper catalysts.

Disaccharide	Catalyst	Solvent	T	P	Conv%	Yield %	Yield %	Ref
Lactose						<i>Lactitol</i>	<i>Sorbitol + Glucose</i>	
	Cu/SiO ₂	Water	180	30	>99		86	[36]
	Cu/SiO ₂	EtOH	180	30	>99	68		[36]
	Ru/HPS	Water	120	49	99.1	97.0		[51]
	Ru-NiO/TiO ₂	Water	120	55	97.0	99.4		[52]
Maltose						<i>Maltitol</i>	<i>Sorbitol</i>	
	Cu/SiO ₂	Water	180	30	98.0		86.3	[53]
	Ru/HPS	Water	140	40	>99	95		[54]
	Ni/Cu/Al/Fe + H ₃ PO ₄	Water	185	30			93.1	[55]

Very similar consideration can be done referring to the one-pot hydrolysis and hydrogenation of maltose. Maltose is a disaccharide of two glucose units linked with a α -(1→4) bond that can be derived from food wastes and agro-industrial residues thanks to the even more mature fermentation

processes designed to valorize starch [56][57]. The possibility to upcycle and exploit the great potential availability of maltose into reduced sugars is therefore an interesting aspect to consider. As already observed in the case of lactose the literature mainly reports on the hydrogenation of maltose into maltitol, the corresponding reduced disaccharide, widely used as sweetener in the food industry [58]. Very few studies are conversely devoted to the one-pot hydrolysis- hydrogenation of maltose into sorbitol.

A Ni/Cu/Al/Fe hydrotalcite precursor synthesized by a co-precipitation method leads to 93% yield in the one-pot transformation of maltose into sorbitol in the presence of diluted H_3PO_4 [55]. The catalyst was proved to be stable and recyclable.

Some of us reported on the use of a silica supported copper catalyst for maltose into sorbitol transformation obtaining 86% yield without any additive or co-catalyst [53].

An important role of the support can be highlighted from both the hydrogenation of maltose and lactose with this class of copper materials. Besides the detrimental effect on selectivity obtained with supports other than silica, such as alumina or acidic mixed oxides already observed with monosaccharides, the proper choice of silica deserves some considerations.

The comparison between two silica materials highlights the importance of the textural properties of the support, with better results obtained with a high SSA/PV ratio, that means a high surface area and a small pore volume.

Again, the very high dispersion of the metallic phase and also the possibility to exploit a moderate acidity imparted just by the copper phase highly dispersed allows to have in hand a very efficient and simple catalyst for these applications.

Conclusions

- The use of copper catalyst still overlooked, deserving more studies and application as alternative to noble metals.

Main points influencing activity and selectivity:

- High dispersion of metallic phase
- Acidity for activation and for isomerisation

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PNRR

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