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Isosorbide: recent advances in catalytic production

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ABSTRACT: This article focuses on the state-of-the-art advancements on the production of isosorbide, a furanic diol exclusively produced via a two-steps dehydrocyclisation of sorbitol; polyol acquired from the catalytic reduction of glucose. Generally, the compound is formed admixed with various types of monocyclic ethers called sorbitans. During the past half century, many researchers tried to explore the underlying mechanistic and kinetic aspects of the reactions involved in its formation with the main objective to increase the selectivity thus

avoiding the formation of 2,5-sorbitan by-product. In the intervening years, new energy-saving and environmental-friendly methods have been developed, especially those that involve heterogeneous catalysts or acidic ionic liquids. In order to improve the catalytic activities of catalysts, it is imperative to measure the impact of their intrinsic acidity strength, porosity and surface hydrophobicity on each stage of the formation of bicyclic furanic compound. Additionally, comparative advantageous features of simple protocols involving acidic deep eutectic solvent employed as catalyst in solvent-free microwave-assisted reaction, are highlighted.

KEYWORDS: *sorbitol, cyclodehydration mechanism, homogeneous catalyst, heterogeneous catalyst, kinetic aspects*

1. Introduction

The major challenges facing humanity today pertain to energy and environment, including energy requirements, scarcity of water and resources [1]. Current population growth and improvement of living standards in developing countries are boosting the demands of energy and materials. Especially, increased world energy consumption have led to depletion of fossil resources, which may results in a global crisis, affecting chemicals, materials, fuels and supplies of polymers [2,3]. Therefore, replacement of petroleum-based industry has become a priority in most of the scientific programs and agendas of researchers worldwide [4, 5, 6]. Besides economical repercussion and even more alarming facts, possible effects on human and environment safety have alerted the scientific society and motivated them to move towards more sustainable processes employing renewable resources. Particularly, due to the public concern on climate change and global warming associated with the increment of CO₂,

[7, 8, 9, 10] one of the main contributors to greenhouse emissions, the establishment of circular economy with a closed carbon cycle has become an optimal and highly desirable alternative (Fig. 1) [11, 12].

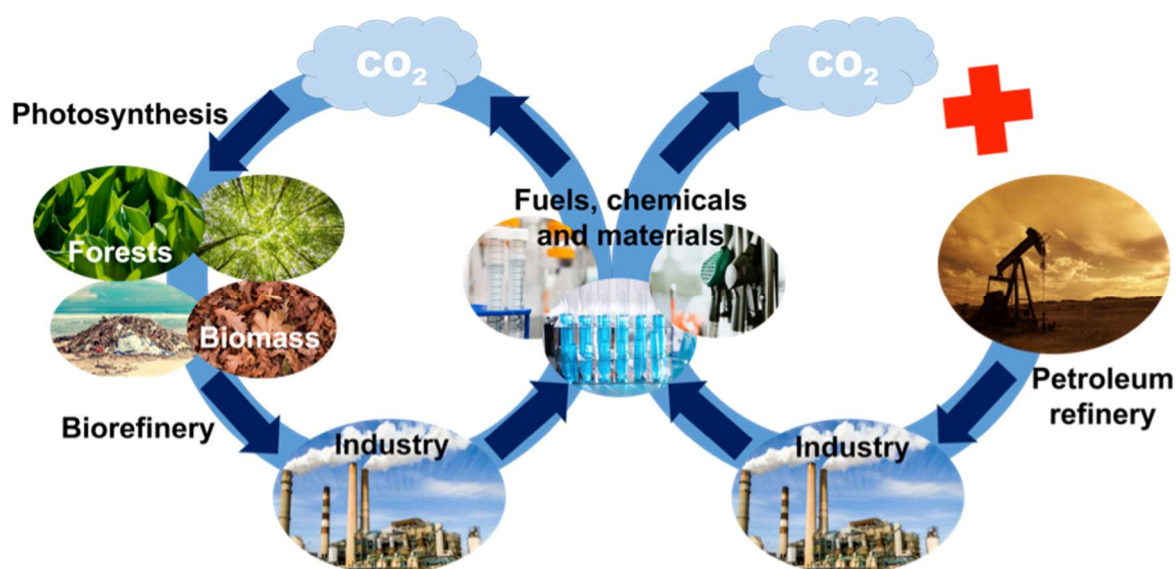


Fig. 1. Comparison of carbon cycles between biorefinery and petroleum refinery.

In this regard, biomass resources, including aquatic cultures, lignocellulosic materials, agricultural, animal and anthropological residues, represent attractive options for the preparation of high-end materials, fuels and chemicals from renewable sources [13-19]. Therefore, biorefinery, which could be defined as the sustainable processing of biomass into energy, chemicals and materials through a closed carbon cycle, have emerged as an alternative to petroleum refinery. Biorefinery mainly comprises two types of feedstocks, namely 1) dedicated feedstocks, including aquaculture, forestry and grasses, and 2) biomass residues. Nonetheless, dedicated feedstocks may result in a food crisis and affect the ecological balance [20].

In contrast, due to its high abundance, lignocellulosic biomass waste, mainly composed of cellulose, hemicellulose and lignin, is an enticing option for the chemical industry [21-23]. Indeed, through both fermentation processes and chemical transformations, lignocellulosic residues could lead to the production of added-value products, which can replace conventional petroleum-derived commodities [24-34]. For instance, ethanol, furans, [35] glycerol, [36, 37] succinic acid, hydroxypropionic acid/aldehyde, levulinic acid, [38] biohydrocarbons, lactic acid, xylitol/arabinitol and sorbitol have been identified as the main 10 promising biomass-derived building blocks for the chemical industry [39-42].

To date, many reports have shown that one-pot and efficient production of bio-based chemicals could be achieved from biomass by optimizing catalysts, solvents, equipment and process technology upgrades. Nonetheless, biorefinery still demands alternative technologies that, at the same time, allow the enhancement of biomass conversion and could be transferred to the industrial scale. Among the alternative technologies currently explored, thermal treatment [43-48], microwave (MW) irradiation [49-63], ultrasound activation [64-66] and photochemistry [67-70] have been successfully developed in academic and research institutes all around the world.

Thermal treatments of biomass include pyrolysis, liquefaction, combustion and gasification; especially, pyrolytic processes that convert biomass into aromatic and aliphatic products, by heating at temperatures between 300 °C and 600 °C, in the absence of O₂ [71, 72]. On the other hand, combustion treatment entail burning of biomass in an oxygen rich atmosphere [73, 74]. Finally, conversion of biomass into liquid compounds could be achieved through thermochemical liquefaction [75-78], requiring wet conditions in presence of catalytic systems.

On the other hand, MW heating techniques are emerging as unconventional treatments for lignocellulosic materials [79, 80]. Polar molecules movements provoke a rapid heating, and in consequence, MW-assisted- methods result in faster reaction times and high yields. Besides the aforementioned advantages, MW irradiation could achieve different reaction pathways and chemistries, which are not attainable under conventional heating processes [81, 82]. However, a deep study of dielectric properties of materials and economic analysis are still necessary in order to boost the application of microwave in the industry.

Although ultrasound irradiation facilitated biomass conversion at the industrial scale is still far from being implemented, the great potential of this methodology has attracted the interest of the scientific community in recent years. Several studies at the lab-scale have indicated that ultrasound irradiation could altered crystalline structure of cellulose molecule, assists organic matter hydrolysis and solubilization, and improves the production yields of bio-ethanol, bio-methane and bio-hydrogen. However the lack of energy efficiency hinder its practical application and therefore, more efforts need to be devoted for exploitation of ultrasound technologies [64].

Photocatalysis is also suitable to valorize lignocellulosic biomass-derived compounds (e.g. alcohols, sugars and organic acids) [83-88]. Selective photocatalytic conversions can be an alternative sustainable pathway for the production of added-value compounds. In this regards, organic photosynthetic reactions such as oxidations, reductions, isomerizations, substitutions, polymerizations and condensations have been reported [83]. For instance, selective production of high valuable compounds, such as benzaldehyde from benzyl alcohol, a model lignin compound, has been broadly investigated by photocatalytic approaches [89-91]. Another reported strategy included a photocatalytic step for the valorization of glucose towards γ -valerolactone. Specifically, the formation of γ -valerolactone from levulinic acid was achieved via a sustainable procedure using visible-light energy and replacing hydrogen

gas by formic acid, which is another biomass-derived entity [92]. Therefore, photocatalytic processes have been considered a crucial technology to resolve environmental related issues. Such processes include not only catalytic biomass upgrading, but also water splitting, CO₂ reduction and air, water and soil remediation through elimination of pollutants. Remarkably, emerging trends focus on the utilization of sunlight energy and LEDs devices, as sustainable light sources, which bodes well for the future of photocatalytic processes [13].

Process intensification and focus on flow chemistry has great potential to be applied on the industrial scale [88, 93]. Continuous flow technologies present several advantages, such as well-controlled mixing and heat exchange, increased multiphase interactions, enhanced selectivity and reproducibility, higher safety and possibility to run serial reactions. Several reports have appeared on the deployment of flow chemistry for the valorisation of levulinic acid and methyl levulinate, among other biomass-derived compounds [28-30, 94].

Sorbitol is a platform molecule derived from biomass, which has been identified by the US Department of Energy as one of the ten more promising bio-based building blocks for the chemical industry; often obtained by polysaccharides depolymerization towards glucose and subsequently hydrogenation. In particular, the first step, namely formation of glucose, is already applied in the industry. Furthermore, sorbitol could be an augmented precursor for the synthesis of sorbitan and isosorbide through dehydration processes (Fig. 2) [95]. Interestingly, the global isosorbide market is predicted at USD 396.4 million in 2018, exhibiting a compound annual growth rate (CAGR) of 8.5% over the forecast period [96]. It should be mentioned that these compounds are currently produced mostly from starch, and cereals, and therefore, a perspective change is required to avoid the competition with food production. In this regard, lignocellulosic biomass appears to be the clear and promising alternative [97-102].

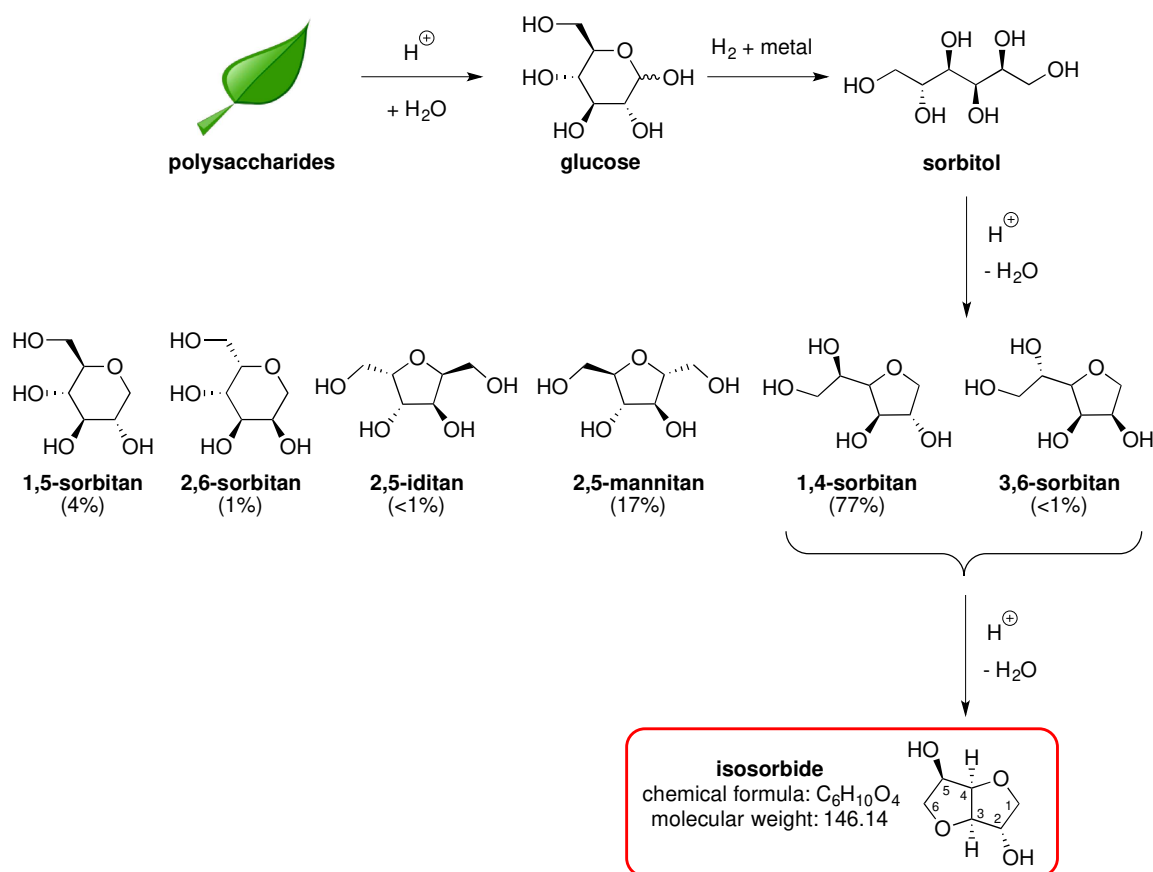


Fig. 2. Illustrative representation of the synthetic pathway for isosorbide preparation from biomass-derived polysaccharides *via* sorbitol formation.

Besides isosorbide, other two isomers could be obtained by cyclodehydration processes, namely isoidide and isomannide (Fig. 3) [103, 104]. Although possible in presence of a metal catalyst such as nickel at 150 bar of hydrogen pressure at 220 °C, catalytic isomerization between these three compounds is currently not economically feasible [105]. The difference among these three isomers is related to the spatial configuration of the two hydroxyl groups in the molecule [103]; hydroxyl groups at carbon-2 and carbon-5 of isosorbide possess *exo* and *endo* configuration, respectively. In turn, both OH groups in isoidide present the same configuration, namely *exo*, while in isomannide, hydroxyl groups exhibit an *endo* spatial arrangement. Such different stereochemistry endows divergent chemical and physical characteristics, regarding for instance the reactivity of OH groups and melting temperatures.

Interestingly, *endo* OH groups could participate to the formation of intramolecular hydrogen bond, while *exo* groups do not present such scenario. Consequently oxygen atom at carbon 5 of isosorbide (endo configuration) possesses a strong nucleophilic behavior, and consequently more reactive in comparison with oxygen in position 2. In contrast, the use of sterically hindered molecules could change preferentially the selectivity towards the reaction with the less reactive, but also less sterically hinder group at carbon 2. The different reactivity of both hydroxyl groups renders isosorbide a very interesting platform molecule, while isomannide is less attractive for industrial applications due to its low reactivity [106]. Isoidide, although highly reactive, cannot be obtained from lignocellulosic biomass [107]. Thus, isosorbide appears to be the most promising option as biomass-derived platform molecule.

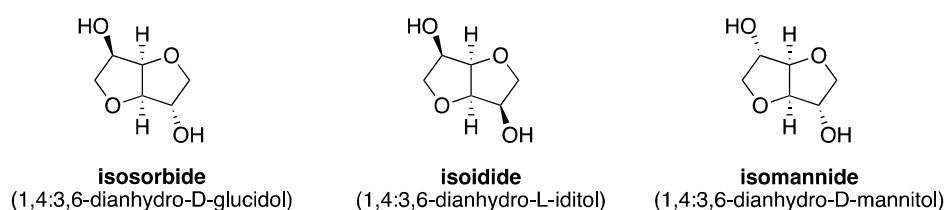


Fig. 3. Structure of the three main diols obtained from double cyclodehydration of their corresponding hexitols.

Table 1

Main physical properties of isosorbide [108].

Molecular weight	146-148 g mol ⁻¹
Melting temperature	61-64 °C
Boiling temperature	160 °C (10 mmHg)
Flash point	>150 °C
Optical rotation	+43.9°
Solubility	Soluble in water, alcohol, dioxane, ketones (solubility in water:

(>850 g.L⁻¹). Almost insoluble in hydrocarbons, esters, and ethers

Isosorbide (1,4:3,6-dianhydro-D-glucitol or 1,4:3,6-dianhydro-D-sorbitol) is rigid diol having a bicyclic fused counterpart and is characterized by two nearly planar 3,4-tetrahydrofuran rings forming a “V-shape” and overall angle of 120 ° [109,110]. The physical properties of isosorbide are reported in the Table 1 having a melting point close to 61 °C. Regarding its stability, at higher temperatures, even warming up in the presence of sulfuric acid, no further dehydration occurs although above 270 ° C, isosorbide starts to degrade [108].

As mentioned before, isosorbide is an essential diol produced industrially on 10⁴ tons scale per year using a three-stage process, comprising 1) enzymatic depolymerization of starch feedstock (or other hexose derivatives) into glucose monomer, 2) hydrogenation (reduction of its C-1 aldehyde function) of glucose to sorbitol over nickel catalyst and 3) double dehydration of sorbitol into isosorbide under vacuum using an acid catalyst (e.g. sulfuric acid). This direct cyclodehydration of sorbitol into isosorbide involves a two-step mechanism [111], initial cyclodehydration could afford one of the two possible intermediates, indeed the 1,4 or 3,6-anhydro sorbitol or sorbitan mixed with negligible amounts of 2,5-sorbitan. On the other hand, it is worth mentioning that by heating at lower pH for prolonged duration, D-glucose could be also converted into 5-hydroxymethyl furfural (HMF)^{32,34} or levulinic acid (LA) [112-114].

In fact, isosorbide is commercially available in two grades: polymer and technical, and produced from the cyclodehydration of its corresponding hexitol. Investigations in this regard are moving forward with the use of alternative resources that do not compete with the food chain. In particular, cellulose, as an abundant biopolymer available in large scale from the

agricultural sector, is a good candidate for the replacement of starch [98, 115]. The controlled hydrolytic depolymerization of cellulose, involving either acids or enzymes, is a source of free D-glucose sub-units. Enzyme-catalyzed saccharification of cellulose give rise to high selectivity values but low yields, which in turn could be circumvented via chemocatalysis [116].

In this regard, acid homogeneous catalysis and acid heterogeneous catalysis are among the main technologies used for the production of isosorbide [117]. Despite their good catalytic activity, the large-scale use of homogeneous catalysts have critical inherent drawbacks related to equipment corrosion, formation of side products by neutralization and therefore difficult product recovery and separation, among others. In contrast, heterogeneous catalytic systems appear to be an ideal and sustainable alternative for the future industrial use. Consequently, numerous researchers have focused on the design of novel solid catalysts, which are easier to recover and reuse, as well as economically viable to avoid treating acid containing wastes [13, 118, 119] thus potentially reducing the cost of isosorbide production. In addition, other parameters such as the acid nature of the catalyst, namely Bronsted or Lewis character, could also influence isosorbide yield and selectivity; successive reduction and dehydration of glucose to produce isosorbide was recently accomplished using an acidic ion exchange resin as catalyst [60]. Not surprisingly, one of the main goals in the research on cellulose-derived isosorbide synthesis have been to identify the bifunctional catalysts containing both, acid and metallic centers for hydrolysis and hydrogenation, respectively. In this context, several explorations have been carried out by supporting noble-metal nanoparticles, such as platinum and ruthenium on different support materials, designed specially to incorporate acidic functionalities [120,121].

The main challenge in chemocatalytic conversion of cellulose, by cleavage of the β -1,4-glycosidic bond, is related to the low solubility of this polysaccharide in most solvents,

due to the presence of hydrogen bonds. Consequently, studies related to the use of newer solvents are highly desirable as exemplified by deployment of sub/supercritical water [122, 123] and ionic liquids (ILs) has been attempted [124-128]. Specifically, the use of sub/supercritical water, although a green reaction media, demands high energy consumption as the reaction is performed at elevated temperatures, ~ 300-400 °C. On the other hand, ILs enable the complete dissolution of cellulose and hence have been the focus of exploration in recent years.

Isosorbide and its stereoisomers possess great potential for various industrial applications ranging from building block in synthesis chemistry to the preparation of bio-based polymers; isosorbide and sorbitan are versatile and key-intermediates in therapeutics, food additive, pharmaceutical, cosmetic and surfactant industry [95]. Regarding biomedical applications, isosorbide mono and dinitrates have been used as in vivo nitric oxide donors, being interesting candidates for the treatment of heart related diseases such as angina pectoris [129]. Isosorbide-derived aliphatic and aromatic biodegradable esters and ethers possess numerous interesting properties such as low-melting points, non-toxicity and amphiphilic nature (highly nonpolar substituents and polar head groups), among others. Such features have motivated the scientific community to employ them as surfactants, fuels, solvents and bioplasticizers. As an example, isosorbide dimethyl ether has been utilized as solvent in pharmaceutical applications due to its non-toxic characteristics [130] whereas short-chain aliphatic isosorbide ethers have been used in the paint industry as hydrotropes or coalescents [112, 131-134]. Applications as fuels and fuels additives have also been explored wherein fuel properties could be tuned, depending on the combustion requirements by modifying the energy content of the molecule through aliphatic substitutions [95].

Due to the rising demand for biodegradable and eco-friendly materials, many industries are making efforts to develop new strategies for producing the target diol in high purity. For

example, the isosorbide diester POLYSORB®, has been developed and already commercialized by ROQUETTE, a French company, for the replacement of phthalates in the production of polyvinyl chloride (PVC) [135]. Furthermore, isosorbide has been used as substitute of ethylene glycol, which is presently used as component for the polyethylene terephthalate (PET), generating polyethylene isosorbide terephthalate (PEIT) (Fig. 4). Through its restricted conformation inside the polymer backbone, monomer isosorbide sub-units are a good alternative to improve the strength and rigidity of polymers as well as the temperature resistance improvement and increased sustainable nature [136-139].

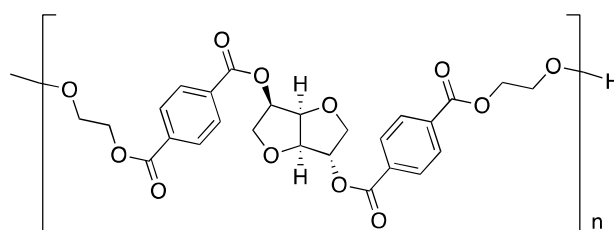


Fig. 4. Overview of a fragment of polyethylene isosorbide terephthalate polymer incorporating isosorbide as a monomer.

Besides PEIT, polycarbonates, polyurethanes and polyamides are among other interesting products in the global isosorbide market. Two isosorbide based polycarbonates have been already commercialized, DURABIO® and PLANEXT® by Mitsubishi chemical and Teijin, respectively; both are engineered plastic with superior characteristic such as improved stiffness and heat resistance, compared to polymethylmetacrylate (PMMA) and poly(bis phenol-A)carbonate [140, 141].

This article summarizes current state-of-the art in the field of isosorbide production from sorbitol and polysaccharides, especially using homogeneous and heterogeneous catalytic strategies, under MW activation in batch and/or under continuous flow conditions.

2. Isosorbide production using homogeneous inorganic acid

Sorbitol is comparable to other hexitols and comprise four successive asymmetric carbons and two primary alcohols at each extremity that could control the varying reaction rates via the interactions in the different transition states [142]. Thus, the formation of isosorbide from sorbitol entails a more complicated mechanism involving additional intermediates (Fig. 5).

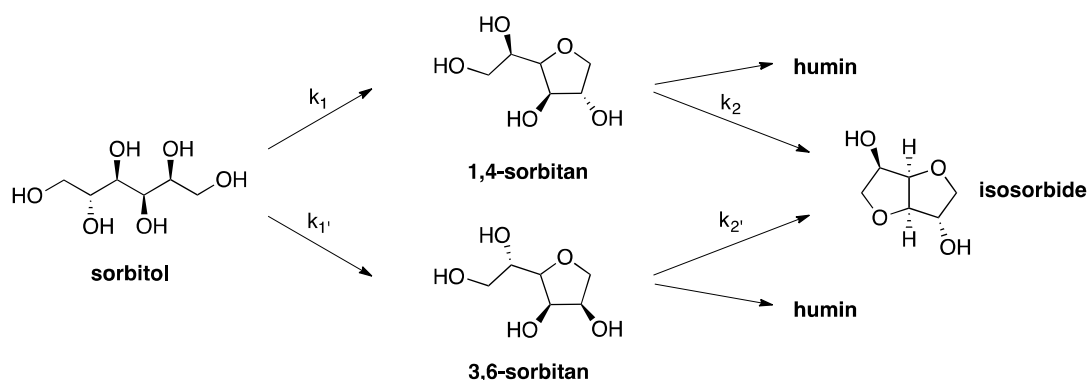


Fig. 5. Principal pathways, formed intermediates and their related kinetic constant rates encountered during the cyclodehydration of sorbitol.

The simplified reaction scheme of the reaction could be represented as follow, assuming the reaction is not the source of undesired degradation side-products or humin, ideally no trace of 2,5-sorbitan were formed and if there is no influence of catalyst H^+ concentration:

$$\frac{d[\text{Sorbitol}]}{dt} = -\left(K_1 + K_1'\right)[\text{sorbitol}]$$

$$\frac{d[\text{Sorbitan}]}{dt} = (K_1 + K_1')[\text{Sorbitol}] - (K_2 + K_2')[\text{Sorbitan}]$$

$$\frac{d[\text{Isosorbide}]}{dt} = \left(K_2 + K_2'\right)[\text{Sorbitan}]$$

In the current literature, researchers have tried to determine the reactions constant rates under various conditions and they have generally found $K_1 \gg K_2$ and $K_1 > K_1'$.

Originally, isosorbide was produced by Backer's method using hydrochloric acid HCl as catalyst [143, 144] and the impact of the entire D-sorbitol configuration on reaction rates was attempted creating tetrahydrofuran rings from commercially available hexitols. From a kinetic point of view, under the influence of a strong acid such as HCl, the pseudo order rate constants of isosorbide formation from sorbitol was clearly inferior to the value obtained from the monocyclodehydration of sorbitol into 1,4-anhydro sorbitol. Unfortunately, in this paper no comments were made about the real yields or selectivities of the reaction. However, the formation of undesired by-products such as 2,5-anhydro-L-iditol could be explained by the formation of preferred 1,2 epoxides intermediates at the end of the molecule during the dehydration process explaining the conversion of configuration at C-2 currently observed in this monoanhydrosorbitanside-product. The global effect of configuration on the rate of 1,4 anhydride ring formation is also observable in case of sorbitol.

When sorbitol is immersed in a boiling 3.0 M sulfuric acid aqueous solution, a S_N2 reaction is said to be responsible of an inversion at the primary carbon C-1 when both 1,4 and 3,6 anhydrides and isosorbide are formed. Isosorbide (64% yield) is formed along with 27% of 1,4-sorbitan when heated at 104 °C under these conditions after 172 h of reaction. [145] while only 2% of 2,5-sorbitan traces are detected for a complete conversion of the substrate. When 1% of H_2SO_4 is employed as the appropriate mineral acid, it affords good yields of isosorbide (70-77%) at 135 °C in batch reactions, with only 8% of the undesired sorbitan formation; reaction barely needs 20 h in average to be completed. Furthermore, a recent patent reports the production of isosorbide using sulfuric acid with unexpected higher yield of 92% [146].

For any hexitol, in case of a monodehydration, it is well known that one of the most important transition states is when the hydroxyl group at C-2 is found in axial position and thus no interaction with the potent leaving group is possibly created (Fig. 6).

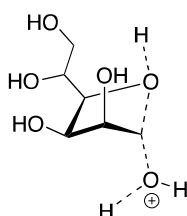


Fig. 6. Model for intramolecular interactions leading to one water molecule elimination and five-membered furanic cycle formation.

Usually in this mechanism, the S_N2 cyclodehydration at the C-1 is also favored due to less steric hindrance and retention of the configuration of sorbitol. Theoretically, S_N1 reaction is more plausible mechanism considering the possible sorbitol protonation of the hydroxyl group at C-4. The cyclodehydration is supposed to occur *via* a carbocationic intermediate species that release water *via* a S_N1 substitution mechanism followed by cyclization.

By replacing HCl with the solid pyridinium chloride, researchers attempted to study the temperature-dependent mono and dicyclodehydration of sorbitol [147]. The reaction was carried out under neat conditions and the optimized conditions were determined to be 160 °C for 20 h of residence time; only 19% of 1,4-sorbitan was detected for an apparent yield of 56% of isosorbide. Interestingly, the authors did not notice trace of 3,6 and 2,5-sorbitan formed during the process, evidence for the high selectivity of the present catalytic system. According to the first kinetic model, these results could be explained by calculated values of each reaction rates constants. Compared to the other rates, $K1'$ is inferior to any other reaction rate and overall lower than $K2'$. This result could expound the rapid consumption of formed

3,6-sorbitan and the absence of other types of side products at the end of the reaction for residence times more than 8 h.

Later, other researchers tried to accelerate the reaction rates and the selectivity by performing the cyclodehydration under MW irradiation [148]. The sorbitol was here immersed in a diluted 0.1 M H₂SO₄ aqueous solution and heated under MW at 170 °C for 10 min. In this work, 21% of isosorbide yield was recorded in mixture with 64% of 1,4-sorbitan while conventional heating leads to 11% of 2,5-sorbitan. By increasing reaction temperature up to 200 °C, and stirred for 20 min, the generated isosorbide yield reached a value of 88% in presence of 0.3 M of sulfuric acid. The double dehydration was performed in 7% water-dioxane and no undesired cleavage of the ether-type solvent was discerned. In another paper, high yield of labelled [U-¹⁴C] isosorbide was produced from sorbitol under MW irradiation using H₂SO₄ as catalyst and undecane as cosolvent for 3 min at 1300 W, final yield being 80% [149].

Yabushita et al. [150] published a revision of the mechanism for the sorbitol dehydration to 1,4-sorbitan. Indeed, sorbitol preferentially forms an adduct with sulfuric acid thereby inhibiting the subsequent dehydration of 1,4 sorbitan to isosorbide. An S_N2 reaction on primary C1 of sorbitol attacked by OH of secondary C4 was proposed.

A recent study pointed out that catalytic activity and yield of isosorbide evolve together depending on pK_a value of the selected acid catalyst [151]; formation of side-products was also influenced by the nature of the catalyst and its acidic strength. In summary, acid catalysts showing pK_a value <1 (H₂SO₄, CF₃SO₃H, *p*-toluene sulfonic acid (PTSA) and methane sulfonic acid MeSO₃H of -3, -15, -6.5 and -1.9 of pK_a values, respectively) are able to produce high yield of isosorbide at 160 °C. However, their catalyst performance is always similar in term of activity and selectivity. After 60 min of stirring, the average yield of

produced isosorbide attained was in a range of 60-70% with complete conversion of sorbitol. On the contrary, by using acid catalysts with $\text{pK}_a > 1$, the catalyst activity and the isosorbide formation tend to decrease gradually in concert with the increase in pK_a value. Moreover, these acids required higher loading concentration, temperature reaction near 180 °C and longer residence time to achieve complete conversion of the substrate. By using weaker acids such as aqueous phosphoric acid solution for dehydrating sorbitol, the cyclodehydration affords only 12% of isosorbide yield with 87% of sorbitol conversion. For batch reaction performed under conventional heating in presence of NaHSO_4 , the treatment yielded 14% of isosorbide and 77% of unsolved mixture of 1,4 and 1,5-sorbitan. Interestingly, if the cyclodehydration is realized in a mixture of 14 wt% H_2O -dioxane in presence of NaHSO_4 , when heated at 210 °C for 90 min the isosorbide yield reached a value of 74% under MW irradiation; MW heating has not only accelerated the reaction rate but also improved the selectivity.

Compared to Brönsted acids, Lewis acids were not really efficient for the dehydration of sorbitol, except $\text{Ti}(\text{SO}_4)_2$ and $\text{Zr}(\text{SO}_4)_2$ which afforded 65-68% of isosorbide and only 16-18% of non-desired sorbitan yield after 60 min of stirring at 160 °C [152]. These catalysts could be easily decomposed by reaction with hydroxyl groups of the polyols releasing the active sulfuric acid in the reaction medium. Besides, despite their recognized higher electronegativity, these catalyst cannot act as usual Lewis acid compared to $\text{Sc}(\text{OTf})_3$. In case of SnCl_4 or AlCl_3 , 1,4-anhydrosorbitan remained the main product rather than the expected isosorbide. Interestingly a recent patent also described the preparation of isosorbide by means of AlCl_3 in 55% yields [153]. Further, when sorbitol was heated at 150 °C for 16 h in the presence of $\text{Bi}(\text{OTf})_3$ or $\text{Sc}(\text{OTf})_3$, 85% of isosorbide yield was obtained. The authors tried to explain the “hidden Brönsted catalytic activity” observed here by the release of triflate with

its low pKa value of 2,6. These results are finally related to the pH of the medium measured at the end of each reaction, in a range of 2.8-4.

For homogenous acid with low pK_a such as acetic acid, they need to be deployed in combination with a stronger acid such as hydrofluoric acid (HF) [154] with a different underlying mechanism. At the beginning, by reacting slowly with HF, the sorbitol and acetic acid are supposed to form complex mixtures of 5,6 acetoxonium ions and 1,2:5,6 diacyloxoniumdions (Fig. 7). This mixture leads mainly to the 3,6-monoanhydride and finally to the 1,4:3,6 dianhydro sorbitol after 6 days of stirring at 20 °C. After hydrolysis, an overall yield of 85% of isosorbide yield was obtained, needing two and three equivalents of acetic acid and HF respectively.

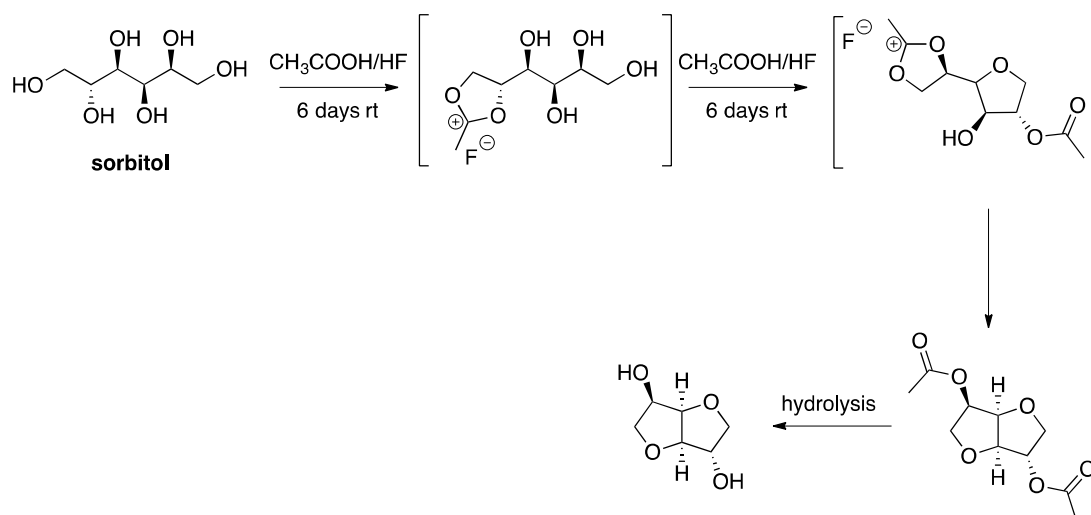


Fig. 7. Revised mechanism for isosorbide production by means of 3 equivalents of HF in acetic acid *via* formation of successive diacyloxonium ions.

3. Miscellaneous acidic catalysts

Alternative pathways have been explored to produce selectively isosorbide. Instead of water, it is possible to use ionic liquids (ILs), especially tetraalkyl ammonium or imidazolium types, recognized today as the next generation solvents with high polarity and low volatility;

reactions can be performed at the higher temperatures. For example, the hydrolysis of number of sugar rich biopolymers such as cellulose or starch could become a major feedstock to convert biomass into chemical platform molecules. Kamimura et al. heated sorbitol in *N,N,N*-trimethyl-*N*-propylammoniumbis (trifluoromethylsulfonyl)amide ([TMPA][NTf₂]) under conventional heating at 180 °C for 10 min in presence of 5% of PTSA, unfortunately sorbitol furnished only 8% of isosorbide yield with no trace of 1,4 anhydrosorbitol but it was admixed with 22% of the useless 1,5 anhydrosorbitol [155]. Higher isosorbide yield was eventually obtained at 200 °C, just after 10 min of irradiation affording 61% for the target material. Interestingly, ILs needs more energy to convert the substrate to isosorbide compared to an aqueous solution, however the authors considered a possible acceleration of the 1,4-anhydrosorbitol formation rate due to the absence of water and the high polarity and non-solvating effect of the IL, the promoted protonation of the hydroxyl group at C-1.

Kamimura et al. used Nafion NR 50 immersed in hydrophobic IL, ([TMPA][NTf₂]), in presence of sorbitol [156] and the mixture was heated up at 180 °C to afford isosorbide in 65% yield. However the reuse of partial or the entire catalytic system shows a decrease of activity which may be explained by a proton exchange between the IL and the sulfonated polymer forming a potent Bronsted triflimic acid HNTf₂, the species really involved in the dehydration. However, the phenomenon could explain the proton concentration drop on the surface.

Recently, another team reported the isosorbide production using different acidic ILs prior to a transfer in a continuous process [157]. Among these catalysts, a system bearing an imidazolium moiety and a sulfonyl group was complexed with a triflate ion which displayed a good performance to dehydrate sorbitol into its isosorbide counterparts; compared to other counter-ions it exhibited the best performance. Besides variation of the molecular structure of the catalyst, such as carbon chain elongation had only a slight effect on the catalyst activity. Sorbitol heated up to 130 °C in presence of 0.6 mol% of the catalyst under solvent-free

conditions produced diol in 84% of yield without trace of usual undesired sorbitan by-products. Due to the formation of a complex between the polyol substrate and the ionic liquid, the reaction rate k_1 of the 1,4-anhydrosorbitol formation was finally lowered and became inferior to the isosorbide formation rate k_2 thus improving the yield of the isosorbide.

Recently, deep eutectic solvents (DESs) comprising simple mixture of quaternary ammonium salts such as choline chloride (CC) and a chosen acidic hydrogen bond donor (HBD) in a defined ratio could be employed as catalyst. For this purpose, we tried to illustrate all above theories reported in this review by using our most recent unpublished results involving a typical DES. Thus, low amount of PTSA was used to promote the dehydration of sorbitol into isosorbide. The mixture of solids in a molar ratio (2:1) was heated up at temperature found between 70 and 90 °C to afford a stable liquid dissolve the generated isosorbide at room temperature (Fig. 8). Sorbitol was heated for 1 h at 160 °C in presence of the catalyst in neat conditions under MW irradiation. When 500 mg of the polyol was treated by 200 mg of the catalyst, after complete conversion of the sugar, isosorbide became the major product mixed with just 7-8% of 1,4-sorbitan. In absence of water, the k_1 reaction rate increases promoting the S_N2 mechanism. However, with increased loading of the sugar, 200 mg of the catalyst was not enough to dehydrate 1,4-sorbitan into target isosorbide. The result was confirmed by HPLC and ^1H and ^{13}C NMR.

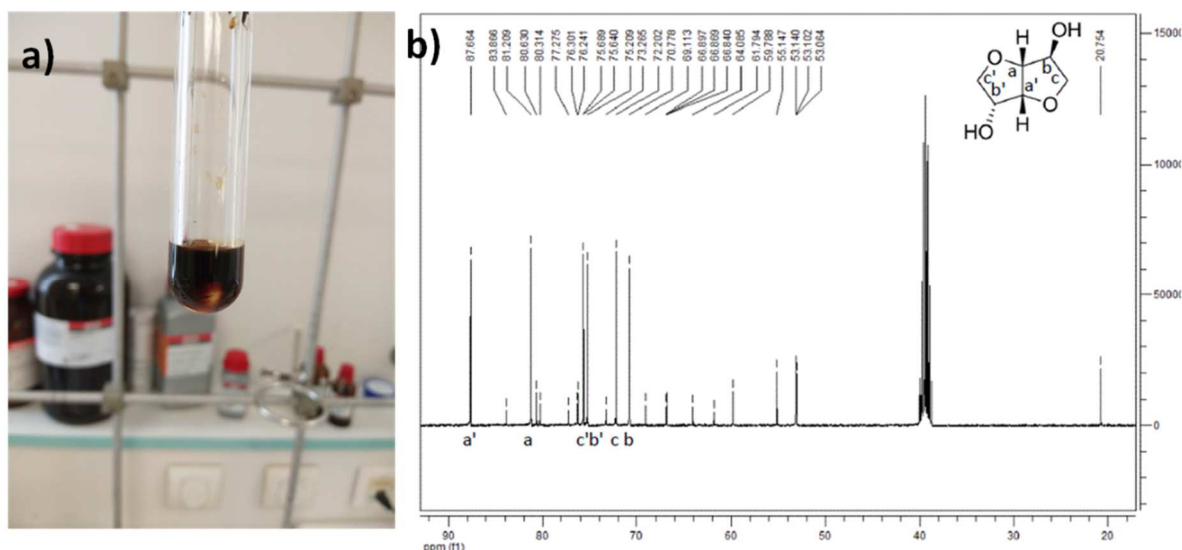


Fig. 8. a) Brown mixture of CC-PTSA (2:1) DES containing the isosorbide (reaction conditions: 200 mg of the catalyst, 500 mg of sorbitol, 160 °C, 1 h MW); b) ¹³C NMR in DMSO-*d*₆ of the sample a).

Returning to water as the reaction solvent, the sorbitol cyclodehydration was reported realized by means of 70 wt % of ZnCl₂ aqueous solution in an autoclave [158]. At 200 °C, once stirred for 70 min, the yield of isosorbide reached a value of 85%. During the process, epimerized side-product galactitol was obtained leading to the formation of its corresponding 1,4 and 3,6 monoanhydrohexitols and a slight amount of 1,4:3,6-isoidide. On the other hand, by using 70 wt% of ZnCl₂ solubilized in water directly on cellulose [159], an *in situ* hydrolysis of the polysaccharide occurred under pressure of hydrogen, the ensuing hydrolyzate containing the free released glucose could be reduced into sorbitol by the pressurized gas. More exactly, at 180 °C, in presence of H₂ (4.0 Mpa) with a substrate to catalyst ratio of 1:12 (wt/wt), isosorbide was obtained as the main product in 95% yield. The complete mechanism here successively involves the production of HCl by reaction between the salt and a neighboring hydroxyl group, and also the formation of an electron acceptor ionic species Zn²⁺, strongly interacting with available hydroxyl groups of the polyol. The consequence is the weakening of the C-O bond on C-1 responsible for promoted nucleophilic

substitution. Interestingly, no 2,5-sorbitan side-product was observed at the end of the reaction. In turn, hydrogen bonding and influence of the hexitol molecular conformation played also a major role for the dehydration selectivity. Herein, the conformation should be retained due to the interaction between the hydroxyl groups and the completely hydrated cationic metal species like for pyridinium chloride salt in neat conditions.

It is possible to obtain isosorbide from sorbitol with a highly concentrated aqueous solution of carbon dioxide (CO₂) [160]. Here, 1.0 mol.dm⁻³ of sorbitol aqueous solution was employed and cyclodehydration of the hexitol was realized under pressurized CO₂ (30 MPa) and heated at 230 °C. However only 8% of isosorbide was formed during a period of 7 h of heating, mixed with about 21% of 1,4-anhydrosorbitol and a small amount of 2,5-anhydrosorbitol. At higher temperatures, 250 and 300 °C, under the same above conditions, Yamaguchi et al. provided the evidence that cyclodehydration of sorbitol has an almost zero order dependence on proton concentration [161]. According their work, the protonation of hydroxyl groups was not a rate-determining step, and by using pressurized CO₂ as a catalyst the real determining step was the attack of C-OH at C-4 on C-1 carbon through the classical S_N2 substitution mechanism. Thus, 1,4-anhydrosorbitol or isosorbide selectivity's of the reaction can be easily controlled due to a temperature dependence of the reaction. Again, the isosorbide formation rate is relatively slow at the lower temperatures whereas at 275 °C, the major product of the reaction became the isosorbide after 5 h of stirring. By increasing the reaction temperature, it was possible to reduce the reaction time in order to obtain a maximum of isosorbide yield of 56% at 300 °C after 8 h of mixing. The reaction also has high pressure requirements. Water molecules interact as a proton donor, and the hydroxyl groups were protonated by carbonic acid H₂CO₃ in subcritical water.

4. Isosorbide formation using heterogeneous sulfonated acid catalysts

In order to solve the problems often encountered with the deployment of the homogeneous inorganic acid catalysts, solid acid catalysts could be good alternatives to produce isosorbide in large yields. The use of Amberlyst 15 as the catalyst for isosorbide production was initially reported where diol is produced as a side product [162]. When sorbitol is directly heated up in MW oven without addition of water at 130 °C or at 170 °C under conventional heating, in case of the MW-assisted reaction 90 min were necessary to achieve 30% of isosorbide selectivity. In contrast, 6 h of conventional heating are required for obtaining superior selectivity. Herein, the value reached 50% and in both cases the conversion of D-sorbitol was complete. Flèche and Huchette [88] have earlier attempted to dehydrate sorbitol with amberlite C200, but at 135 °C for 20 h of residence time [143]; isosorbide with 55% yield was obtained. The presence of 29% of 1,4-sorbitan corroborates previous results and indicates that high temperatures are required to increase the isosorbide selectivity in the same neat conditions.

Another study reported the use of Amberlyst 35 [163] wherein researchers tried to establish a valuable correlation between its structure and catalytic potential. This polymer displayed an average pore diameter of 300 Å and a concentration of acid sites of 5 moles of proton per kilogram. Generally, by using strong homogeneous acid such as H₂SO₄, a slight amount of humins was formed on the surface of the acidic resins that become the main source of catalyst deactivation. In fact, this black carbonaceous material could deposit on the surface of the catalyst blocking the access to the sulfonyl groups. With Amberlyst 35, when the hexitol was heated at 140 °C for 5 h upon MW irradiation approximatively 68% of isosorbide yield was recorded. At this temperature, there was no difference between the respective reactions rates under conventional heating or MW irradiation. Notably, the sorbitan formation rate is also superior by using sulfuric acid as the acidic catalyst in the same unchanged neat conditions.

Gozlan et al. reported the efficient loading of Amberlyst 15 onto 110 mmol of sorbitol [164]. The resulted mixture was heated at 140 °C for 24 h giving an average selectivity for isosorbide with a normal sorbitol conversion of 86%. In another experiment, a dispersion of sorbitol in a mixture of dry 1,4-dioxane-ethyl acetate (1:1, v/v) was refluxed for 24 h in presence of sulfonic acid exchange resin at 78-84 °C, the dehydration gave 39% of isosorbide yield [165].

Purolite CT 269, a commercial acidic ion-exchange resin, has been used and compared to different type of Amberlyst's resins in the isosorbide production [166]. When heated at 140 °C for 12 h at the atmospheric pressure, in melted conditions, with 5 wt% of the catalyst, sorbitol is converted into isosorbide with 75% yield. The catalytic activity improvement could be explained by enhanced acid capacity and high porosity of the solid promoting the good protonation of the hexitol; as expected, the current value of k_1 is superior to k_2 .

Clearly, that it is possible to take advantage of modified silica particles for dehydrating sorbitol instead of solid acidic resins under solvent-free conditions. Compared to perfluorinated sulfated polymer referred as Nafion NR-50 or Nf-Sac, due to the hydrophobicity of their active surface the sorbitol, conversion is enhanced up to 75% with 16% of isosorbide selectivity. The sorbitol dehydration level is also influenced by the catalyst acid strength and the nature of the acid sites, the conversion is also related to the pKa of the catalyst and the number of Brönsted acid sites. For instance, sulfonated resins show macroporous structures, but with very hygroscopic nature and low active surface area. All characteristics could explain that a part of the substrate, especially from the hydrophilic hexitols, is able to enter in the cavities of the material and finally being converted into isosorbide which is decomposed without being released in the reaction medium.

As a first example of modified silica material shown in the Fig. 9, the particle surface was functionalized with arene sulfonic acid moieties [167]. A complete study of its cavity revealed that the optimized conditions of sorbitol dehydration was determined as follows: 33 mmol of sorbitol was heated in presence of 10% molar of the catalyst for 2 h at 170 °C affording 71% isosorbide yield. Finally, it needs shorter residence time compared to Amberlyst 15 to acquire similar results in the same range of temperature.

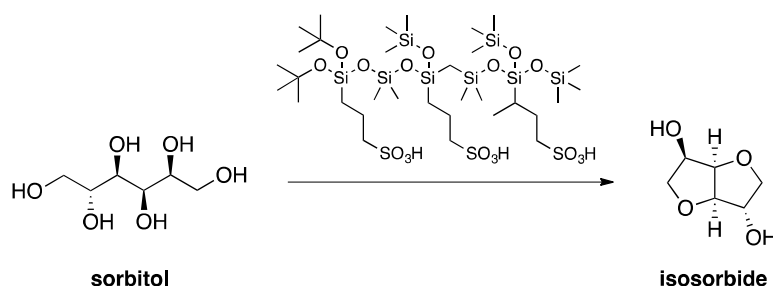


Fig. 9. Modified silica beads with surface displaying sulfonic acid moieties able to dehydrate sorbitol to isosorbide.

Another type of modified silica catalyst was also synthesized and evaluated for its performance for dehydrating sorbitol into isosorbide under solvent-free and vacuum conditions [168]. To produce the catalyst, the solid surface was silylated by 3-(mercaptopropyl)trimethoxysilane (MPTS) and followed by oxidation of the exposed thiol functions into their corresponding sulfonic acid groups by reaction with hydrogen peroxide (H₂O₂) in acetic acid. Although the catalyst did not provide maximum acidity, it was potent enough to afford higher yield of the target diol presumably due to the large pore size and highly active surface area. The best catalytic performance was observed at 120 °C stirred for 10 h under vacuum in presence of 2% of one of the best catalysts candidates reported; [168] complete conversion of sorbitol was accompanied by 84% of isosorbide yield. This result was explained by the specificity of the catalyst, which exhibits a more hydrophilic surface displaying stronger affinity for sorbitol compared to isosorbide. The diol leaves the active site

rapidly, avoiding possible undesirable side reaction, which causes large humin production. The exceptional catalyst performance could be also be explained by its total acidity determined by the current temperature programmed desorption ammonia (NH_3 -TPD) method. These series of catalyst give a value of 840 mmol g^{-1} of protons, a number far lower compared to Amberlyst 15H⁺ displaying 4530 mmol g^{-1} in parallel to a superior acidity density of 93 mmol m^{-3} [124]. Although isosorbide yield was improved to 71% under vacuum conditions, but it failed to prevent of the undesired degradation of the product.

Mesoporous SBA-15 was successively functionalized by propylsulfonic acid and hydrophobitized by various methyl chlorosilanes reagents to improve the acid strength of the catalyst [169]. Consequently, in view of the reduced affinity of the polar sorbitol on the surface, it can lower the first reaction rate k_1 and promote the conversion of sorbitan intermediate into isosorbide. Under solvent-free conditions, in a pressurized reactor, when heated at 150°C for 24 h, isosorbide was produced from sorbitol with a catalyst to substrate ratio of 3:1. Interestingly, the major intermediate was the 1,4-sorbitan and the final isosorbide yield reached 72%.

A hybrid methodology involving a silica supported latex-type sulfated polymer was also studied [170]. This kind of material displayed a total acidity varying between 1.82 and 3.25 mmol g^{-1} and was identified as a potent system for the cyclodehydration of sorbitol; usually, 1.65 mmol of sorbitol was mixed with 0.27 mmol of the present solid catalyst. The reaction was carried out at 150°C for 4 h to secure 95% of sorbitol conversion. However, the reaction was mainly limited to 1,4-sorbitan formation under mild and anhydrous conditions. Besides, if the total acidity of the catalyst was enhanced from 0.48 to 4.86 mmol g^{-1} , the sorbitol conversion increased from 31 to 100%, while the selectivity toward 1,4-sorbitan decreased from 91 to 22%; concurrently, the isosorbide selectivity increased from 0 to 65% More acidic and highly hydrophilic catalytic surface can interact with the primary dehydrated products

such as 1,4-sorbitan despite the strong water adsorption in neat conditions. For starting the second cyclodehydration step, it is necessary to go over a great barrier controlled by a subtle hydrophilic-hydrophobic balance between substrates and catalyst surface to guide the reaction in desired direction.

Another category of sulfated solid catalyst could be considered as a potent alternative of the sulfonated materials. For example, sulfated titania oxides are reported to be enough active in aqueous solution to form anhydrides of sugars [171]. The initial paper describing this type of material indicates that sulfur contents, given here in percentage, depend on calcinations temperature during the preparation process. When heated at 180 °C for 2 h a dispersion of 0.2 g of the present catalyst in an aqueous solution containing 10 g of sorbitol, 65% of isosorbide selectivity was obtained. For extended residence time up to 4 h no improvement of the selectivity was recorded. Besides, only a small amount of sorbitan was also detected in the vessel. Another type of sulfated material was prepared by Ahmed and his collaborators *via* a sol-gel procedure involving titanium IV isopropoxide and concentrated sulfuric acid which shows a final concentration of total acidity of 4.4 mmol g⁻¹ in average. Its catalytic activity was measured in liquid phase loaded with 10 g of sorbitol and 0.4 g of the catalyst. Then, under conventional heating at 210 °C for 2 h, the maximum of isosorbide selectivity reached 75% and the complete conversion of 1,4-anhydrosorbitol formed during the process was limited.

Hwang et al. followed a co-precipitation method for the preparation of a different kind of calcined and sulfated titanium oxide catalyst for the dehydration of sorbitol into isosorbide [172]. Compared to the other results documented in the literature, they obtained 70 % of isosorbide yield after warming up a melted sorbitol feed containing the catalyst. The reaction was carried out at 180 °C for 2 hours in presence of 0.2 g of their best catalyst candidate; a

good catalyst apparently needs to display sufficient porosity level with the higher amount of sulfur contents to attain its main objective.

Sulfated tin oxide is another catalyst prepared by direct calcinations at different temperatures of stannous sulfate, in a range of temperature from 350 to 600 °C [173]. Some studies indicated the best catalytic activity for material formed at 450 °C. Unfortunately, no comments were made about the relationship between structures and their associated catalytic activity or selectivity. When a mixture showing a catalyst to sorbitol ratio (wt/wt = 25) is stirred for 2 h at 180 °C, the conversion was complete with an isosorbide selectivity of 65%. For all previous solid catalysts, it is evident that both porosity level control and the number of sulfonyl groups attached on the surface could contribute to the enhancement of the catalytic activity, but we have to bear in mind the surface hydrophilicity is generally promoted by the presence of these sulfonyl groups.

By changing the nature of the metal oxide, different catalysts were tested for realizing the cyclodehydration of the hexitol performed in liquid phase reaction [174]. The best reaction conditions were found using a 10 wt % sorbitol aqueous solution. The first metal selected was the abundant and cheaper copper, one of the best derived sulfated copper oxide was prepared by calcinations of its metal sulfate precursor at 650 °C and the ensuing optimized sorbitol dehydration were as follow. The reaction carried out in its presence gave 99% of the hexitol conversion and 68% of isosorbide selectivity when heated up at 200 °C under a flow of the sorbitol aqueous solution directly in the reaction vessel. Interestingly, a sulfated aluminium oxide gave similar catalytic activity at the same reaction temperature. For sulfated copper oxide, the activity of the catalyst was also directly connected to its temperature of preparation. Unfortunately, no correlation between porosity and the isosorbide selectivity have been discussed in this work.

Khan et al. reported the preparation of a sulfated zirconia by coprecipitation of zirconium (IV) hydroxide and sulfuric acid, followed by calcinations of the solid at 600 °C for 5 h [175]. Then the sorbitol dehydration was performed in liquid-phase conditions where the optimized catalyst candidate showed pore volume of 0.11 cm³ g⁻¹ with 1.31% of sulfur content. A 0.2 g loading of the catalyst for a reaction carried out at 230 °C gave fastest sorbitol conversion and best isosorbide selectivity. However, at 201 °C, in presence of 0.5 g of the catalyst, 100% of conversion and 61% of isosorbide selectivity was finally obtained within 2 h. Two additional patents explored the deployment of sulfonated TiO₂ leading to the production of isosorbide with obtained yields around 69% [176, 177].

The catalytic performance of a sulfonated activated carbon catalyst was tested at 150 °C [178] which holds 0.5 mmol g⁻¹ of sulfur content for dehydration and the material displayed higher surface area of 710 m² g⁻¹. Its activity was comparable to Amberlyst-36 that hold 5.4 mmol g⁻¹ of proton at 150 °C. The hydrophobicity of the material could be the main reason for the strong adsorption of the isosorbide just after its production and thus causing its resinification. In fact, after 8 h of stirring, the reaction afforded 52 and 25% of isosorbide and 1,4-sorbitan selectivity, respectively. When compared to sulfated zirconium oxide with 0.9 mmol g⁻¹ of sulfur content for a similar complete conversion of sorbitol, employed at 150 °C, the isosorbide formation rate was lower and could be explained by the pronounced hydrophilic character of the sulfated metal oxide.

Affiliated to the previous catalyst, a sulfated carbonaceous solid acid was developed started from cellulose biomaterial [179]. The preparation of the material includes a hydrothermal carbonization followed by the direct sulfonation of the resulted black powder. An analytical study of the ensuing material revealed that it remains too hydrophobic despite a large number of hydroxyl groups as detected by FT-IR and displayed on the solid surface. Its acidity was characterized by 0.8 mmol g⁻¹ of weak acid sites and 1.8 mmol g⁻¹ of medium

strong sites. The sorbitol conversion under neat conditions remained incomplete at 190°C. However, for temperatures superior to 220 °C, the isosorbide yield and selectivity decreased due to the hydrophobicity of the catalyst. This property is mainly responsible for the isosorbide self-polymerization or cross-polymerization between sorbitan and isosorbide. Finally, the maximum value of isosorbide selectivity of 67% was obtained at 200 °C. By increasing the amount of loaded catalyst only a slight improvement of the total isosorbide yield was reported.

A hydrophobic sulfonated carbon-based acid catalyst was synthesized by carbonization of a commercial polysulfonated styrene (sodium type) or sodium *p*-styrene sulfonate PSSNa in an autoclave and encapsulated with tetraethyl orthosilicate (TEOS) [180]. Then, varying the conditions of this treatment, porous and non-porous sulfate moieties holding carbonaceous materials were prepared with 0.76 and 0.083 mmol g⁻¹ of acid sites, respectively. The solid displaying high porosity was able to deliver complete conversion of hexitol into isosorbide with selectivity of 88%, however its non-porous counterparts was apparently insufficiently polar with probably stronger affinity for isosorbide. This phenomenon was the main cause for the degradation of the diol. In addition, a great number of weak acids sites was favorable to improve the 1,4-sorbitan selectivity of 48% with only 4% of associated isosorbide selectivity. The optimized cyclodehydration conditions were set up at 140 °C, using 2.0 g of solid sorbitol mixed with 0.1 g of one of the catalysts under a pressure of 0.1 bar.

Dussenne and his co-workers produced the original metalized sulfonic resins as catalyst for the production of isosorbide via dehydrocyclization of sorbitol [181]. These catalysts were easily produced by mixing various metallic salt precursors with PTSA in acetonitrile. All materials (M(OTs)_n) were simply recovered as solids by filtration or evaporation under reduced pressure of the solvent. The crude solids were simply dried under vacuum or employed for producing the hybrid catalyst using various sulfonic resins. As a preparative

experiment, 1 % of each produced tosylate salt was added to 2.5 g of melted sorbitol. Using $\text{Bi}(\text{OTs})_3$ at 115°C , the hot solution of sorbitol was stirred under inert atmosphere to afford 100 % of sorbitol conversion and 67 % of isosorbide selectivity. In the next stage of their study, they intended to improve the isosorbide yield by means of a combined catalytic system involving a polymeric sulfated resin such as Nafion NR50, Dowex or Amberlyst 70. Unfortunately, a non-desired deactivation of the sulfated resins ensued by metallic chelation of their sulfonic acid moieties all around the catalyst, especially with Fe^{3+} , Al^{3+} or Ga^{3+} . This unintended poisoning of the sulfated resins did not permit the expected yield improvement.

In a more complicated pathway, the direct conversion of glucose in three steps was performed by means of a Dowex acid resin decorated with ruthenium nanoparticles (RuNPs) [182]. In the first step, glucose was completely converted into sorbitol by contact with RuNPs under 30 bar of hydrogen pressure, followed by the *in situ* cyclodehydration of the resulted hexitol into target isosorbide *via* sorbitan intermediate. At 190°C , full conversion of sorbitol was also observed with 10% of sorbitan and 85% of the diol. The reaction was carried out in liquid-phase conditions using 0.1 M of C-6 sugar aqueous solution in presence of 0.2% of RuNPs as a part of the catalyst. The simple hydrogenation of glucose is favored compared to the isomerization side-reaction, due to the normal strength of the Brönsted acid sites. Once reduced by hydrogen on the metallic nanoparticle, the acidic moieties of the resin can easily dehydrate the non-isolated hexitol without any trace of HMF potentially formed from the direct dehydration of glucose.

A nickel oxide supported on activated carbon catalyst has also been studied [183]. The generated catalyst showed medium strength acidity, after introduced at 250°C in a 25 wt% of sugar aqueous solution under hydrogen pressure of 8 MPa; the sorbitol conversion was almost complete with a value of 92%. Besides, the selectivity for 1,4-anhydrosorbitol decreased in

favor to isosorbide that reached a final value of 29%, but always mixed with anhydro sugars. Interestingly, despite the conditions, no isomerization of sorbitol was measured.

Metal IV phosphates of tin, titanium and zirconium (SnPO, TiPO, and ZrPO) were reported to be potent catalysts for dehydrating sorbitol into isosorbide [184]. The reaction was realized using 10% aqueous sorbitol solution which was vaporized and diffused by a stream in a range of temperature from 200 and 300 °C. The best candidates were both SnPO and TiPO catalysts giving 72 and 97%, respectively of sorbitol conversion. However, the best yields of isosorbide were obtained with only SnPO at 300 °C with a value of 65%. In fact, SnPO displayed higher surface acidity in accord with the common normal understanding that strong acid sites are necessary to dehydrate the 1,4-sorbitan into isosorbide to promote the second slower dehydration. Here, the total amount of strong acid sites has a value of 4.60 mmol g⁻¹. A quarter of the solid SnPO surface is recovered by strong acid sites. In summary, just a small amount of humin was formed, due to the lack of affinity of the formed isosorbide. On the other hand, bimetallic acids were also found to be potent for sorbitol conversion into isosorbide. The preparation of three types of bimetallic catalysts was achieved starting from various metallic salt precursors and associated methods. Thus, Cu-Ru and Cu-Pt catalysts were obtained by reaction between a metallic salt precursor and a NaOH-leached copper/aluminium alloy. On the other hand, Ru-Cu was generated by reduction of copper salt in presence of 10 % carbon supported catalyst [185,186]. Like for the other metallic catalysts, it is possible to use hydrogen pressure to avoid the formation of some undesired by-products, but the unexpected hexitol isomerisation persists during the reduction process. The reaction was carried out as follows: 0.11 M of sorbitol aqueous solution was heated up in presence of the catalyst under hydrogen pressure (4 MPa) at a well-selected temperature found to be in a narrow range between 220 and 260 °C. Especially over Cu/Ru at 260 °C, 71% of isosorbide yield was obtained but 10% of 2,5-anhydroiditol and 2,5-anhydromannitol were detected in

the crude reaction. Not surprisingly, no trace of 3,6-monoanhydrosorbitol was recorded, only 11% of 1,4-sorbitan remained as the main intermediate. The acidity of these bimetallic catalysts was generated from the interaction of ruthenium and platinum with copper. This proximity creates new sites able to catalyze successive cyclodehydrations. Thus, the acidity could originate from the heterolytic dissociation of the hydrogen gas on the bimetallic surface, generating a great number of protons. Then, the protonation of the hydroxyl group on C-1 could occur prior to the typical S_N2 reaction with hydroxyl group on C-4. The bimetallic Cu/Pt catalyst activity could be enhanced when the salt precursor is a chloride salt. Remaining chloride in the catalyst could act through some kind of halogenated copper active site.

Another highly structured and layered niobium-molybdate solid acid was prepared by calcination and studied against sorbitol aqueous solution [187]. A typical procedure involves 0.27 mmol of sorbitol dissolved in 3.0 ml of water in presence of layered niobium molybdate (HNbMoO_6) heated up at 160 °C. After 60 h of contact, the isosorbide yield was low. A complete analysis of the solid catalyst by XRD highlighted the lack of affinity of both 1,4-sorbitan and isosorbide on the surface of the metallic oxide, a phenomenon responsible for all side-reactions inhibition. Eventual resinification or cross-polymerization of the furanic products appeared to be impossible. The 1,4-sorbitan formation rate was reported to be faster than the reaction employing sulfuric acid as the catalyst, due to a plausible molecular recognition of sorbitan inside the layer of the material full of strong Brönsted acid sites.

A phosphorylated niobium oxide catalyst was also developed to produce isosorbide [188]. Produced by calcination of hydrated niobium oxide in presence of phosphoric acid, this material shows capacity for dehydrating hexitol under liquid phase conditions. Indeed, ratio between oxide and grafted phosphoryl groups are an important point for modulating the catalytic power of the solid acid. The relative catalytic activity was tested for various catalysts with different composition ratios in a pressurized vessel and 10 wt % of aqueous sorbitol

solution was injected in the reactor using a constant flow-pump. At 2~25 °C, one of these catalyst gave 63% of isosorbide selectivity with only 0.5% of sorbitan selectivity being finally recorded. The best catalytic performance depends on the most appropriate calcination temperature that could define the number of acidic sites on the surface. The most powerful catalyst required stronger acid sites formation and larger surface area.

A tantalum oxide modified by condensation with phosphoric acid has been described in the literature [189]. Again, a 10% sorbitol aqueous solution is injected in a closed and pressurized reactor with an average flow of 24 mL.h⁻¹. In general experiment, usually 0.5 g of catalyst were employed, and the reaction was stopped after 6 h of residence time. The reaction temperature ranged between 200 and 275 °C. One of the catalyst reported in the paper expressed a remarkable activity for dehydrating sorbitol; the catalytic performance of Ta₂O₅ was improved significantly by mixing with different concentrations of H₃PO₄. The best result showed a sorbitol conversion of 98% with the highest selectivity for isosorbide of 48% at 225 °C. The physico-chemical characterization of the material showed that the introduction of the phosphate groups has transformed the tantalic acid into two kinds of new crystalline phase. For the material displaying highest amount of medium acidic sites (10.45 mmol g⁻¹), the P-OH species in TaH(PO₄)₂ were mainly responsible of the catalytic performance. Besides, ratio between phosphorous and tantalum inside the solid define its activity. For a ratio P/Ta<0.8, the phosphoryl groups are said to be mainly localized outside of the material, the solid is supposed to be more hydrophilic retaining water. Compared to sorbitol, the less hydrophilic sorbitan's short-lived residence on the surface should be responsible for the high sorbitan selectivity. On the contrary, for P/Ta>0.8, the surface became more hydrophobic because of a great number of covalent bonds formed between the highly populated and adjacent phosphoryl groups. Authors also remarked on the high affinity of the formed isosorbide for the catalyst surface leading to the production of humins.

Different trivalent and quadrivalent metal phosphates were studied under liquid phase conditions in a pressurized autoclave reactor at various temperatures [190, 191]. The experiments were carried out in a range of temperature from 150 to 250 °C. Herein, 70 wt% of an aqueous sorbitol solution was employed as the substrate and the reaction was conducted during a period comprised between 0.5 and 24 h. The optimized conditions were investigated and clarified for boron phosphate. When 0.23 g of the catalyst was warmed up for 8 h at 250 °C in the sorbitol aqueous solution; 99.5% of sorbitol conversion and 80% of isosorbide selectivity was attained with a lower selectivity of 1% for 1,4-sorbitan. Oddly, 14% of unknown monoanhydrosorbitan mixture was reported. Once again, the catalytic activity appears to be connected to the number of acidic sites, their size and also to some degree with the number of moderate acid sites available on the surface. No detail has been provided on the porosity of these materials. A patent issued by Huang reports the deployment of quadrivalent tin phosphates to produce isosorbide from sorbitol. The catalyst was prepared reaction between SnCl_4 with phosphoric acid [190].

When heated in presence of zeolite, several hexitols could be converted into various furanic compounds [192]. The exact protocol involves 1.0 g of sugar heated at different temperatures found in a range between 260 and 300 °C for a period of 1 or 2 h under inert atmosphere in presence of 0.4 g of 3 Å type molecular sieves. Starting from sorbitol, when the solid was heated up at 290 °C for 2 h, isosorbide was obtained as the main product in 45% yield with a total conversion of the hexitol of 98%. According to a related paper, a revised mechanism for the dehydration of isosorbide and its intermediates was forwarded [192]. The formation of the target diol could involve the creation of unsaturated species obtained by the first elimination of a molecule of water. Related to this work, another study employed a silica-aluminium material, raising the Si/Al ratio found in the zeolites [193]. The increase of the ratio improved drastically the activity of the catalyst until a limit was reached. The

cyclodehydration of sorbitol was performed using sorbitol aqueous solution with 76% yield at 127 °C for two hours of contact; reaction produced trace (4%) of sorbitan. A great number of “strong “ acid sites and enough hydrophobicity were required to get conversion superior to 99%. The authors reported that the increase of Si/Al ratio improves the hydrophobicity thus thermodynamically enhancing to remove the water from the reaction intermediates. In this work, the effect of solid porosity was considered as a minor factor. It is important to mention that the catalysts remained active up to five cycles.

Morales et al. realized a study of isosorbide production using various heterogeneous catalysts such as sulfonated resins and zeolites [194]. The best candidates were SBA-15-Pr-SO₃H and Amberlyst recognized for their pore sizes found between 73 and 220 Å of diameter and higher capacities. On the other hand, Sung et al. compared the acidity of heteropolyacids (HPAs) deposited on different metallic oxides such as silicon (SiO₂) or aluminium (Al₂O₃) [195]. Thus, 30 wt% of 12-phosphotungstic acid (H₃PW₁₂O₄₀) supported on SiO₂ expressed the strongest acidity leading to the highest sorbitol conversion and selectivity for isosorbide. Porosity of the material (0.5 cm³ g⁻¹) defines the nature and the degree of the interactions with the substrate, but also the strong acidity of the solid. The optimized reaction conditions was finally determined experimentally, where an aqueous solution of sorbitol was injected in flow and heated in presence of 0.5 g of the catalyst at 150 °C for 6 h to give conversion of sorbitol of 96% with 18 and 58% respectively of 1,4-sorbitan and isosorbide selectivity. On the other hand, free heteropolyacid was also reported to catalyze the formation of isosorbide under liquid conditions when 50 mL of water containing 5.6 g of sorbitol was warmed up for 30 min at 230 °C; reaction gave mainly a mixture of sorbitan for an isosorbide selectivity of 60%.

Recently, Zhang and collaborators realized the incorporation of silver atoms via a simple ion exchange process between silver nitrate and a commercial HPW leading to the formation

of modified catalysts with varying silver contents [196]. For this study, three catalysts of different molecular compositions were generated and well-characterized. Among them, one expressed remarkable potential to convert sorbitol into isosorbide. Finally, by using 0.3 g of the best catalyst candidate at 140 °C, 1 hour of contact is necessary to consume all sorbitol substrate. The conversion was superior (99 %) with an isosorbide selectivity of 83 % and up to 5 cycles, the catalytic activity remained unchanged to produce isosorbide in good yields but with an apparent slight decrease.

5. Isosorbide preparation via direct conversions of glucose and its related homopolymers

Many research teams are now trying to produce isosorbide *via* the direct conversion of glucose via different types of one-pot conversion methods. But the competitive and inexpensive production strategy for the diol from cellulose or woody wastes remains a challenge. In one case, starting pure cellulose biopolymer was pretreated and hydrolyzed by a heteropolyacid into variable amount of glucose subunits [197]. By using $\text{H}_4\text{SiW}_{12}\text{O}_4$ (SiW), the isosorbide was produced without any further purification under the conditions when glucose was exposed to hydrogen pressure. The carbonyl function on C-1 is reduced under H_2 pressure by means of a ruthenium catalyst and then normal cyclodehydration can occur easily in the acidic conditions. The reaction was performed in liquid phase by using 0.8 g of microcrystalline cellulose, dispersed in 40 mL of water in presence of 200 mg of additional metal supported Ru/C catalyst. The reaction was carried out at the initial H_2 pressure of 5 MPa and heated at 210 °C. By increasing the proton concentration on the surface of the catalyst both sorbitol and sorbitan dehydration rates were improved. At the end, 52% of isosorbide was generated from the native cellulose.

Milled crystallized cellulose was easily converted into isosorbide by means of Amberlyst 70 associated with 4% Ru/C, employed for its potential to hydrolyze the polysaccharide and

dehydrate the ensued hexitol intermediate [198, 199]. The entire dispersion was heated at 190 °C under hydrogen pressure of 5 MPa for 16 h. During the process, 56% of isosorbide yield was formed admixed with 17% of its 1,4-sorbitan precursor. Interestingly, 3% of isomannide was formed due to the possible isomerization occurring during the reduction of carbonyl group. Starting from the lignocellulosic biomass, using similar protocol, Yamaguchi and collaborators were able to produce 26% yield of isosorbide with 13% of sorbitan; the optimized temperature being 190 °C.

A recent paper reports the dual action of homogeneous mineral sulfuric acid associated with Ru/C catalyst [200]. In presence of hydrogen, heated at 170 °C for two h a solution of 0.5 M H₂SO₄ loaded with 5 wt% of Ru/C containing cellulose or other glucose-based polysaccharides afforded isosorbide in 57% yield with a tiny amount of 1,4-sorbitan.

The last example for converting cellulose to isosorbide entails supported ruthenium metal or nanoparticle (RuNPs) deposited on mesoporous niobium phosphate (NbPO) [201, 202]. Furthermore, when both mesoporous structure of the catalyst and the molecular weight of cellulose are examined carefully in terms of the global accessibility of the acid sites, the polysaccharide hydrolysis can take place only on the external surface of the niobium phosphate. Initially, a Ru/NbOPO₄ catalyst with 5% loading amount of Ru could transform cellulose into isosorbide under hydrogen pressure of 4 MPa when the mixture was heated for 24 h at 170 °C; 62% of isosorbide selectivity was observed. The authors noticed the isomerization of sorbitol into mannitol on the Ru active sites under hydrogen atmosphere. To improve its activity, especially for the second dehydration occurring just after the reduction, the solid catalyst necessitates higher amount of acid sites including Brönsted and Lewis acid sites; more Brönsted acid sites are essential to increase the isosorbide yield. Best isosorbide selectivity could be obtained when 0.24 g of milled cellulose was introduced in 15 mL of water in presence of 0.1 g of catalyst. The resulting dispersed mixture was the heated at

170 °C for 24 h and 57% of isosorbide yield was recorded, unfortunately contaminated by other sorbitans. When small-size RuNPs of 0.9 nm of diameter were introduced into niobium phosphate catalyst, one of the major effects is the reduction of the pore size. However, the incorporation of the RuNPs only slightly improved the isosorbide yield (26%). From sorbitol, the acidity of the solid catalyst was not inhibited despite the presence of RuNPs. Besides, starting from 0.6 g of microcrystalline cellulose, in presence of 0.06 g of 5 wt% RuNPs-NbPO, the transformation of the biopolymer performed at 220 °C for 60 min under hydrogen pressure afforded a final isosorbide yield of 43%.

Table 2 summarizes the results and highlight the performance of each category of catalyst; we have listed the most representative catalysts, their optimal operating conditions and the corresponding isosorbide yields attained.

Table 2

Optimized conditions and catalytic activities of each catalyst for producing isosorbide via cyclodehydration of sorbitol.

Entry	Catalyst	T (°C)	Time (h)	Isosorbide (%)	ref
1	HCl	nd	nd	nd	[143,144]
2	H ₂ SO ₄ (3.0 M)	100	172	64-67	[145,146]
3	Pyr, HCl ^a	160	200	88	[147]
4	H ₂ SO ₄ (3.0 M), water-cyclohexane ^a	200	20	88	[148]
5	H ₂ SO ₄	1300 W	3	80	[149]
6	H ₂ SO ₄ , CF ₃ SO ₃ H, or PTSA	160	60	60-70	[151]
7	NaHSO ₄ , H ₂ O-dioxane ^a	210	90	74	[151]

8	Ti(SO ₄) ₂ , Zr(SO ₄) ₂	160	1	16-18	[154]
9	Acetic acid/HF (3 eq)	20	6 ^e	85	[154]
10	[TPMA][NTf ₂]-5% PTSA	200	10	61	[155]
11	Triflate Imidazolium (0.6 mol%)	130	nd	84	[156]
12	Nafion NR50/IL	180	nd	65	[157]
13	ZnCl ₂ (70%)	200	70 ^f	85	[158]
14	ZnCl ₂ (70%), H ₂ (4MPa) ^b	180	nd	95	[159]
15	CO ₂ (30 MPa), H ₂ O	200-250	7	8	[160,161]
16	Amberlyst 15 ^a	170	1.5	nd	[162,164]
17	Amberlyst 15	140	24	86	[162,164]
18	Amberlyst C200	135	20	55	[143]
19	Amberlyst 35 ^a	140	5	68	[163]
20	Amberlyst 70 (5 mol %)	115-145	4	72	[181]
21	Purolite CT 269 (5wt %)	140	12	75	[166]
22	Sulfonated silica type 1 (10 % molar)	170	2	71	[167]
23	Sulfonated silica type 1 (2 % molar)	120	10	84	[168]
24	Sulfonated mesoporous SBA-15	150	24	72	[169]
25	Sulfated latex-type polymer	150	4	nd	[170]
26	Sulfated titania oxide	180	2	65-70	[171,172]
27	Sulfated tin oxide	180	2	65	[173]
28	Sulfated copper oxide ^c	200	na	67	[174]
29	Sulfated zirconium	201	2	61	[175]
30	Sulfonated carbon catalyst	150	8	51	[178]
31	Sulfated carbonaceous solid	200	nd	67	[179]
32	Silicon-calcined PSSNa composite	140	6	88	[180]

33	Bi(OTs) ₃ (1.0 mol %)	115-145	4	67	[181]
34	Dowex acid resin/RuNPs ^d	190	nd	85	[182]
35	C/ nickel oxide	250	nd	27	[183]
36	SnPO, TiPO or ZrPO ^c	300	na	65	[184]
37	Cu-Ru, Cu-Pt or Ru-Cu	260	nd	71	[185-186]
38	[HNbMoO ₆]	160	60	nd	[187]
39	Phosphorylated nobium oxide	2-25	nd	63	[188]
40	Ta ₂ O ₅ /H ₃ PO ₄ , 225°C, 6 h	225	6	47	[189]
41	Boron phosphate	250	8	79	[190,191]
42	Zeolite	127-190	2	45	[192,193]
43	Metallic oxide supported HPAs	150	6	55	[195]
44	Silver exchanged phosphotunstic acid	140	1	82	[196]

^a microwave activation

^b directly from cellulose

^c under a flow solution of aqueous sorbitol

^d from glucose

^e days

^f minutes

6. Most recent and non-acidic alternative methods for isosorbide preparation

Among the chemical transformations of the major biosourced platform chemicals such as furanic compounds (5-HMF, furfural), glycerol and organic acids (lactic, succinic and

levulinic acids), new strategies have been devised for the synthesis of high-value chemical derivatives using dimethylcarbonate (DMC) under mild conditions [204]. A good example is the attempt for preparing various industrially relevant cyclic ether from polyols or butanediol starting materials. As shown in Fig. 10, the cyclization of a substituted 1,4-butane-diol is reliant on the versatility of DMC as a reagent. Initially, the methoxycarbonylation of a hydroxyl group on terminal carbon occurs by a B_{AC}2 (base catalyzed, bimolecular and acyl-oxygen fission ester hydrolysis) mechanism in presence of sodium methoxide (NaOMe) which is followed by an intramolecular cyclization through a B_{AI}2 (base catalyzed, bimolecular and alkyl oxygen fission ester hydrolysis) pathway, in which a methyl carbonate anion is released [204].

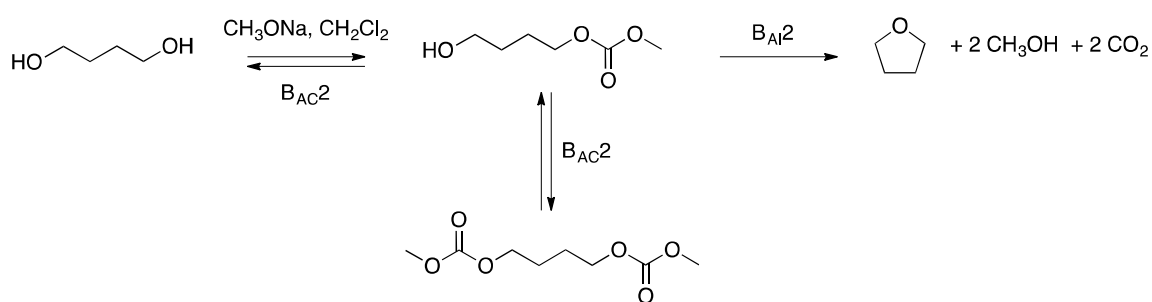


Fig. 10. Classic scheme for 5 five-membered furanic ring formation from 1,4-butanediol in presence of DMC and NaOMe.

The formation of mono- and dimethoxycarbonyl derivatives from a diol starting material is a thermodynamically controlled equilibrium reaction, whereas the intramolecular B_{AI}2 cyclization is kinetically driven. In fact, the direct conversion of the diol into cyclic ether or furanic derivatives by means of “DMC methodology” shows the advantage of being conducted without isolation of any intermediate namely sorbitan.

In case, when D-sorbitol, it was reacted with two equivalents of base and an excess of DMC, isosorbide formation ensued in relatively low yields, the explanation being that once

isosorbide is formed it could react once again with DMC leading to the formation of both methoxycarbonyl and methyl derivatives. However, when methanol was employed as the solvent, the reaction equilibrium got shifted towards the isosorbide preventing of the non-desired side reactions. Under these conditions, isosorbide was obtained in high yields and an excess of NaOMe allowed the one-pot double-cyclization that requires two equivalents of base for each cyclic ether produced.

Moreover, the B_{Al}2 mechanism reported here was not responsible of isosorbide isomerisation. Using 4 equivalents of NaOMe and 8 equivalents of DMC in MeOH, the yield of isosorbide formed was 98%. However, other bases have been explored in the literature, the first one being in presence of K₂CO₃ for the formation of isosorbide from sorbitol using 10 equivalents of DMC; base is relatively easy to handle compared to sodium methoxide [205]. The mixture is introduced in dioxane and heated at 90 °C. After purification, the yield of the reaction was limited to 42%. Another procedure was carried out without any solvent in presence of 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) as catalyst in stoichiometric amounts. The reaction was accomplished in methanol with 8 equivalents of DMC and heated up at 90 °C quantitative conversion of sorbitol was realized after 8 h delivering 98% of isosorbide yield [206].

As a recent alternative, Wang et al developed a new pathway involving the combination of a reticulated ammonium-type latex polymer and DCM [207]. Here, the polymer plays the role of a basic heterogeneous catalyst instead of DBU usually employed in the homogeneous strategy. The best performance is connected to both high porosity level and nitrogen contents. To obtain the maximum isosorbide yield, the reaction needs 8 equivalents of DCM and the mixture of sorbitol and DCM was stirred in presence of 200 mg of the catalyst at 140°C for 14 h to reach the complete conversion of the hexitol. The isosorbide yield reached a value of 83 %

7. Conclusions

Isosorbide could be easily produced from D-sorbitol by means of homogeneous acid under neat conditions of liquid-phase reaction. Due to its high solubility in both water and organic solvents, it appears to be difficult to develop an efficient biphasic system to extract and isolate the target compound from the catalyst. For homogeneous catalysts, strong acids with lower pKa values, as low as possible, afford the diol rapidly under mild conditions. Besides subcritical water preloaded with carbon dioxide seems to be a cleaner pathway and a good alternative to access isosorbide. Unfortunately, this method is high energy consuming process. In addition, microwave irradiation heating is not able to improve the normal isosorbide yield furnished by the conventional reaction, but it can easily accelerate the reaction by improving the relative reactions constant rates. For the use of heterogeneous catalysts, scientists have to consider two important equilibria to define their catalytic performance. The first one involves the hydrophilic-lipophilic equilibrium observed on the surface, responsible of the adsorption strength for each intermediate present in the medium. Indirectly it could influence and control the yields of both sorbitan and isosorbide. The second one entails the global amount of stronger and mild acid sites necessary to transform all monoanhydrosorbitan formed from the initial faster monocyclodehydrations. In our opinion, considering the increasing and challenging industrial needs, an effort could be made for developing innovative and process intensive systems based on continuous flow or microfluidic devices embedded with nanosized catalysts.

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