



The peculiar role of copper in the saccharides hydrogenation in aqueous phase

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ABSTRACT

The paper reports on the use of heterogeneous supported Cu catalysts in the aqueous phase reduction of mono and disaccharides to reduced sugars. The huge availability of the starting materials present also in many side streams of the agri-food industry and the growing interest in polyols not only in the food and pharma sectors but also in the polymer one make this reaction a relevant one in the current scenario. Although less active than Ru and Ni based ones, low loaded Cu catalysts show very interesting performance. Conversions up to 100 % can be reached in the hydrogenation of galactose at 160 °C and 40 bar of H₂. Moreover, they allow to directly obtain reduced sugars in the hydrogenation of disaccharides through a one pot bifunctional hydrolysis-hydrogenation process. The high dispersion of the Cu metallic phase and the presence of weak acidic sites on the catalyst surface can give account of the observed activity and selectivity.

1. 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] (Fig. 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.

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 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] (Fig. 2).

A particular case is represented by sorbitol, one of the most 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 isosorbide, its bicyclic ether. Isosorbide 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 polymethylmethacrylate (PMMA) and poly(bisphenol-A) carbonate, and in

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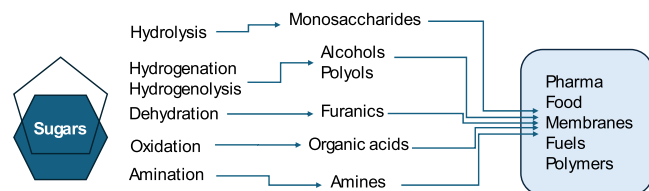


Fig. 1. From carbohydrates to chemicals.

the preparation 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] (Fig. 3).

However, most of sorbitol is produced through hydrogenation of corn starch-based glucose thus competing in some way with the food supply chain, therefore, to find more sustainable raw materials is crucial. Side streams 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 catalyst for sugar alcohols manufacturing method [9] but although convenient from the economic point of view, it is quite easily poisoned and deactivated [10].

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 [12].

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 associated with the use of metal-based systems in aqueous environment related to sintering, oxidation, leaching and nanoparticles collapse problems. [13] Moreover the poor hydrothermal stability of many oxides commonly used as supports in solid catalysis cannot be an afterthought aspect in designing efficient systems. [14] This is the case of Al_2O_3 or ZrO_2 that can undergo phase changes and in consequence significant loss in surface area [15, 16], as well as the occurrence of ordered structure collapse observed with mesoporous materials such as SBA-15 [17].

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

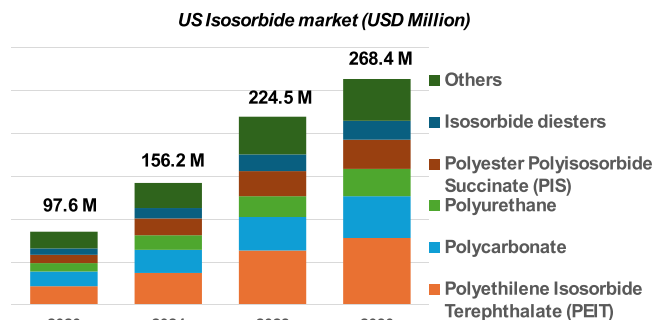


Fig. 3. US market for isosorbide-based materials (adapted from www.grandviewresearch.com).

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.

It is just in this respect that Ruthenium catalysts reveal outstanding performances due to their superior activity in the aqueous-phase hydrogenation of carbonyl compounds. Besides the several advantages related with the use of aqueous conditions, the promotional role of water in accelerating the reaction steps has been highlighted in the hydrogenation of diverse oxygenated substrates and in particular in levulinic-derived ones. [18] The beneficial effect of water was proved to be ascribable to its participation as a reactant after a dissociation process occurring during the hydrogenation of levulinic acid (LA) into γ -valerolactone (GVL). Experiments carried out under D_2O actually showed the incorporation of D atoms in GVL derived from LA hydrogenation. [19] The hypothesis of this dissociation phenomenon occurring during the hydrogenation of carbonyl compounds with Ru catalysts in water was already pointed out in a previous review [20] and is strongly corroborated by theoretical studies relying on the stability of half-dissociated monolayer of water on Ru(0001) increasing the surface concentration in H atoms [21]. On the other hand, the interaction via hydrogen bonds between the $\text{C}=\text{O}$ group adsorbed on the metal surface and adjacent water molecules could contribute to the lowering of energy barriers, thus explaining the highly superior activity of Ru catalysts with respect to less oxophilic metals.

Several aspects have been envisaged to design efficient noble metal based systems and in particular ruthenium ones. Among these, 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

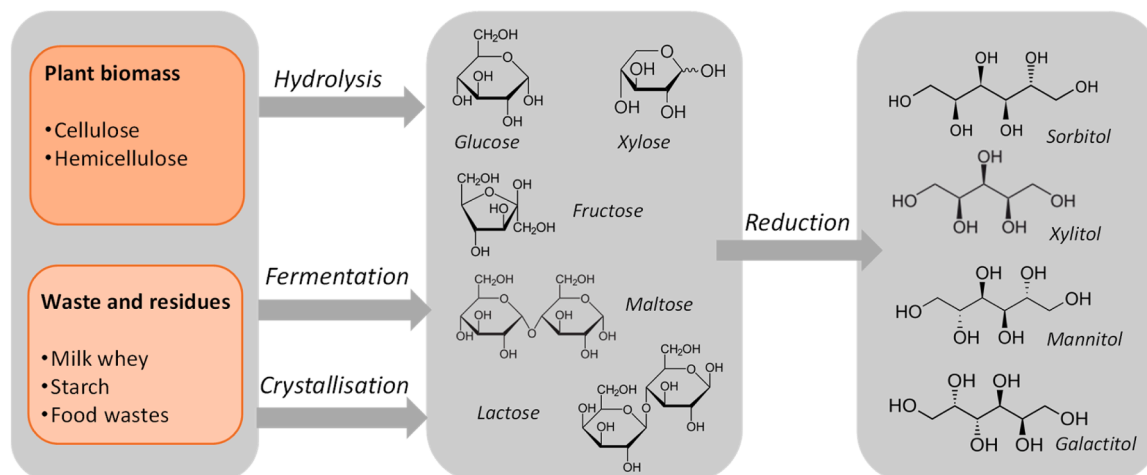


Fig. 2. Main streams from biomass to sugar alcohols.

nanoparticles ranging from 2 to 4 nm. [22] The very high performances in terms of activity and stability were also obtained with a commercial Ru/Al₂O₃ mainly ascribed to the particle sizes of Ru around 2 nm and to the control of secondary reactions [23]. 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 [24]. This preparation technique generates a multimodal size distribution of the metal nanoparticles, stabilized by the interaction with both the support and the reaction environment.

In some cases, *the combination of noble metals* with Ni allows to design a trade-off system able to face with both economic and efficiency needs [25,26]. The activity of Ru catalyst on a NiO modified TiO₂ has been proposed in the liquid phase catalytic hydrogenation of xylose to xylitol [27].

The direct transformation of lignocellulosic biomass into sugar alcohols has been also reported. [28,29] For example, it has been reported that xylitol can be produced directly by an hydrogenation of a hydrolysate obtained from sugarcane bagasse residues [23]. In another work, polyols production was used as a mean to purify sugar streams after biomass hydrolysis [30].

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 [31]. Mainly Cu/SiO₂ and Cu/Al₂O₃ have been explored in the hydrogenation of aliphatic and aromatic ketones under mild conditions [32–34], 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 [35,36].

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 groups as reduction target. Cu/MgO has been proposed for the hydrogenation of furfural [37], Cu/SiO₂ for γ -butyrolactone [38] and γ -valerolactone [39].

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. Some main factors influencing the catalytic activity and deserving to be more deeply studied will be highlighted and compared with the much more studied Ru and Ni systems

2. Reduction of monosaccharides

2.1. Glucose reduction

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

Sorbitol is listed by the US National Renewable Laboratory (NREL) among the top value-added chemicals from biomass [40].

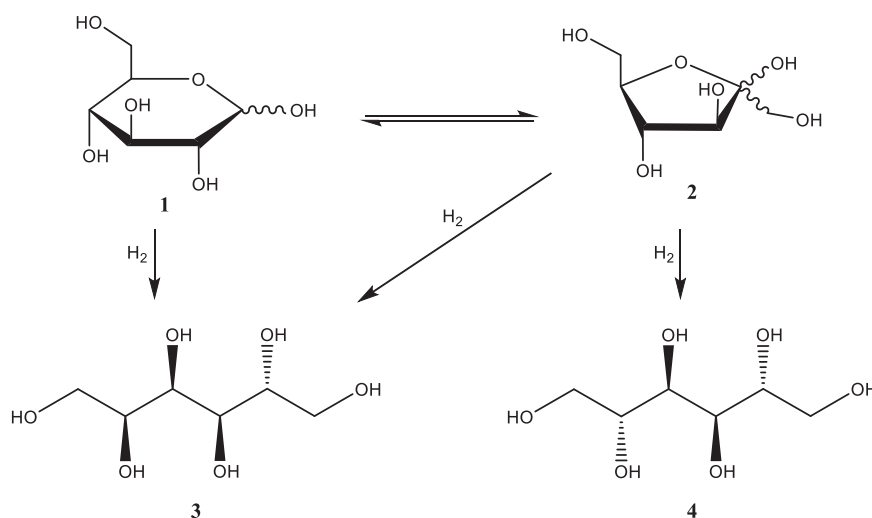
Glucose hydrogenation into sorbitol is mainly performed with noble metal-based catalysts, namely Pt and Ru [11]. It is worth underlining that even when using noble metals this kind of reductions need harsh conditions in terms of temperature and specially of hydrogen pressure, usually ranging from 15 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, although also in this respect technological aspects can have dramatic effect on the overall economics of these processes [41]

The great part of the studies on monosaccharides hydrogenation with non-noble metals relies on Nickel catalysts [42], that offer economic advantages and high activity, but suffer from poor stability and easy poisoning [43]. These issues have important effects on the overall process and on the quality of the final products [44] and prompted to find solutions in designing the catalysts by using promoters or supports able to enhance the stability of the active metal. The addition of Mo and Cr/Fe has been proposed to increase the surface area of RANEY® Ni [45] obtaining a synergistic effect with the promoters, a higher adsorption capacity and the possibility to tune the chemical structure and the electron distribution of the active sites. The effect of the support has been also explored by using SiO₂ [46] or carbon [46]. Also unsupported Ni/NiO systems have been reported to be highly active and advantageous due to their magnetical separation from the products [47].

On the other hand, among non-noble based opportunities, the activity of copper as both active reductive metal and/or as co-catalyst is known although much 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 [48] elucidating some important aspects related with the coordination of the substrates on the catalyst surface, as also underlined in latest works [49].

The strong *effect of the support* when using copper catalyst and in particular the outstanding effect obtained with silica, has been also recently highlighted in a comparative study of glucose hydrogenation



Scheme 1. – The hydrogenation products from glucose and fructose.

with Cu and Ni by using SiO₂ or Al₂O₃ [50]. 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, 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 [51]. 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 not only influences the Cu properties, but also affects 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.

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 [52]. 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*.

The effect of acid-base properties emerges as an important factor also in noble-metal based systems supported on activated carbon. A comparison between two series of Pt and Ru catalysts studied in the hydrogenation/hydrogenolysis of D-glucose, shows the effect of acidity on selectivity induced by the electronic properties of some Ru samples [53]. Nonetheless, the positive effect of a mild Lewis acidity given by the support in the activation of the substrates is reported in the use of Ru supported on phosphate zirconia and zirconia-alumina [54].

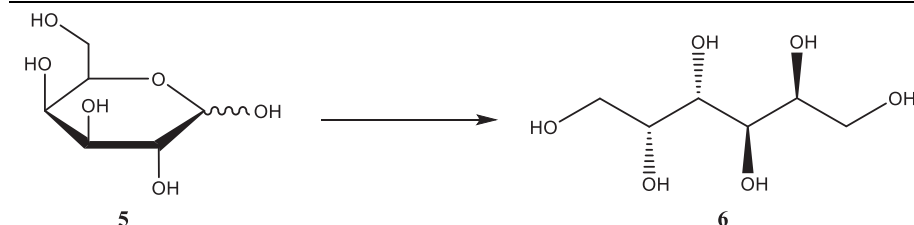
Some of us also reported on the use of Cu/SiO₂ prepared with a chemisorption-hydrolysis technique in the hydrogenation of glucose obtaining 90 % conversion and 82 % selectivity in sorbitol [55].

2.2. Galactose reduction

Very high activity and selectivity were 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 wt% of ZrO₂,

Table 1

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



Entry	Catalyst	T (°C)	P (atm)	Conv %	Yield %	Sel %
1	Cu/SiO ₂ ^a	180	30	98	62	63
2	Cu/Al ₂ O ₃ ^a	180	30	99	22	22
3	Cu/SiO ₂ -ZrO ₂ ^a	180	30	97	10	10
5	Cu/SiO ₂ ^a	160	40	100	69	69
6	Cu/SiO ₂ ^b	160	30	95	62	65
7	Cu/SiO ₂ ^b	160	40	100	76	76
8	Cu/SiO ₂ ^b	160	50	100	76	76

^a 8 % Cu loading catalyst

^b 16 % Cu loading catalyst

clearly shows 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).

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 (Fig. 4). A yield of 80 % can be reached for a starting concentration of 50 mg/mL.

It is worth underlining that the hydrogenation of galactose is not widely reported, with main examples relying once again on the use of Ru [56–58]. In the case of Ru/C the size of metal clusters is considered one of the main factors affecting the catalytic activity [59]. As far as non-noble metals are concerned the use of bimetallic nickel-iron based nanoparticles [60] and of nickel/nickel oxide hetero-structural catalyst [61] has been proposed.

2.3. Xylose reduction

The very great influence of the support used and the potentialities of copper catalysts as interesting substitutes to noble metal-based systems have been also investigated in the reduction of xylose 7, that is the main component of xylan derived from hemicellulose. By virtue of this it is

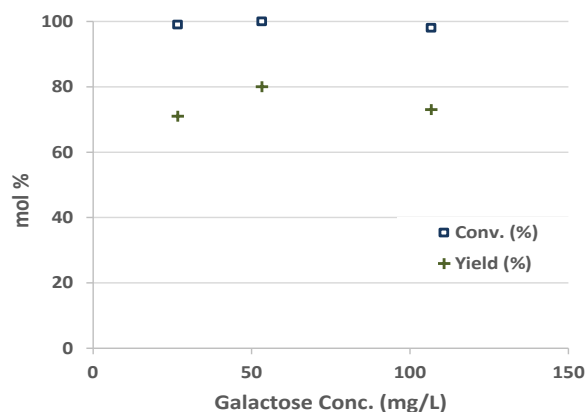


Fig. 4. Effect of galactose concentration on conversion and yield.

considered a key platform to produce furfural, furan dicarboxylic acid (FDCA), glycols and xylitol **8** [62,63]. 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 [64]. Main studies rely on the use of ruthenium solid catalysts for the transformation of xylose into xylitol [65].

Some new results obtained with Cu/SiO₂ in the hydrogenation of xylose revealed the formation of xylitol with excellent selectivity into xylitol (Fig. 5), at 120°C and 40 atm.

The comparison with Cu/ZrO₂-SiO₂ (SiO₂ = 3.5 wt%) and Cu/TiO₂ clearly shows the outstanding effect in terms of selectivity obtained by using silica as the support. By-products corresponding to lyxose and xylulose, derived from isomerization processes are formed (Scheme 2) 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 favour the isomerisation processes. 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 (Fig. 6).

On the other hand, furfural was continuously produced during reaction with a final 13 % yield, conversely to its absence when working with the corresponding copper catalyst.

Silica was found to be a good choice also for Ni-based catalysts in xylose hydrogenation. A silica supported nickel system derived from nickel phyllosilicate was found to be highly efficient giving higher xylose conversion if compared to the corresponding nickel oxide derived one prepared by impregnation and to the commercial Raney Ni just due to the high dispersion. Moreover, the strong interaction between nickel species and silica support, due to the unique property of phyllosilicate precursor imparts very high stability [66]. The strong effect of the support on activity is put in evidence even in the studies relying on Ruthenium systems. Activity and selectivity of Ru/TiO₂ dramatically depends on the titania phase [65], titania anatase supported system being much less selective due to the formation of multiple by-products on the support catalytic sites, including several pentoses isomers of xylose. Ruthenium supported aluminosilicate mesoporous materials also revealed best selectivity with respect to Ru/C [67].

2.4. Fructose reduction

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 makes 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 [48]. A CuO-ZnO catalyst containing 61 % of CuO and 39 % of ZnO gave 60–68 % selectivity in mannitol [68]. 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 [69]. The catalyst is recyclable, and the authors underline the importance of the complete reduction of Cu²⁺ to Cu⁰.

This aspect represents an important distinction between copper catalysts and ruthenium-based ones. In glucose hydrogenation the use of a series of Ru systems prepared over activated carbon shows that the coexistence of metallic nanoparticles with amorphous Ru(O)₂⁺ species on the support promotes the molecular H₂ adsorption on Ru(0) on one hand and the H atoms spilling over to amorphous species on the other, thus leading to high activity in glucose hydrogenation, although to variable selectivity [53]. Moreover, Ruthenium valence regulation has been exploited on multiwalled carbon nanotubes (Ru/MWCNTs) catalysts for the selective sugar hydrogenation with high selectivity and yield [57]. The simultaneous presence of Ru⁰ and Ru³⁺ sites on the surface respectively activates hydrogen and coordinates the C=O group of the sugar aldehyde.

On the other hand the importance of Ru reducibility in Ru-SiO₂ has been invoked as an important feature for activity and stability [24].

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 [70]. 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 depresses 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 comparison with a silica supported Cu catalyst prepared with an Incipient Wetness technique characterised by larger and less dispersed metal particles shows an initial product formation rate one order of magnitude lower, thus also confirming the importance of the metallic phase dispersion in turn determined by the preparation method. In particular the material prepared by precipitation-deposition method showed Cu metal particle size estimated to be around 3.3 nm vs the 32 nm estimated for the catalyst prepared by the Incipient Wetness method, resulting in a fructose conversion of 98 % vs 37 %. [70] The relationship between catalytic activity in hydrogenation and copper dispersion derived from the preparation method moreover finds clear evidence in other applications. In the 1,3-COD reduction over Cu/TiO₂ for example, the turnover frequency increased by two order of magnitude when the Cu specific surface area increased from 11 m²/g_{Cu} for the sample prepared by IW to 64 m²/g_{Cu} of a system prepared with an

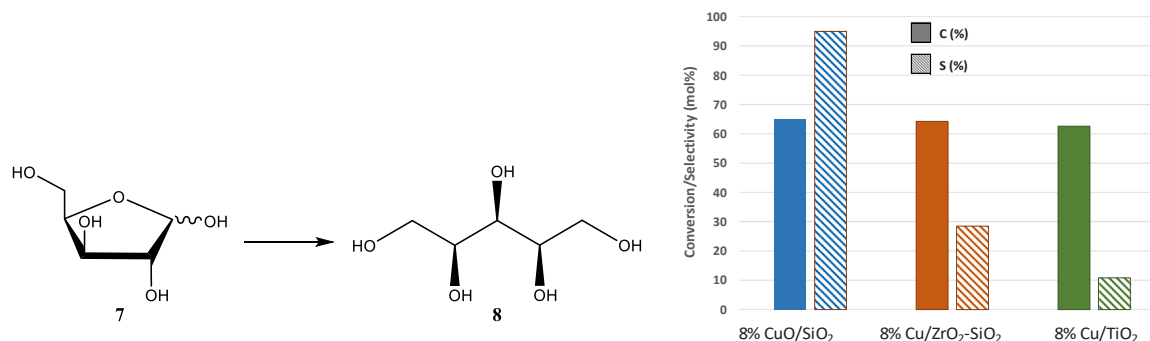
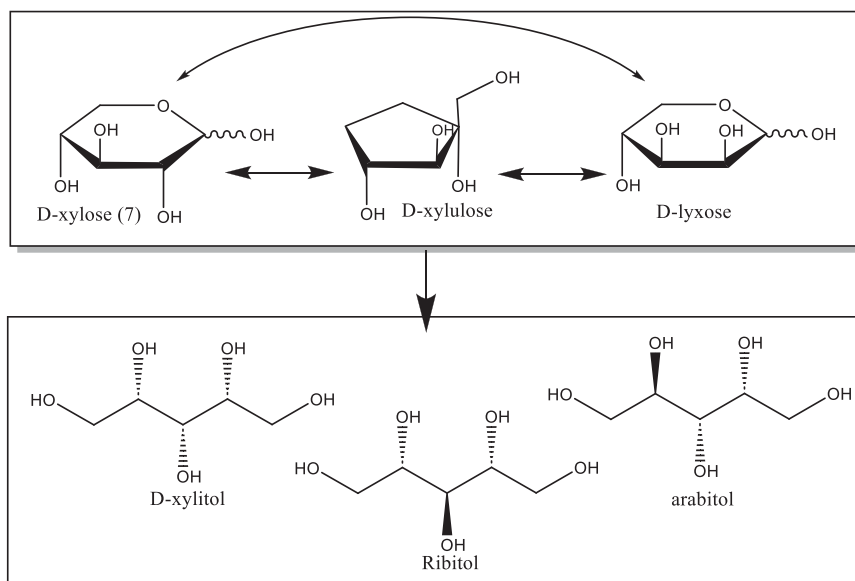
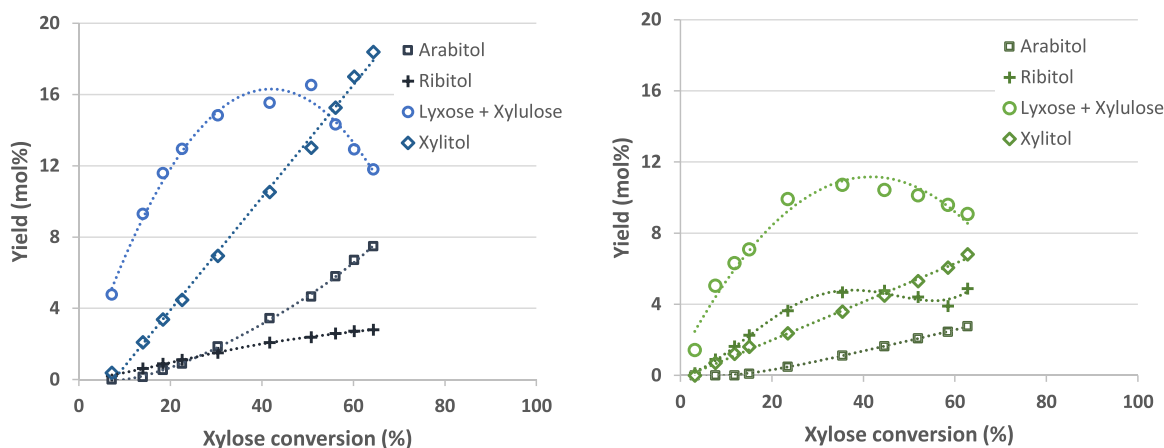


Fig. 5. Hydrogenation of xylose with three heterogeneous catalysts (120°C, 40 bar H₂).



Scheme 2. Hydrogenation of xylose.

Fig. 6. By-products yield during xylose hydrogenation over Cu/ZrO₂-SiO₂ (left) and Cu/TiO₂ (right) (120°C, 40 bar).

electrostatic interaction technique.[71]

The group of Marchi also reported an improvement in activity by using a bi-metallic CuNi/SiO₂ system prepared with the same technique [72]. 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 monometallic 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 derived Cu-Ni-Al catalyst used as hydrogen transfer system [73]. 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-butanediol as hydrogen donor is reported, obtaining yields in the corresponding reduced sugars ranging from 60 % (mannitol and xylitol), to 61 % (sorbitol) and 66 % arabitinol. The use of 1,4-butanediol as hydrogen source has the advantage of giving 2 moles of H₂ while forming γ -valerolactone as the by-product.

The examples selected and reported allow to note down some main points concerning the development of copper catalysts. The *dispersion* of the metallic phase seems to be the most critical aspect to be considered to obtain good activity that in the case of copper must be mainly ascribed to the hydrogenative capacity of the metallic phase. The plus given by the water dissociation phenomenon is a pure peculiarity of Ruthenium catalysts. Complete reduction of the copper phase is moreover related to its dispersion and it is an important parameter. The effect of the *support* is therefore definitely critical to determine high dispersion but is also intervenes in acid/base properties that need to be properly tuned to facilitate the activation of the carbonyl group of the substrate on one hand, and to limit isomerization, dehydration and cleavage side reactions on the other. In this respect silica appears to be the elective support for copper catalysts so far. Moreover the possible role of copper as cocatalyst or promoter is an important field of study.

3. Reduction of disaccharides

Among disaccharides, **lactose** deserves attention as it is a main constituent of milk whey. It is worth noting that the use of milk whey as starting material entails a double advantage. In fact, first it is an abundant source of proteins and carbohydrates, and second 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) [74]. 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 [75].

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 (**pathway 1**), and the hydrogenation of the hydrolyzed monosaccharides on the other (**pathway 2**). 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 3**).

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 [76]. Nickel and Ruthenium based catalysts play a major role in this transformation [77] [78], 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 [79]. 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 [55]. The use of Cu/SiO₂ for this application puts in light the difference obtained just by changing the solvent from EtOH to water. As shown in **Table 3** the use of water allows one 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.

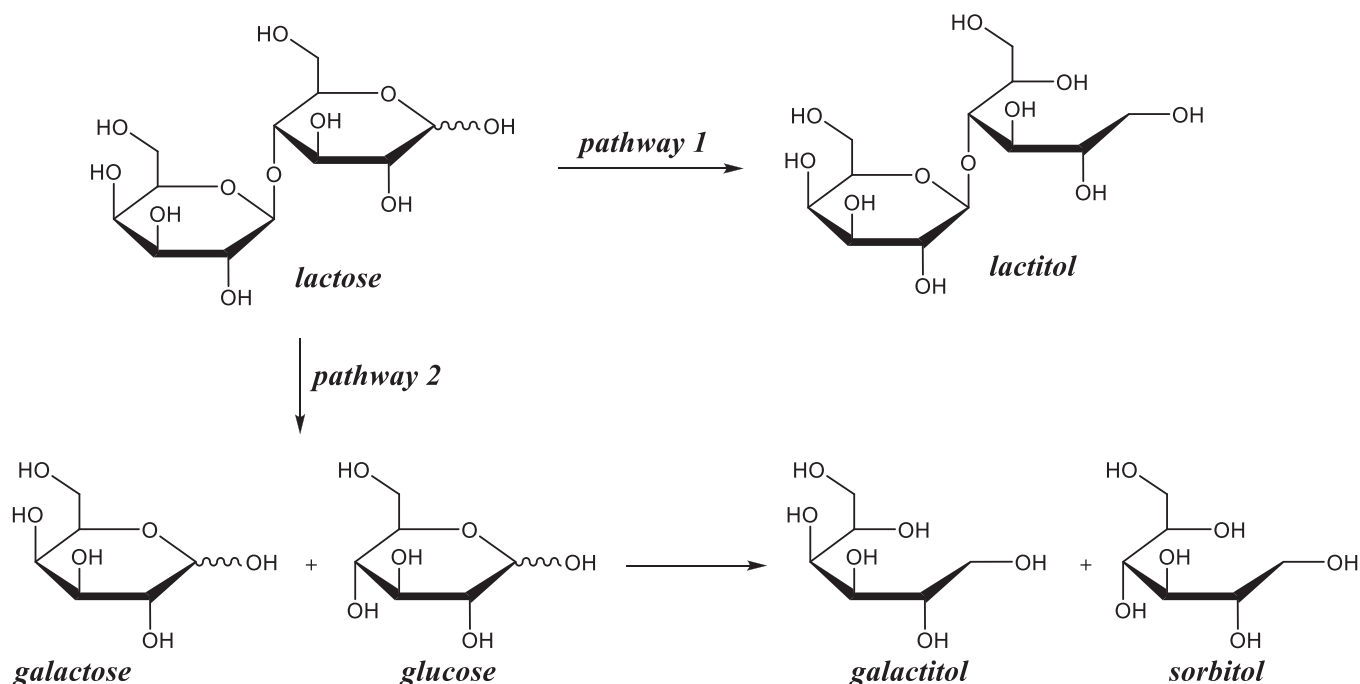
It is interesting to note that using Cu/SiO₂, even when operating at lower temperatures (150–160°C), therefore less favorable for the hydrolysis step, the reduced monosaccharides mixture represents the main product.

Very similar considerations 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 [84,85]. 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 [86]. 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 coprecipitation method leads to 93 % yield in the one-pot transformation of maltose into sorbitol in the presence of diluted H₃PO₄ [83]. 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 [81].

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.



Scheme 3. – Reduction of lactose.

Table 2
Comparison of selected examples of catalytic systems reported for the hydrogenation of monosaccharides.

Substrate	Catalyst	T (°C)	P (atm)	time (min)	Conv (%)	Yield (%)	ref
Glucose	Cu/SiO ₂	130	30	240	50	40	[50]
	Cu/SiO ₂	180	30	360	90	74	[55]
	Ru/Al ₂ O ₃	100	30	150	100	97	[23]
	Ru/C	120	20	120	100	96	[22]
	Ru/C	120	20	300	100	>98	[49]
	(RuO ₂) _{0.04} (SiO ₂) _{0.96}	120	20	300	100	94	[24]
	Ru/ZP-A	90	12	420	99	97	[54]
	RaneyNi-Cr/Fe	120	40		100	>98	[45]
	Ni/NiO	130	50		95	84	[47]
Pt/AC	180	16	60–180	97–100	90–95	[53]	
Galactose	Cu/SiO ₂	160	40	360	100	76	This work
	Ru/C	120	20	360	100	>98	[56]
	Ru/MWCNTs	110	30	120	99	98	[57]
	Ni ₃ Fe ₁ BMNPs	100	20	180	100	99	[59]
	SiO ₂ @Ni/NiO	120	hydrogen transfer	180	99	82	[61]
Xylose	Cu/SiO ₂	120	40	360	65	62	This work
	Ru/TiO ₂	120	40	120	100	99	[65]
	Ni ₃ Fe ₁ BMNPs	100	20	180	99	98	[60]
	Ni/SiO ₂	100	40	120	96	95	[66]
	Ru/Al-MCM-41	90	40	240	>99	99	[67]
Fructose	CuO/ZnO	130	50		>99	67	[68]
	Cu/SiO ₂	100	40	360	98	76	[70]
	Ni/Cu/Al/Fe	110	30	120	100	57	[69]
	CuNi/SiO ₂	100	40	60	90	73	[72]
	Cu-Ni-Al	150	hydrogen transfer	11	85	60	[73]

Table 3
Hydrogenation of disaccharides over different solid systems compared to copper catalysts.

Disaccharide	Catalyst	Solvent	T (°C)	P (atm)	Conv (%)	Yield (%)	Yield (%)	Ref
Lactose	Cu/SiO ₂	Water	180	30	>99	<i>Lactitol</i>	<i>Sorbitol + Glucose</i>	[55]
	Cu/SiO ₂	EtOH	180	30	>99	68	86	[55]
	Ru/HPS	Water	120	49	99	97		[79]
	Ru-NiO/TiO ₂	Water	120	55	97	96		[80]
Maltose	Cu/SiO ₂	Water	180	30	98	<i>Maltitol</i>	<i>Sorbitol</i>	[81]
	Ru/HPS	Water	140	40	>99	95	86	[82]
	Ni/Cu/Al/Fe + H ₃ PO ₄	Water	185	30			93	[83]

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 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. Cu/SiO₂ used in that application analysed by HR-TEM actually showed particles with a mean diameter lower than 3 nm. This resulted in a markedly higher dispersion with respect to the Cu/SiO₂-Al₂O₃ system, showing an inhomogeneous particle size dimension ranging from 3.2 to 13 nm of mean diameter and in a overwhelming higher catalytic performance. [81]

4. Conclusions

Copper has been always playing the poor relative among the hydrogenation active metals due to its much lower activity with respect to Ni and noble metals. For this reason, only very high loading Cu catalysts such as Cu/ZnO/Al₂O₃ and Cu/Cr₂O₃ are used at industrial level. However, the use of Ni and noble metals catalysts in food, agrochemicals, pharmaceutical and cosmetic applications is strictly regulated due

to their toxicity and suspected carcinogenicity.

On the other hand, low loading supported Cu catalysts can give excellent results in hydrogenation of a variety of unsaturated compounds under mild experimental conditions[87]. From data reported in this review it is apparent that Cu catalysts have been undeservedly neglected with respect to noble metals, particularly Ru, also in carbohydrate reduction in the aqueous phase.

The activity and selectivity observed can be ascribed to several factors. The preparation method allows to obtain a high dispersion of the metallic phase, in turn leading to very small and active Cu particles. The mild acidity present on the catalyst surface has also a pivotal role particularly in the hydrogenolysis/hydrogenation reaction of disaccharides. Finally the textural features of the support in particular its surface area and hydrophobic/hydrophilic nature can actively influence the reaction pathway. A fine tuning and balance of these three factors are the key to obtain high performant catalysts for the reduction of saccharides in the aqueous phase, a more and more relevant transformation in the circular economy scenario.

CRediT authorship contribution statement

Valeria Pappalardo: Writing – review & editing, Data curation.

Nicoletta Ravasio: Writing – review & editing, Funding acquisition, Conceptualization. **Federica Zaccheria:** Writing – original draft, Investigation, Conceptualization. **Léa Vilcoq:** Writing – review & editing, Investigation, Conceptualization. **Nicola Scotti:** Writing – review & editing, Data curation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

References

- [1] K.S. Arias, A. Vely, M.J. Climent, S. Iborra, Valorization of biomass platform molecules through one-pot cascade processes using heterogeneous catalysts, *Tetrahedron Green Chem.* 3 (2024) 100037, <https://doi.org/10.1016/j.tgchem.2024.100037>.
- [2] R.R. De Souza, R. Bergamasco, S.C. da Costa, X. Feng, S.H.B. Faria, M.L. Gimenes, Recovery and purification of lactose from whey, *Chem. Eng. Process.: Process. Intensif.* 49 (2010) 1137–1143, <https://doi.org/10.1016/j.cep.2010.08.015>.
- [3] C.S.K. Lin, L.A. Pfaltzgraff, L. Herrero-Davila, E.B. Mubof, S. Abderrahim, J. H. Clark, A.A. Koutinas, N. Kopsahelis, K. Stamatelatou, F. Dickson, S. Thankappan, Z. Mohamed, R. Brocklesby, R. Luque, Food waste as a valuable resource for the production of chemicals, materials and fuels. Current situation and global perspective, *Energy Environ. Sci.* 6 (2013) 426–464, <https://doi.org/10.1039/c2ee23440h>.
- [4] A.M. Ruppert, K. Weinberg, R. Palkovits, Hydrogenolysis goes bio: From carbohydrates and sugar alcohols to platform chemicals, *Angew. Chem. - Int. Ed.* 51 (2012) 2564–2601, <https://doi.org/10.1002/anie.201105125>.
- [5] X. Zhang, K. Wilson, A.F. Lee, Heterogeneously catalyzed hydrothermal processing of C5–C6 Sugars, *Chem. Rev.* 116 (2016) 12328–12368, <https://doi.org/10.1021/acs.chemrev.6b00311>.
- [6] C. Marques, R. Tarek, M. Sara, S.K. Brar, Sorbitol production from biomass and its global market, Elsevier Inc, 2016, <https://doi.org/10.1016/B978-0-12-802980-0.00012-2>.
- [7] F. Delbecq, M.R. Khodadadi, D. Rodriguez Padron, R. Varma, C. Len, Isosorbide: recent advances in catalytic production, *Mol. Catal.* 482 (2020), <https://doi.org/10.1016/j.mcat.2019.110648>.
- [8] Y. Zhou, R.L. Smith, X. Qi, Chemocatalytic production of sorbitol from cellulose via sustainable chemistry - a tutorial review, *Green Chem.* 26 (2023) 202–243, <https://doi.org/10.1039/d3gc04082h>.
- [9] K. Van Gorp, E. Boerman, C.V. Cavenaghi, P.H. Berben, Catalytic hydrogenation of ne chemicals: sorbitol production, 52 (1999) 0–12..
- [10] J.P. Mikkola, R. Sjöholm, T. Salmi, P. Mäki-Arvela, Xylose hydrogenation: kinetic and NMR studies of the reaction mechanisms, *Catal. Today* 48 (1999) 73–81, [https://doi.org/10.1016/S0920-5861\(98\)00360-5](https://doi.org/10.1016/S0920-5861(98)00360-5).
- [11] M.J. Ahmed, B.H. Hameed, Hydrogenation of glucose and fructose into hexitols over heterogeneous catalysts: A review, *J. Taiwan Inst. Chem. Eng.* 96 (2019) 341–352, <https://doi.org/10.1016/j.jtice.2018.11.028>.
- [12] J. Lee, Y. Xu, G.W. Huber, High-throughput screening of monometallic catalysts for aqueous-phase hydrogenation of biomass-derived oxygenates, *Appl. Catal. B: Environ.* 140–141 (2013) 98–107, <https://doi.org/10.1016/j.apcatb.2013.03.031>.
- [13] X. Liu, G. Lan, Z. Li, L. Qian, J. Liu, Y. Li, Stabilization of heterogeneous hydrogenation catalysts for the aqueous-phase reactions of renewable feedstocks, *Chin. J. Catal.* 42 (2021) 694–709, [https://doi.org/10.1016/S1872-2067\(20\)63699-3](https://doi.org/10.1016/S1872-2067(20)63699-3).
- [14] H.N. Pham, A.E. Anderson, R.L. Johnson, K. Schmidt-Rohr, A.K. Datye, Improved hydrothermal stability of mesoporous oxides for reactions in the aqueous phase, *Angew. Chem. - Int. Ed.* 51 (2012) 13163–13167, <https://doi.org/10.1002/anie.201206675>.
- [15] R.M. Ravenelle, J.R. Copeland, W.G. Kim, J.C. Crittenden, C. Sievers, Structural changes of γ -Al₂O₃-supported catalysts in hot liquid water, *ACS Catal.* 1 (2011) 552–561, <https://doi.org/10.1021/cs1001515>.
- [16] D.D. Nematov, A.S. Burhonzoda, K.T. Kholmurodov, A.I. Lyubchik, S.I. Lyubchik, A detailed comparative analysis of the structural stability and electron-phonon properties of ZrO₂: mechanisms of water adsorption on t-ZrO₂ (101) and t-YSZ (101) surfaces, *Nanomaterials* 13 (2023), <https://doi.org/10.3390/nano13192657>.
- [17] A. Galarneau, M. Nader, F. Guenneau, F. Di Renzo, A. Gedeon, Understanding the stability in water of mesoporous SBA-15 and M CM-41, *J. Phys. Chem. C* 111 (2007) 8268–8277, <https://doi.org/10.1021/jp068526e>.
- [18] A. Seretis, P. Diamantopoulou, I. Thanou, P. Tzevelekidis, C. Fakas, P. Lilas, G. Papadogiannakis, Recent advances in ruthenium-catalyzed hydrogenation reactions of renewable biomass-derived levulinic acid in aqueous media, *Front. Chem.* 8 (2020) 1–22, <https://doi.org/10.3389/fchem.2020.00221>.
- [19] J. Tan, J. Cui, T. Deng, X. Cui, G. Ding, Y. Zhu, Y. Li, Water-promoted hydrogenation of levulinic acid to γ -valerolactone on supported ruthenium catalyst, *ChemCatChem* 7 (2015) 508–512, <https://doi.org/10.1002/cctc.201402834>.
- [20] C. Michel, P. Gallezot, Why Is ruthenium an efficient catalyst for the aqueous-phase hydrogenation of biosourced carbonyl compounds? *ACS Catal.* 5 (2015) 4130–4132, <https://doi.org/10.1021/acscatal.5b00707>.
- [21] P.J. Feibelman, Partial dissociation of water on Ru(0001), *Science* 295 (2002) 99–102, <https://doi.org/10.1126/science.1065483>.
- [22] A. Aho, S. Roggan, O.A. Simakova, T. Salmi, D.Y. Murzin, Structure sensitivity in catalytic hydrogenation of glucose over ruthenium, *Catal. Today* 241 (2015) 195–199, <https://doi.org/10.1016/j.cattod.2013.12.031>.
- [23] I. Bonnin, R. Méreau, T. Tassaing, F. Jérôme, K. De Oliveira Vigier, Hydrogenation of sugars to sugar alcohols in the presence of a recyclable Ru/Al₂O₃ catalyst commercially available, *ACS Sustain. Chem. Eng.* 9 (2021) 9240–9247, <https://doi.org/10.1021/acssuschemeng.1c01422>.
- [24] S. Esposito, B. Silvestri, V. Russo, B. Bonelli, M. Manzoli, F.A. Deorsola, A. Vergara, A. Aronne, M. Di Serio, Self-activating catalyst for glucose hydrogenation in the aqueous phase under mild conditions, *ACS Catal.* 9 (2019) 3426–3436, <https://doi.org/10.1021/acscatal.8b04710>.
- [25] A. Romero, A. Nieto-Márquez, E. Alonso, Bimetallic Ru/Ni/MCM-48 catalysts for the effective hydrogenation of D-glucose into sorbitol, *Applied Catalysis A: General* 529 (2017) 49–59, <https://doi.org/10.1016/j.apcata.2016.10.018>.
- [26] D.K. Mishra, J.M. Lee, J.S. Chang, J.S. Hwang, Liquid phase hydrogenation of d-glucose to d-sorbitol over the catalyst (Ru/NiO-TiO₂) of ruthenium on a NiO-modified TiO₂ support, *Catal. Today* 185 (2012) 104–108, <https://doi.org/10.1016/j.cattod.2011.11.020>.
- [27] M. Yadav, D.K. Mishra, J.S. Hwang, Catalytic hydrogenation of xylose to xylitol using ruthenium catalyst on NiO modified TiO₂ support, *Appl. Catal. A: Gen.* 425–426 (2012) 110–116, <https://doi.org/10.1016/j.apcata.2012.03.007>.
- [28] A. Yamaguchi, O. Sato, N. Mimura, M. Shirai, Catalytic production of sugar alcohols from lignocellulosic biomass, *Catal. Today* 265 (2016) 199–202, <https://doi.org/10.1016/j.cattod.2015.08.026>.
- [29] Q. Liu, T. Zhang, Y. Liao, C. Cai, J. Tan, T. Wang, S. Qiu, M. He, L. Ma, Production of C5/C6 sugar alcohols by hydrolytic hydrogenation of raw lignocellulosic biomass over Zr based solid acids combined with Ru/C, *ACS Sustain. Chem. Eng.* 5 (2017) 5940–5950, <https://doi.org/10.1021/acssuschemeng.7b00702>.
- [30] J.M. Robinson, C. E. Burgess, M. A. Bently, C. D. Brasher, B. O. Horne, D. M. Lillard, J. M. Macias, H. D. Mandal, S. C. Mills, K.D. O'Hara, J. T. Pon, A. F. Raigoza, E. H. Sanchez, J. S. Villarreal, The use of catalytic hydrogenation to intercept clean carbohydrates in a dilute acid hydrolysis of biomass to effect a clean separation from lignin, *Biomass-- Bioenergy* 26 (2004) 473–483, <https://doi.org/10.1016/j.biombioe.2003.09.005>.
- [31] R. Watari, Y. Kayaki, Copper catalysts unleashing the potential for hydrogenation of carbon–oxygen bonds, *Asian J. Org. Chem.* 7 (2018) 2005–2014, <https://doi.org/10.1002/ajoc.201800436>.
- [32] N. Ravasio, F. Zaccheria, A. Fusi, R. Psaro, One pot selective hydrogenation and dynamic kinetic resolution over Cu / Al₂O₃: a way to (À)-menthol starting from low value mint oils 315 (2006) 114–119, <https://doi.org/10.1016/j.apcata.2006.09.010>.
- [33] N. Ravasio, R. Psaro, F. Zaccheria, Cu / SiO₂ catalyzed hydrogenation of cyclohexanones under very mild conditions, 2 (n.d.).
- [34] F. Zaccheria, N. Ravasio, R. Psaro, A. Fusi, Heterogeneous selective catalytic hydrogenation of aryl ketones to alcohols without additives, *Tetrahedron Lett.* 46 (2005) 3695–3697, <https://doi.org/10.1016/j.tetlet.2005.03.159>.
- [35] A.J. Marchi, D.A. Gordo, A.F. Trasarti, C.R. Apesteguía, Liquid phase hydrogenation of cinnamaldehyde on Cu-based catalysts, *Appl. Catal. A: Gen.* 249 (2003) 53–67, [https://doi.org/10.1016/S0926-860X\(03\)00199-6](https://doi.org/10.1016/S0926-860X(03)00199-6).
- [36] Y. Cao, B. Chen, J. Guerrero-Sánchez, I. Lee, X. Zhou, N. Takeuchi, F. Zaera, Controlling selectivity in unsaturated aldehyde hydrogenation using single-site alloy catalysts, *ACS Catal.* 9 (2019) 9150–9157, <https://doi.org/10.1021/acscatal.9b02547>.
- [37] B.M. Nagaraja, V. Siva Kumar, V. Shasikala, A.H. Padmasri, B. Sreedhar, B. David Raju, K.S. Rama Rao, A highly efficient Cu/MgO catalyst for vapour phase hydrogenation of furfural to furfuryl alcohol, *Catal. Commun.* 4 (2003) 287–293, [https://doi.org/10.1016/S1566-7367\(03\)00060-8](https://doi.org/10.1016/S1566-7367(03)00060-8).
- [38] P. Kasinathan, D.W. Hwang, U.H. Lee, Y.K. Hwang, J.S. Chang, Effect of Cu particle size on hydrogenation of dimethyl succinate over Cu-SiO₂ nanocomposite, *Catal. Commun.* 41 (2013) 17–20, <https://doi.org/10.1016/j.cattcom.2013.06.034>.

- [39] D. Cavuoto, N. Ravasio, N. Scotti, A. Gervasini, S. Campisi, M. Marelli, G. Cappelletti, F. Zaccheria, A green solvent diverts the hydrogenation of γ -valerolactone to 1, 4 - pentandiol over Cu / SiO₂, *Mol. Catal.* 516 (2021) 111936, <https://doi.org/10.1016/j.mcat.2021.111936>.
- [40] T. Werry, G. Petersen, Top value added chemicals from biomass volume I (pages), *Us Nrel* 76 (2004), <https://doi.org/10.2172/15008859>.
- [41] D. Gericke, D. Ott, V.G. Matveeva, E. Sulman, A. Aho, D.Y. Murzin, S. Roggan, L. Danilova, V. Hessel, P. Loeb, D. Kralisch, Green catalysis by nanoparticulate catalysts developed for flow processing? Case study of glucose hydrogenation, *RSC Adv.* 5 (2015) 15898–15908, <https://doi.org/10.1039/c4ra14559c>.
- [42] E. Redina, O. Tkachenko, T. Salmi, Recent advances in C5 and C6 sugar alcohol synthesis by hydrogenation of monosaccharides and cellulose hydrolytic hydrogenation over non-noble metal catalysts, *Molecules* 27 (2022), <https://doi.org/10.3390/molecules27041353>.
- [43] B. Kusserow, S. Schimpf, P. Claus, Hydrogenation of glucose to sorbitol over nickel and ruthenium catalysts, *Adv. Synth. Catal.* 345 (2003) 289–299, <https://doi.org/10.1002/adsc.200390024>.
- [44] B. García, A. Orozco-Saumell, M. López Granados, J. Moreno, J. Iglesias, Catalytic transfer hydrogenation of glucose to sorbitol with raney Ni catalysts using biomass-derived diols as hydrogen donors, *ACS Sustain. Chem. Eng.* 9 (2021) 14857–14867, <https://doi.org/10.1021/acsschemeng.1c04957>.
- [45] B.W. Hoffer, E. Crezee, F. Devred, P.R.M. Mooijman, W.G. Sloof, P.J. Kooyman, A. D. Van Langeveld, F. Kapteijn, J.A. Moulijn, The role of the active phase of Raney-type Ni catalysts in the selective hydrogenation of D-glucose to D-sorbitol, *Applied Catalysis A: General* 253 (2003) 437–452, [https://doi.org/10.1016/S0926-860X\(03\)00553-2](https://doi.org/10.1016/S0926-860X(03)00553-2).
- [46] S. Schimpf, C. Louis, P. Claus, Ni/SiO₂ catalysts prepared with ethylenediamine nickel precursors: influence of the pretreatment on the catalytic properties in glucose hydrogenation, *Appl. Catal. A: Gen.* 318 (2007) 45–53, <https://doi.org/10.1016/j.apcata.2006.10.034>.
- [47] H. Singh, A. Rai, R. Yadav, A.K. Sinha, Glucose hydrogenation to sorbitol over unsupported mesoporous Ni/NiO catalyst, *Mol. Catal.* 451 (2018) 186–191, <https://doi.org/10.1016/j.mcat.2018.01.010>.
- [48] M. Makkee, A.P.G. Kieboom, H. van Bekkum, Hydrogenation of d-fructose and d-fructose/d-glucose mixtures, *Carbohydr. Res.* 138 (1985) 225–236, [https://doi.org/10.1016/0008-6215\(85\)85106-5](https://doi.org/10.1016/0008-6215(85)85106-5).
- [49] E. Crezee, B.W. Hoffer, R.J. Berger, M. Makkee, F. Kapteijn, J.A. Moulijn, Three-phase hydrogenation of D-glucose over a carbon supported ruthenium catalyst - Mass transfer and kinetics, *Applied Catalysis A: General* 251 (2003) 1–17, [https://doi.org/10.1016/S0926-860X\(03\)00587-8](https://doi.org/10.1016/S0926-860X(03)00587-8).
- [50] L. Silvester, F. Ramos, J. Thuriot-Roukos, S. Heyte, M. Araque, S. Paul, R. Wojcieszak, Fully integrated high-throughput methodology for the study of Ni- and Cu-supported catalysts for glucose hydrogenation, *Catal. Today* 338 (2019) 72–80, <https://doi.org/10.1016/j.cattod.2019.05.041>.
- [51] C. Liu, Z. Zhang, X. Zhai, X. Wang, J. Gui, C. Zhang, Y. Zhu, Y. Li, Synergistic effect between copper and different metal oxides in the selective hydrogenolysis of glucose, *N. J. Chem.* 43 (2019) 3733–3742, <https://doi.org/10.1039/c8nj05815f>.
- [52] G. Bagnato, M. Signoretto, C. Pizzolitto, F. Menegazzo, X. Xi, G.H. Ten Brink, B. J. Kooi, H.J. Heeres, A. Sanna, Hydrogenation of biobased aldehydes to monoalcohols using bimetallic catalysts, *ACS Sustain. Chem. Eng.* 8 (2020) 11994–12004, <https://doi.org/10.1021/acsschemeng.0c02623>.
- [53] P.A. Lazaridis, S. Karakoulia, A. Delimitis, S.M. Coman, V.I. Parvulescu, K.S. Triantafyllidis, D-Glucose hydrogenation/hydrogenolysis reactions on noble metal (Ru, Pt)/activated carbon supported catalysts, *Catalysis Today* 257 (2015) 281–290, <https://doi.org/10.1016/j.cattod.2014.12.006>.
- [54] J.J. Musci, M. Montaña, E. Rodríguez-Castellón, I.D. Lick, M.L. Casella, Selective aqueous-phase hydrogenation of glucose and xylose over ruthenium-based catalysts: influence of the support, *Mol. Catal.* 495 (2020) 111150, <https://doi.org/10.1016/j.mcat.2020.111150>.
- [55] F. Zaccheria, M. Mariani, N. Scotti, R. Psaro, N. Ravasio, Catalytic upgrading of lactose: a rest raw material from the dairy industry, *Green. Chem.* 19 (2017) 1904–1910, <https://doi.org/10.1039/c7gc00741h>.
- [56] G. Araujo Barahona, K. Eränen, D. Murzin, J. García Serna, T. Salmi, Reaction mechanism and intrinsic kinetics of sugar hydrogenation to sugar alcohols on solid foam Ru/C catalysts - From arabinose and galactose to arabitol and galactitol, *Chem. Eng. Sci.* 254 (2022) 117627, <https://doi.org/10.1016/j.ces.2022.117627>.
- [57] X.J. Zhang, H.W. Li, W. Bin, B.J. Dou, D.S. Chen, X.P. Cheng, M. Li, H.Y. Wang, K. Q. Chen, L.Q. Jin, Z.Q. Liu, Y.G. Zheng, Efficient synthesis of sugar alcohols under mild conditions using a novel sugar-selective hydrogenation catalyst based on ruthenium valence regulation, *J. Agric. Food Chem.* 68 (2020) 12393–12399, <https://doi.org/10.1021/acs.jafc.0c03873>.
- [58] V.A. Sifontes Herrera, O. Oladele, K. Kordás, K. Eränen, J.P. Mikkola, D.Y. Murzin, T. Salmi, Sugar hydrogenation over a Ru/C catalyst, *J. Chem. Technol. Biotechnol.* 86 (2011) 658–668, <https://doi.org/10.1002/jctb.2565>.
- [59] I.L. Simakova, Y.S. Demidova, E.V. Murzina, A. Aho, D.Y. Murzin, Structure sensitivity in catalytic hydrogenation of galactose and arabinose over Ru/C catalysts, *Catal. Lett.* 146 (2016) 1291–1299, <https://doi.org/10.1007/s10562-016-1752-3>.
- [60] N. Ullah, F. Jérôme, K.D.O. Vigier, Efficient Nickel-Iron bimetallic nanoparticles catalysts for the selective hydrogenation of biomass-derived sugars to sugar alcohols, *Mol. Catal.* 529 (2022), <https://doi.org/10.1016/j.mcat.2022.112558>.
- [61] L. Qin, S.H. Lee, K.H. Kim, O. Lun Li, Selective hydrogenation of reducing sugars over SiO₂/Ni/NiO hetero-structured nanoreactor in Mg-driven aqueous phase, *Appl. Surf. Sci.* 587 (2022) 152849, <https://doi.org/10.1016/j.apsusc.2022.152849>.
- [62] V. Narisetty, R. Cox, R. Bommarreddy, D. Agrawal, E. Ahmad, K.K. Pant, A. K. Chandel, S.K. Bhatia, D. Kumar, P. Binod, V.K. Gupta, V. Kumar, Valorisation of xylose to renewable fuels and chemicals, an essential step in augmenting the commercial viability of lignocellulosic biorefineries, *Sustain. Energy Fuels* 6 (2022) 29–65, <https://doi.org/10.1039/d1se00927c>.
- [63] J.P. Lange, Purfural manufacture and valorization – a selection of recent developments, *Catal. Today* 435 (2024) 114726, <https://doi.org/10.1016/j.cattod.2024.114726>.
- [64] xylitol-market @ (www.imarcgroup.com), (n.d.). (<https://www.imarcgroup.com/xylitol-market/>).
- [65] L. Vilcoq, A. Paez, V.D.S. Freitas, L. Veyre, P. Fongarland, R. Philippe, Unexpected reactivity related to support effects during xylose hydrogenation over ruthenium catalysts, *RSC Adv.* 11 (2021) 39387–39398, <https://doi.org/10.1039/d1ra08193d>.
- [66] H. Du, X. Ma, M. Jiang, P. Yan, Y. Zhao, Z. Conrad Zhang, Efficient Ni/SiO₂ catalyst derived from nickel phyllosilicate for xylose hydrogenation to xylitol, *Catal. Today* 365 (2021) 265–273, <https://doi.org/10.1016/j.cattod.2020.04.009>.
- [67] G. Araujo-Barahona, N. Shcherban, K. Eränen, I. Kopa, I. Bezverkhy, M. Martínez-Klimov, Z. Vajglová, A. Aho, J. García-Serna, T. Salmi, D.Y. Murzin, Ruthenium supported on silicate and aluminosilicate mesoporous materials applied to selective sugar hydrogenation: xylose to xylitol, *Chem. Eng. J.* 485 (2024), <https://doi.org/10.1016/j.cej.2024.150019>.
- [68] J. Kuusisto, J.P. Mikkola, P.P. Casal, H. Karhu, J. Väyrynen, T. Salmi, Kinetics of the catalytic hydrogenation of d-fructose over a CuO-ZnO catalyst, *Chem. Eng. J.* 115 (2005) 93–102, <https://doi.org/10.1016/j.cej.2005.09.020>.
- [69] J. Zhang, S. Xu, S. Wu, Y. Liu, Hydrogenation of fructose over magnetic catalyst derived from hydrotalcite precursor, *Chem. Eng. Sci.* 99 (2013) 171–176, <https://doi.org/10.1016/j.ces.2013.06.002>.
- [70] J. Zelin, C.I. Meyer, S.A. Regenhart, V. Sebastian, T.F. Garetto, A.J. Marchi, Selective liquid-phase hydrogenation of fructose to D-mannitol over copper-supported metallic nanoparticles, *Chemical Engineering Journal* 319 (2017) 48–56, <https://doi.org/10.1016/j.cej.2017.02.1272017>, 485610.1016/j.cej.2017.02.127.
- [71] F. Bocuzzi, A. Chiorino, Preparation, characterization, and activity of Cu/TiO₂ Catalysts, *I. C.* 139 (1997) 129–139.
- [72] J. Zelin, S.A. Regenhart, C.I. Meyer, H.A. Duarte, V. Sebastian, A.J. Marchi, Selective aqueous-phase hydrogenation of D-fructose into D-mannitol using a highly efficient and reusable Cu-Ni/SiO₂ catalyst, *Chemical Engineering Science* 206 (2019) 315–326, <https://doi.org/10.1016/j.ces.2019.05.042>, 31532610.1016/j.ces.2019.05.042.
- [73] D. Scholz, C. Aellig, C. Mondelli, J. Pérez-Ramírez, Continuous transfer hydrogenation of sugars to alditols with bioderived donors over Cu-Ni-Al catalysts, *ChemCatChem* 7 (2015) 1551–1558, <https://doi.org/10.1002/cctc.201403005>.
- [74] P.M.R. Guimarães, J.A. Teixeira, L. Domingues, Fermentation of lactose to bioethanol by yeasts as part of integrated solutions for the valorisation of cheese whey, *Biotechnol. Adv.* 28 (2010) 375–384, <https://doi.org/10.1016/j.biotechadv.2010.02.002>.
- [75] S. Cheng, S.I. Martínez-Monteagudo, Hydrogenation of lactose for the production of lactitol, *Asia-Pac. J. Chem. Eng.* 14 (2019) 1–18, <https://doi.org/10.1002/apj.2275>.
- [76] S.I. Martínez-Monteagudo, M. Enteshari, L. Metzger, Lactitol: production, properties, and applications, *Trends Food Sci. Technol.* 83 (2019) 181–191, <https://doi.org/10.1016/j.tifs.2018.11.020>.
- [77] J. Kuusisto, J.P. Mikkola, M. Sparv, J. Wärnä, H. Heikkilä, R. Perälä, J. Väyrynen, T. Salmi, Hydrogenation of lactose over sponge nickel catalysts-kinetics and modeling, *Ind. Eng. Chem. Res.* 45 (2006) 5900–5910, <https://doi.org/10.1021/ie0601899>.
- [78] J. Kuusisto, J.P. Mikkola, M. Sparv, J. Wärnä, H. Karhu, T. Salmi, Kinetics of the catalytic hydrogenation of d-lactose on a carbon supported ruthenium catalyst, *Chem. Eng. J.* 139 (2008) 69–77, <https://doi.org/10.1016/j.cej.2007.07.084>.
- [79] V.Y. Doluda, J. Wärnä, A. Aho, A.V. Bykov, A.I. Sidorov, E.M. Sulman, L. M. Bronstein, T. Salmi, D.Y. Murzin, Kinetics of lactose hydrogenation over ruthenium nanoparticles in hypercrosslinked polystyrene, *Ind. Eng. Chem. Res.* 52 (2013) 14066–14080, <https://doi.org/10.1021/ie401778y>.
- [80] D.K. Mishra, A.A. Dabbawala, C.C. Truong, S.M. Alhassan, J. Jegal, J.S. Hwang, Ru-NiOx nanohybrids on TiO₂ support prepared by impregnation-reduction method for efficient hydrogenation of lactose to lactitol, *J. Ind. Eng. Chem.* 68 (2018) 325–334, <https://doi.org/10.1016/j.jiec.2018.08.003>.
- [81] V. Pappalardo, F. Zaccheria, N. Scotti, N. Ravasio, Heterogeneous copper catalysts in the aqueous phase hydrogenation of maltose to sorbitol, *Catalysts* 13 (2023), <https://doi.org/10.3390/catal13081183>.
- [82] E.M. Sulman, M.E. Grigorev, V.Y. Doluda, J. Wärnä, V.G. Matveeva, T. Salmi, D. Y. Murzin, Maltose hydrogenation over ruthenium nanoparticles impregnated in hypercrosslinked polystyrene, *Chem. Eng. J.* 282 (2015) 37–44, <https://doi.org/10.1016/j.cej.2015.04.002>.
- [83] J. Zhang, J. Li, S. Wu, Y. Liu, Efficient conversion of maltose into sorbitol over magnetic catalyst in extremely low acid, *BioResources* 8 (2013) 4676–4686, <https://doi.org/10.15376/biores.8.3.4676-4686>.
- [84] R. Araujo-Silva, A.C.O. Mafra, M.J. Rojas, W. Kopp, R. de C. Giordano, R. Fernandez-Lafuente, P.W. Tardioli, Maltose production using starch from cassava bagasse catalyzed by cross-linked β -amylase aggregates, *Catalysts* 8 (2018), <https://doi.org/10.3390/catal8040170>.
- [85] Y.R. Oh, Y.A. Jang, G.T. Eom, Valorization of waste cooked rice into value-added maltobionic acid using genetically engineered pseudomonas taetrolens, *ACS*

- Sustain. Chem. Eng. 10 (2022) 810–815, <https://doi.org/10.1021/acssuschemeng.1c06208>.
- [86] A. Saraiva, C. Carrascosa, D. Raheem, F. Ramos, A. Raposo, Maltitol: analytical determination methods, applications in the food industry, metabolism and health impacts, Int. J. Environ. Res. Public Health 17 (2020) 1–28, <https://doi.org/10.3390/ijerph17145227>.
- [87] W. Li, X. Cui, K. Junge, A.E. Surkus, C. Kreyenschulte, S. Bartling, M. Beller, General and chemoselective copper oxide catalysts for hydrogenation reactions, ACS Catal. 9 (2019) 4302–4307, <https://doi.org/10.1021/acscatal.8b04807>.