

## Recent advances in catalytic production of sugar alcohols and their applications

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Conversion of non-edible biomass into fuels and value-added chemicals has achieved great attention to cope the world's energy requirements. Lignocellulose based sugar alcohols such as sorbitol, mannitol, xylitol, and erythritol can be potentially used as emerging fuels and chemicals. These sugar alcohols can be converted into widely used products (e.g. polymer synthesis, food and pharmaceuticals industry). The heterogeneous catalytic production of sugar alcohols from renewable biomass provides a safe and sustainable approach. Hydrolysis, coupled with hydrogenation and hydrogenolysis has been proved to be more effective strategy for sugar alcohols production from biomass. This review summarizes the recent advances in biomass upgrading reactions for the production of sugar alcohols and their comprehensive applications.

**sugar alcohols, mannitol, xylitol, sorbitol, erythritol**

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### 1 Introduction

Demands for fossil based transportation fuel and chemicals would significantly increase in upcoming decades. The consequent environmental problems are becoming more serious [1]. Exploration of sustainable and green resources as feedstocks, instead of crude oil for the production of fuels and chemicals is extremely important [2]. As an alternative and environment friendly resource, the renewable lignocellulose biomass has received an increasing attention. Lignocellulose biomass consists of 40 wt%–50 wt% cellulose (polymer of glucose linked by  $\beta$ -1,4-glycosidic bonds), 16 wt%–

33 wt% hemicellulose (heteropolymer containing various different sugar monomers, mainly xylose) and 15 wt%–30 wt% lignin (deeply cross-linked, complex polymer with coniferyl, coumaryl and sinapyl alcohols as monomers) [3]. Due to the complexity of lignocellulose biomass and its high resistance to chemical transformation, the energy-efficient and cost effective preparation of liquid fuels and chemicals from lignocellulose are still challenging.

Lignocellulose biomass transforms into liquid fuels and chemicals through thermal, biological and chemical methods [3,4]. The whole biomass can be converted into liquid fuel precursors and synthetic gas by using thermal techniques, such as pyrolysis and gasification. However, thermal techniques still suffer from some disadvantages such as low selectivity and high energy consumption, which made it difficult to achieve the requirement of liquid fuel and chemical

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productions [5]. On the other hand, in the case of biological conversion of biomass, the compulsory losses of carbon and oxygen lead to low selectivities and desired products yield. Catalytic conversion of lignocellulose biomass using chemical methods showed good application prospects. In general, the feeding raw materials possess high oxygen contents (up to 50%) [6]. To achieve required C-skeleton of value-added chemicals, relatively mild reaction conditions with a high selectivity are required [6].

Sugar alcohols, including sorbitol, mannitol, xylitol and erythritol are vital chemicals with wide applications. The applications of these sugar alcohols in food, pharmaceutical, cosmetics and polymer industries have been widely reported [7]. Presently, sorbitol and mannitol can be synthesized through hydrogenation of fructose and glucose [8]; xylitol and erythritol can be prepared by conversion of xylose and glucose, respectively [5,7,9,10] (Scheme 1). New strategies for the valorization of these sugar alcohols have also been established. For instance, glycol was used to generate fuel-cells electricity [11]. Similarly, steam reforming process of glycol also produced hydrogen [12].

In this review, we concentrate mainly on recent advances in one-pot heterogeneous catalytic conversion of biomass to sorbitol, mannitol, xylitol, erythritol and their applications. Herein, the effect of functional supporting materials combined with noble or non-noble metals for the hydrogenation/hydrogenolysis reactions and their interactions under mild reaction conditions were studied.

## 2 Recent advances in production of sorbitol and mannitol from cellulose and their applications

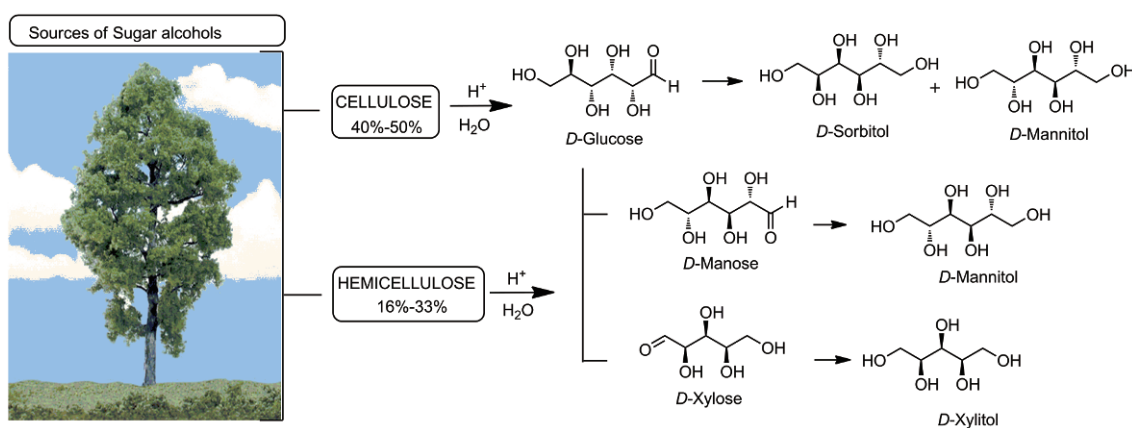
### 2.1 Sorbitol and mannitol

Sorbitol and mannitol are isomers, having same chemical formula ( $C_6H_{14}O_6$ ) and molecular weight (182.17 g/mol). Both

are non-cariogenic, odorless, diffuent and white crystalline powders. Compared with sucrose, sorbitol and mannitol show 60% and 50% relative sweetness respectively. Commercially sorbitol and mannitol are widely used compounds that have been used in food, pharmaceutical, and chemical industries as moisturizer, sweetener, softener, texturizer and dietetic food for diabetic patients. It can be used as platform molecules for the production of biofuel. In comparison with mannitol, sorbitol is regarded as one of top 12 important target chemicals which could be obtained from biomass [13].

Along with awareness regarding benefits to consumers, the global demand for sorbitol is continuously growing with 2%–3% annual increase [14]. According to annual report of 2015, the world's sorbitol production capacity has reached to 1.8 million tons per year and it is estimated that it will reach 2.34 million tons by 2020 [15]. Sorbitol holds a great market share which was valued in 8433.9 million US dollars (USD) in 2013 and expected to rise up about 15977.5 million USD by 2020 with a compound annual growth rate of 9.5% [15]. Similarly, mannitol is the second most abundantly used sugar alcohol and holds about 209.4 million USD market shares, which were valued in 2015 market analysis report [16]. China, US and Western Europe are the main producers of sorbitol and mannitol which cover about 50% requirements of the world [17].

Depending on agricultural resources, sorbitol and mannitol are mainly manufactured from cassava, corn and wheat, which all are from edible feed-stock. Alternatively, reforming the non-edible biomass to sorbitol via cost-efficient technology could not only fulfill the sorbitol demands but also will prevent the food shortage. Both of them can be synthesized through hydrolysis followed by hydrogenation of non-edible biomass materials such as cellulose. Universally, a large amount of agricultural and forestal raw materials are readily available for this purpose. Among the components of lignocellulose biomass, cellulose is the main part which can be widely converted into sorbitol and mannitol. Many catalytic systems and methods have been developed for the conversion



**Scheme 1** Route for nonstop conversion of biomass feedstock into sugar alcohols (color online).

of cellulose into sorbitol and mannitol through hydrolysis followed by hydrogenation. A series of homogenous and heterogeneous catalytic systems have been introduced for sorbitol synthesis, however, heterogeneous catalytic systems are more suitable for industrial applications. Herein, the heterogeneous catalytic conversion of biomass into sorbitol and mannitol in recent years is reviewed and summarized. Moreover, the advances in the applications of sorbitol and mannitol were specially emphasized.

The catalytic conversion of cellulose to sorbitol and mannitol is mainly carried out through two-step reactions, as shown in Scheme 1. First cellulose is hydrolyzed into glucose which could be further transformed into sorbitol through hydrogenation or mannitol through epimerization then hydrogenation [18,19]. The hydrolysis is catalyzed by acidic sites of catalysts while the hydrogenation is mostly carried out on metallic sites [20].

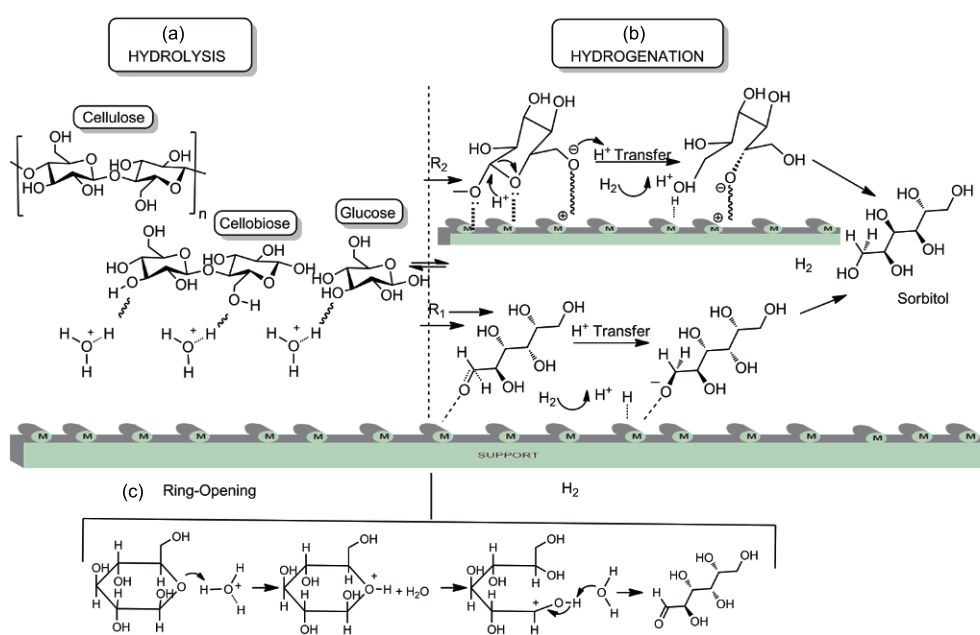
Generally, it is considered that the acid sensitive linkages i.e.  $\beta$ -1,4-glucosidic bond in cellulose molecule undergoes acid hydrolysis and breaks into shorter chain fragments (e.g. cellobiose) with the addition of water molecules. Later, glucose molecules form through successive hydrolysis of cellobiose [21]. Possible mechanism for this process is that glucosidic oxygen attaches or adsorbs on acidic site, then slow cleavage takes place by insertion of water molecule [21].

An understanding of mechanistic pathway for the conversion of glucose to sorbitol is reported by Zhang *et al.* [22], using Ru/MCM-41 as catalyst (**R2**, Scheme 2(b)). It has been suggested that  $H_2$  first absorbs and activates on the active sites of the catalysts, instead of reacting with carbonyl group of glucose. Consequently, glucose reacts with activated hydro-

gen ( $H^+$ ) on the catalyst surface (an irreversible process) and sorbitol has been formed as the final product in liquid phase. The whole mechanism for the hydrogenation of glucose on Ru/MCM-41 catalyst proceeds through dissolution and diffusion of hydrogen in the reaction medium, its absorption on catalyst surface followed by activation, and finally interaction with glucose's carbonyl group to produce sorbitol.

On the other hand, Zhang *et al.* [23], reported another mechanism for the conversion of glucose to sorbitol over 1.5 wt% Pt/SBA-15 catalyst (**R1**, Scheme 2(b)). *D*-glucose mostly exists in  $\alpha$  or  $\beta$  anomer and the ratio of open chain aldehyde form is less. As the sorbitol can only be obtained from open-chain aldehyde, which would be obtained via H-transfer to etheric-oxygen of glucopyranose ring followed by  $C_{(1)}-O_{(5)}$  cleavage shown in Scheme 2(c). Density functional theory (DFT) calculations also recommended the conformational changes, starting in water through deprotonation of anomeric  $-OH$  group, followed by H-transfer to etheric-oxygen atom [24,25]. Catalytic properties such as particle size and acid/metal balance [26,27] of catalyst were investigated for the synthesis of sorbitol. Chen *et al.* [27] synthesized a supported Ru-PTA/MIL-100(Cr) catalyst with specific acid sites through controlled loadings of PTA in MIL-100(Cr). Resultantly, the prepared bifunctional Ru-PTA/MIL-100(Cr) catalyst was used for the conversion of cellulose and cellobiose into sugar alcohols. In optimized conditions, sorbitol yields reached to 95% and 57.9% using cellobiose and cellulose as starting materials, respectively.

Pt-nanoparticle with smaller size showed higher selectivity for the conversion of *D*-glucose towards *D*-fructose. With a  $\eta^1O$  configuration, the weakly bonds towards electron-defi-



**Scheme 2** One-pot conversion of cellulose into sorbitol. (a) Hydrolysis of cellulose to glucose; (b) hydrogenation of glucose (aldose) to sorbitol on Pt/SBA-15 (**R1**) and hydrogenation of glucose ( $\alpha$  or  $\beta$  anomers) to sorbitol on Ru/MCM-41 (**R2**); (c) conversion of  $\alpha/\beta$ -anomer to aldose via ring opening.

cient Lewis acidic sites [28] on small Pt nano-particles are responsible for this isomerization. Moreover, DFT calculations also proved that hydrogen bonding to hydroxyls on Pt/silica surface is important in the mechanism of isomerization [29]. The models of glucose interaction with Pt catalyst are shown in Scheme 2(b) **R1**.

## 2.2 Preparation of sorbitol and mannitol over non-noble metal catalysts

It is crucial to study the non-noble metal based catalysts for low cost at large scale synthesis of sorbitol and mannitol. Recently, the cheaper non-noble metal catalysts such as nickel with different supporting materials (e.g. TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, ZnO, MgO, and ZrO<sub>2</sub>) have been found to be effective to convert cellulose into sugar alcohols (sorbitol and mannitol) [30]. The effect of Ni loading, its oxidation states and the presence of supporting materials on the conversion of cellulose, has been widely investigated. The above factors have significant influences on the catalytic activity and product distribution.

Liang *et al.* [31] developed a unique flower shaped highly effective Ni/ZSM-5 catalyst, which was tested for the hydrolytic hydrogenation of cellulose to sugar alcohols. A maximum portion (60%) of hexitols with high selectivity (i.e. 91.2%) of sugar alcohols was obtained using Ni/ZSM-5 catalyst. The high selectivity of this catalyst was imagined due to its flower like structure, with rich Ni (111) facet and possessing a strong metal-support interaction [31].

Activated carbon supported different nickel phosphide (Ni<sub>2</sub>P) catalysts were tested for the hydrogenation of cellulose in aqueous medium. During catalyst screening, the nickel phosphide (16% Ni<sub>2</sub>P/AC) was found to be the most active. About 92% cellulose was converted at 230 °C under 5 MPa H<sub>2</sub> pressure into 60% sorbitol and 4.5% mannitol. Interestingly, as the reaction temperature rises, phase changing occurs in the catalyst from crystalline to amorphous. High activity of catalysts attribute to attain the amorphous phase during reaction, however, leaching of P leads to low recyclability [32].

To increase the accessibility of active Ni-sites, carbon nanofiber supported Ni (Ni/CNF) with a specific morphology was fabricated, which held Ni nanoparticles on the tip of CNF. The fast-intermediate glucose hydrogenation was obtained possibly due to the entanglement of flower petals like CNF which surrounds the water-insoluble oligosaccharide matrixes. At optimum condition, 50% and 7% sorbitol and mannitol were produced respectively. In the same environment, ball-milled cellulose was mostly converted (92%) at 190 °C for 24 h with Ni/CNF treatment [33,34].

Van de Vyver *et al.* [35] generated 7.5 wt% Ni/CNF catalyst by chemical vapor deposition (CVD) of methane over Ni ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) followed by oxidization with HNO<sub>3</sub>. About 76% sugar alcohol yields were produced with this catalyst.

It showed 69% selectivity towards sorbitol and 13% towards mannitol respectively. These promising results depict the accurate selection of acidic surface oxygen-containing groups, which could accelerate the acid catalyzed hydrolysis. Meanwhile, the uniform dispersion of Ni also accelerates the hydrogenation reactions. Other non-precious transition metals (e.g. Fe, Co and Mo) were also supported on CNF and tested for the polysaccharide conversion to C<sub>4</sub> and C<sub>6</sub> sugar alcohols [33]. Under the same reaction conditions, some of the non-precious metal catalysts showed similar results for cellulose conversion with Ru based catalysts, which revealed the significant potential of non-precious metal catalyst for large scale production of sorbitol and other sugar alcohols. The main drawback of Ni based nano-catalysts comes from their sintering. This problem has been solved by increasing Ni content from 10% to 70% supported on carbon. Moreover, Ni crystalline form also explored significant effect over product [36]. In addition, by increasing the amount of Ni, paramagnetic character was also increased, which makes catalysts separation much easier after reactions.

Recently, Zhang *et al.* [37] fabricated a series of Ni catalysts with different combinations such as Al<sub>2</sub>O<sub>3</sub>, ZSM-5, SiO<sub>2</sub>, TiO<sub>2</sub>, kieselguhr and bentonite. Consequently, the catalysts were tested for the untreated microcrystalline cellulose (MCC) conversion. The highest yield of sugar alcohols was achieved over Ni/ZMS-5 catalyst, which reached up to 48.6% under optimized conditions. Strong acidic sites and three-dimensional microporous channel structure of ZSM-5 were proved to be responsible for the good performance. However, the zigzag channels of ZSM-5 with 0.53 nm×0.56 nm are not suitable for the diffusion and transport of large molecules such as cellulose and glucose (the length along the C<sub>1</sub> and C<sub>4</sub> axis for the glucose units of cellulose is 0.58 nm) [38]. To make this process possible, nano crystalline cellulose (NCC) was used as a hard template to control the pore structure and acidic sites in mesoporous ZSM-5 supports. A suitable mesoporous structured NCC-ZSM-5 supports were successfully synthesized and were further used for preparation of Ni/NCC-ZSM-5. This catalyst showed excellent catalytic performance, yielding 60%–79% C<sub>6</sub> sugar alcohols from cellulose.

## 2.3 Preparation of sorbitol and mannitol over bimetallic and noble metal based catalysts

The low yields of sugar alcohols (sorbitol and mannitol) were usually obtained over single-metallic non-noble metal catalysts. Basically, two reasons were accounted for such a low yield. First, the subsequent hydrogenolysis of C<sub>6</sub> sugar alcohols into C<sub>2</sub> and C<sub>3</sub> polyols [33], while the second reason is the rapid deactivation of catalyst due to metal leaching caused by hot and compressed water at 230 °C, which is

necessary for cellulose depolymerization. To solve this problem, collective studies were carried out by combining both precious and non-precious metals into a single catalyst. Furthermore, a series of Ni-containing bi-metallic catalysts such as Ir-Ni, Rh-Ni, Ru-Ni, Pt-Ni and Pd-Ni were supported on mesoporous carbon (MC) [39–41].

Good sorbitol (51.5%) and mannitol (8.3%) yields were obtained by Pang *et al.* [41] using Rh-Ni/MC catalyst. This catalyst can catalyze both hydrolysis and hydrogenation steps simultaneously. It was supposed that hydrolysis and hydrogenation have been facilitated by unique three-dimensional open structure of MC and by highly dispersed bi-metallic nano particles respectively.

Precious metal (Pt, Pd, Ru, Rh, and Ir) modified Ni/HZSM-5 catalyst surfaces with different chemicals and electrical properties were also fabricated and showed higher activity for cellulose hydrogenation. But these catalysts were quite inactive for hydrogenolysis of 1,2-propylene glycol and ethylene glycol. Comparatively a better hexitols yield (76.9%) was gained over Pt-Ni/ZSM-5 catalyst. This catalyst showed good stability and the yield was remained above 55% until completing the fourth cycle. So for the stable activity of this catalyst, the specific structure of Pt-Ni nano composite holding Pt-enriched alloy surface in hot water was considered to be responsible [40].

Moreover, high selectivity towards hexitols (82.7%) was achieved when Pt-SnO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> was used for the conversion of cellulose. The selectivity reported over this catalyst was double to that which was gained over Pt/Al<sub>2</sub>O<sub>3</sub> catalyst in the same reaction environment. It was considered that the electron shift from SnO<sub>x</sub> species to Pt at low Sn/Pt ratios of 0.1–1.0 is the main reason for this excellent performance [42].

The behavior of different mono and bi-metal based catalysts was examined for glucose hydrogenation. A product selectivity difference between mono and bimetallic catalysts has been observed. Glucose was proficiently hydrogenated into sorbitol with a selectivity of 100% over bimetallic Ru-Ni/MCM-48 catalyst. However, the selectivity towards sorbitol was observed from 93% to 95% when Ni/MCM-48 was used for hydrogenation. The minor decrease in selectivity was ascribed to the isomerization of sorbitol into mannitol [43,44].

Single noble metal supported catalysts were also investigated for the conversion of cellulose. A series of metals were loaded on reduced graphene oxide (RGO) and tested for the conversion of cellobiose and cellulose into sorbitol. Among this series, Pt loaded reduced graphene oxide (Pt/RGO) catalyst showed a remarkable activity. When cellobiose and cellulose were used for this process, high yields (91.5% and 58.9% for cellobiose and cellulose, respectively) of sorbitol have been achieved. The active catalytic performance of Pt/RGO was noticed when compared with different Pt/silica and Pt/carbon materials. The order of activities were found

as Pt/RGO>Pt/CNT>Pt>Pt/AC>Pt/SiO<sub>2</sub>>Pt/G. Furthermore, the small sized particles of catalysts were found to be more active compared to large sizes when the effect of particle size was investigated for the catalytic performance [45].

Ribeiro *et al.* [46] developed an activated carbon supported Ru catalyst (Ru/C) which was assessed for the conversion of cellulose to sorbitol. The conversion of microcrystalline cellulose reached to 36% in 5h, while 40% selectivity towards sorbitol was reported. Moreover, 90% conversion of ball-milled cellulose with 50% sorbitol selectivity was gained. The selectivity towards sorbitol was further enhanced upto 80% when the catalyst was ball-milled together with cellulose. Two reasons were counted for the increase in sorbitol selectivity. First, decrease in crystalline size and crystallinity of cellulose without affecting its degree of polymerization. While the second reason is the presence of catalysts throughout ball-milling in reaction medium for extended time [45,47].

Almeida *et al.* [48] prepared a bi-functional RuNPs/A15 catalyst by impregnating pre-manufactured Ru nanoparticles (RuNPs) with Amberlyst-15 (A15). Later, its catalytic activity for cellulose conversion was compared with 5% Ru/C and the mixture of 5% Ru/C and A15, respectively. It was revealed that the catalytic activity and the selectivity towards sorbitol were better over RuNPs/A15. More than 80% yield of sorbitol was obtained in 5h using this catalyst. They also studied the performance of acid functionalized SBA-15 materials (e.g. SBA-15-P-0.6, SBA-15-P-0.3, SBA-15-P-0.15, SBA-15-S-0.3) for cellobiose hydrolysis. It was found that all SBA-15 materials were severely suffered from leaching, which was mostly ignored in previous work especially for silica-based materials. It could result in deactivation by making the catalyst non-dispersible.

Recently, different meso- and micro-porous materials supported Ru catalyst were prepared and studied for the hydrolytic hydrogenation of cellulose [49]. Most of the catalysts showed an efficient conversion (>75%) of cellulose within 5h. The Ru/CNT showed comparatively more effective selectivity (60%) for sorbitol within 5h. When Ru/CNT was ball-milled with cellulose, similar selectivity was reported with complete cellulose conversion in only 1h. Moreover, the catalyst was also found to be stable during recycling experiments. To get rid of the successive purifying steps for sorbitol production, it is necessary to design heterogeneous catalyst which can handle the conversion of cellulose to sorbitol in single pot, which would reduce the purification processes. It might be possible by using excess metal loaded catalysts with a controlled acidity at high reaction pressure.

High hydrogen pressure has been verified to prevent the successive hydrogenolysis of glucose to ethylene glycol through the hydrogenation of C=O bond of glucose [50]. However, the problem mentioned in some studies is how

to decrease the isomerization of glucose and prevent the conversion of glucose into mannitol. In this regard, the most favorable result for the production of sorbitol was obtained by Ni<sub>2</sub>P/AC [20] and sorbitol was the main product. The difficulty in constraining the isomerization of glucose remains an obstacle to obtain high sorbitol yield.

## 2.4 Applications of sorbitol

Sorbitol shows a significant potential for the synthesis of numerous valuable chemicals. The presence of hydroxyl groups in sorbitol allows its further functionalization or direct processing via dehydration, hydrogenolysis or aqueous phase reforming reactions. Moreover, the sorbitol itself revealed wide applications. The important applications of sorbitol are summarized in the following part.

### 2.4.1 Dehydration of sorbitol into isosorbide

Isosorbide is a well-known important industrial chemical, normally produced by dehydration of sorbitol over strong acid catalyst. The dehydration of sorbitol into isosorbide includes two steps: (1) the cyclodehydration of sorbitol into intermediates 3,6-sorbitan and 1,4-sorbitan; (2) further dehydration of 3,6-sorbitan and 1,4-sorbitan into isosorbide (Scheme 3).

In initial stages, isosorbide was mainly prepared by homogeneous catalytic dehydration of sorbitol over various inorganic acids such as H<sub>2</sub>SO<sub>4</sub>, HF, and HCl at 20–140 °C. However, the separation and operating procedures of these homogeneous catalysts were hazardous and costly. In this regard, the heterogeneous solid acid catalysts were treated as potential alternatives to homogenous catalytic systems. A variety of heterogeneous catalysts have been discovered and showed obvious advantages for the industrial production of isosorbide in many aspects. Some zeolites modified metal oxides supported heteropolyacids, metal phosphates, ion-exchange resins and supported metal catalysts were prepared and studied [51].

Xiao *et al.* [52] studied the mesoporous polymer based cat-

alyst with SO<sub>3</sub>H groups for the dehydration of sorbitol in vacuum and got 88% yield of isosorbide. The high catalytic activity of P-SO<sub>3</sub>H was mainly attributed to the high porosity and super hydrophobicity of the catalyst. The catalyst showed an excellent stability, high yield of isosorbide (78%) was obtained after five recycles.

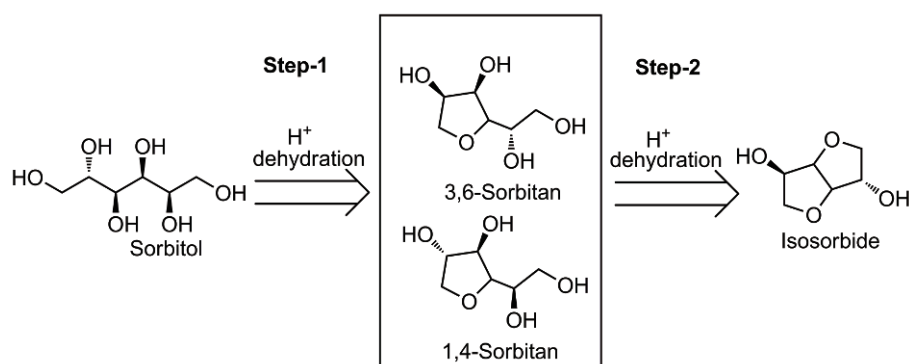
Fukuoka *et al.* [53] reported 76% yield of isosorbide over H $\beta$  zeolite catalysts that possessing a high ratio of Si/Al, under neat conditions. By optimizing various zeolite based catalysts, the H $\beta$  catalyst with a Si/Al ratio of 75 was unexpectedly discovered to be the most active for the dehydration of sorbitol.

Makkee *et al.* [54] produced high yield of isosorbide from cellulose in the presence of molten salt hydrates such as ZnCl<sub>2</sub>, CaCl<sub>2</sub>, and LiCl. These salt hydrates accelerate the reaction by solubilizing cellulose. An interaction established between the hydroxyl groups of cellulose and these ionic species which could help with breaking the hydrogen bonds.

Otomo *et al.* [51] studied the dehydration of sorbitol in aqueous phase by using different types of zeolite catalysts. The BEA-type aluminosilicate zeolite ( $\beta$ ) catalysts were disclosed with remarkable catalytic activity. Especially, the yield of isosorbide reached to 80% over the zeolite with a Si/Al ratio of 75. High catalytic activity was considered to be attributed to the three dimensional large pores structure and high hydrophobicity of zeolite catalysts.

A series of low cost catalysts were prepared by altering the loading amount of (3-mercaptopropyl) trimethoxysilane (MPTS) and named as sulfonic acid functionalized micro-bed silica (SA-SiO<sub>2</sub>) and tested for the dehydration of sorbitol to isosorbide. The SA-SiO<sub>2</sub> showed a good hydrophilic property and performance for the conversion of sorbitol to isosorbide.

The activity and selectivity of catalysts synthesized with different MPTS loadings were monitored and the SA-SiO<sub>2</sub> catalyst with 60.5% MPTS loadings was found to be the most active. When the reaction was carried out at 120 °C under vacuum for 10h, the conversion of sorbitol was 100% and the yield of isosorbide reached 84%. The catalyst showed good stability and can be recycled for 10 times without signi-



**Scheme 3** Dehydration of sorbitol to isosorbide.



ficant loss of activity. The excellent performance of SA-SiO<sub>2</sub>-60.5 might be due to its suitable large diameter, acidic nature and structural properties [55].

Moreover, the acidic and structural properties of various porous zirconium phosphate catalysts were investigated for sorbitol conversion [56]. Full conversion of sorbitol and a 73% selectivity towards isosorbide were obtained in 2 h at 210 °C. The porosity and acidic property of Zr-P catalysts might be responsible for its enhanced catalytic activity.

A cellulose based solid acid catalyst which comprises stronger Bronsted acid sites compared to conventional solid acid catalysts was also investigated for the conversion of sorbitol. 100% yield of isosorbide has been achieved at 200 °C for 1 h. Moreover, this catalyst can easily be prepared and reused for several times without significant loss in catalytic activity [57]. However, developing novel catalytic materials which can directly catalyze the conversion of cellulose into isosorbide is still necessary.

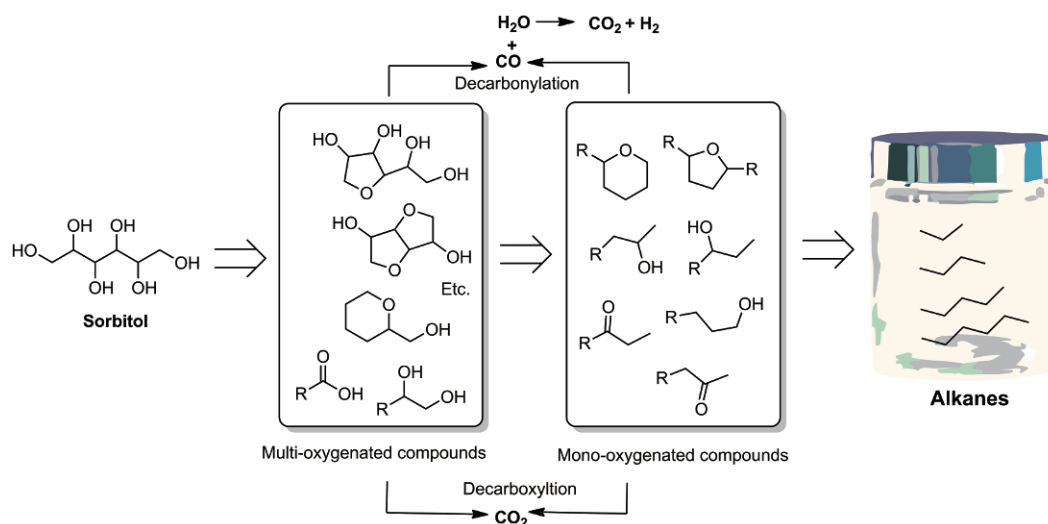
#### 2.4.2 Sorbitol to alkanes

The removal of oxygen from starting materials such as sugars alcohols is the inevitable step to get fuels. Lower molecular weights and high volatile products can be prepared through deoxygenation. According to the reported literature, H<sub>2</sub> and alkanes could be generated from methanol and ethylene glycol through aqueous phase reforming (APR) processes over supported noble metal catalysts [8]. The conversion of sorbitol into biofuel has a great significance for the concern of energy shortage. It can be an alternative source for energy and might replace fossil fuels and natural gas resources in the future. The catalytic mechanism for the synthesis of alkanes and H<sub>2</sub> (Scheme 4) through APR of sugar alcohols involves the cleavage of C–C, C–H and O–H bonds on the surface of catalysts. Group VIII metals such as Rh and Pd are suitable for the cleavage of such bonds [8].

In 2002 Dumesic *et al.* [12] reported that H<sub>2</sub> can be formed by the APR of sugar alcohols over Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, and a mixture of paraffin was produced in this process. The reaction system was complex due to side reactions. The selectivity towards alkanes and H<sub>2</sub> reached to 15% and 66%, respectively, and the selectivity of H<sub>2</sub> was improved by adding ethanol to the reaction system [58].

Among the non-noble metal catalysts, Raney Ni-Sn catalyst showed high selectivities for alkanes and H<sub>2</sub> which were 19% and 65%, respectively. It was shown that a cheap non-noble metal catalysts can be used instead of expensive Pt/Al<sub>2</sub>O<sub>3</sub> [59]. Subsequently, Zhang *et al.* [60] investigated the aqueous-phase transformation of sorbitol to isoparaffins in the presence of Ni/HZSM-5 catalyst. The effect of calcination temperature on the catalytic activity of Ni/HZSM-5 was studied. A remarkable higher activity was observed when the calcination temperature of the catalyst increased from 400 °C to 500 °C. The optimum selectivity of *i*-C<sub>6</sub>H<sub>14</sub> was 45.4% and the total yield of *i*-C<sub>6</sub>H<sub>14</sub> and *i*-C<sub>5</sub>H<sub>12</sub> was 32.3% [60]. In addition, the catalytic activity decreased when the calcination temperature increased to 700 °C [60]. A possible explanation for this phenomenon is the change of pore volumes and sintering of the catalyst at high temperature. In addition, the sintering of Pt in the presence of water and steam was first reported by Vilcoq *et al.* [61]. Metal dispersion was decreased in the presence of water even at room temperature [61]. Steaming pretreatment on Pt/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> was applied to increase the particle size of the catalyst which would prevent metal movement that caused sintering effects in hydrothermal environment.

Xi *et al.* [62] reported multifunctional Pt/NbOPO<sub>4</sub> catalyst for the production of alkanes through aqueous phase hydrodeoxygenation of sorbitol. It was concluded from the results that the maximum total yield of C<sub>6</sub> and C<sub>5</sub> alkanes was 60% at 250 °C under 4 MPa H<sub>2</sub>. Dehydration, hydrogenolysis



**Scheme 4** Catalytic conversion of sorbitol to alkanes (color online).

and cleavage of C–C bonds were carried out in this process. Isosorbide was produced as an intermediate which then went through ring opening and hydrogenolysis and finally produced hexane. Some other studies also reported the production of hydrogen from sorbitol [63], and indicated the importance of sorbitol valorization in different fields.

### 2.4.3 Sorbitol to glycols

Glycols, such as ethylene glycol (EG), 1,2-propylene glycol (1,2-PG) and 1,3-propylene glycol (1,3-PG) are very important industrial chemicals. These chemicals are extensively used for the manufacturing of polymers such as polyethers, polyester resins, and polyurethanes. Annually, more than 20 million tons of EG is used in petroleum industry [33]. Because of this importance, it is vital to achieve the production of glycols from sustainable sorbitol. The most broadly accepted mechanism for the conversion of sorbitol into glycols is the metal catalyzed dehydrogenation of sorbitol which passes through aldose intermediate (Scheme 5). This process can be accelerated by the addition of a basic promoter into the medium, which would facilitate the C–C bond cleavage by reducing the energy barrier and promote glycol selectivity through tuning up the retro-aldol condensation [64]. Calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) is the most common solid base promoter used in this reaction because it is partially insoluble in aqueous media [65].

Ru and Ni based catalysts are the most commonly used catalysts for the hydrogenolysis of sorbitol to glycols [66,67]. However, when nickel-based catalysts were used, high  $\text{H}_2$  pressure was required to attain the desired conversion rate. Therefore, Ru catalysts with low loading capacity in combination with alkaline medium are extensively used. Yet the applications of Ni based catalysts for the cleavage of C–C bonds are highly desirable [68].

Sohounloue *et al.* [69] reported a pioneering work by using  $\text{SiO}_2$  supported Ru catalysts. The effects of pH and temperature on the hydrogenolysis of sorbitol over Ru/ $\text{SiO}_2$  were studied. It was reported that in the basic medium, the hydrogenolysis of sorbitol goes through retro-aldol condensation reaction. Later, Ru supported on carbon nanotubes (CNT) and activated carbon (AC) were found to be quite

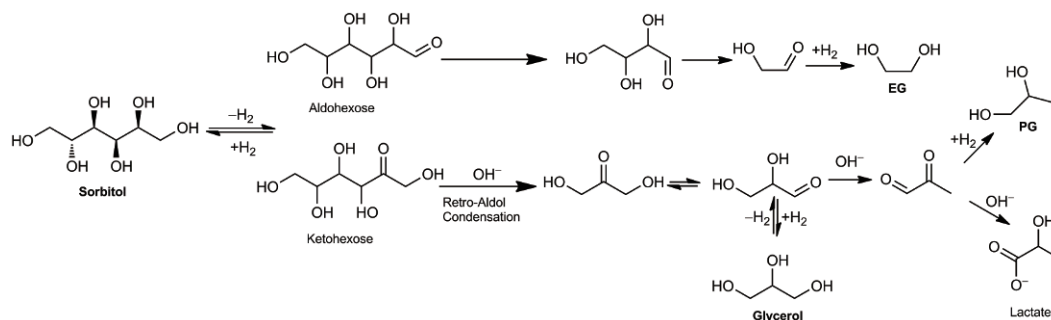
active for sorbitol hydrogenolysis, and the yield of glycols reached 43% under 8 MPa  $\text{H}_2$  at 493 K for 4 h.

Further, Leo *et al.* [66] studied the catalytic behavior of Ru metal supported on different metal oxides such as  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$  and  $\text{TiO}_2$  for the hydrogenolysis of sorbitol under base-free conditions. On optimization, the Ru/ $\text{Al}_2\text{O}_3$  catalyst was found to be the most suitable for glycerol synthesis. As most of the selected oxides (e.g.  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ , and  $\text{TiO}_2$ ) were neutral or acidic in nature, some basic oxides such as MgO were also tested as supporting materials. However, the basic oxide supported catalysts were not active. Meanwhile, leaching of the catalyst was observed during the reaction process. On the other hand, the reason for high activity of Ru/ $\text{Al}_2\text{O}_3$  catalyst was disclosed after its characterization. The presence of high surface acidity, partially oxidized Ru and high Ru/Al atomic ratio were considered to be responsible for the good yield and high selectivity of glycols.

Murillo Leo *et al.* [67] prepared and tested different Ru based catalysts for the conversion of sorbitol to glycols. A good yield of glycerol was obtained over  $\text{Ca}(\text{OH})_2$  supported Ru catalyst, which showed a better catalytic activity than alumina supported Ru catalyst where additional basic promoters were used [70]. Moreover, when Ni was introduced to  $\text{Ca}(\text{OH})_2$  supported Ru catalyst, a promoting efficiency was experienced. This phenomenon is possibly due to presence of Ni which facilitates the reduction of Ru by mutual interaction among both metals. A 40% yield of glycerol was obtained over NiRuCa catalyst for 4 h. However, this catalyst have lost its stability when it was used in a reaction medium which solubilized the  $\text{Ca}(\text{OH})_2$  during reaction.

Similarly, Jia *et al.* [71] found that the combination of carbon supported Ru clusters and  $\text{Ca}(\text{OH})_2$  could efficiently catalyze the selective hydrogenolysis of sorbitol to propylene glycol and ethylene glycol. Moreover, the Ru/C catalysts with identical particle size were found to be superior to many other metal oxides supported Ru catalysts [66]. Reaction conditions such as temperature,  $\text{H}_2$  pressure and the amount of  $\text{Ca}(\text{OH})_2$  shown strong effects on the activity of Ru/C and selectivity towards glycols.

Guo *et al.* [72] observed the catalytic activities of different functionalized CNTs (e.g. AMCN, CMCN, HMCN and NMCN,



**Scheme 5** Conversion of sorbitol into glycols.



where AM, CM, HM, and NM represents  $-\text{NH}_2$ ,  $-\text{COOH}$ ,  $-\text{OH}$  and nitrogen doping respectively) supported Ru catalysts for the hydrogenolysis of sorbitol. From the results, it can be concluded that mentioned functionalities act as a fastening of Ru metal particles and prevent it from sintering. In all cases, the Ru nanoparticles were well dispersed over CNTs while the acidity or basicity of the functional groups were found to be quite significant for the catalytic activity of sorbitol hydrolysis. In the presence of 6MPa hydrogen pressure and solid base promoter (NaOH), the conversion and selectivity of the hydrodeoxygenation reaction reached maximum at 210°C. The base promoters facilitate the dehydration and deoxygenation of sugar alcohols and restrained the production of methane. Among these catalysts, Ru/AMCN showed the best catalytic activity and selectivity towards glycols.

#### 2.4.4 Sorbitol as food

Sorbitol has broad applications in food industry. It is mainly used as a flavor in dried roasted nuts, chewing gum, pet foods, cured meat products, icing and toppings, coconut, beverages and dietary foods. Sorbitol is also considered as a nutritive sweetener as it provides 2.4–2.6 kcal/g nutritional energy. Because of its low calorific value and stability, sorbitol is widely used as a substitute of sugars and it does not cause dental caries [73]. It can also be used for the production of non-ionic surfactants, which provides an excellent stabilizing and emulsifying effects [74].

#### 2.4.5 Pharmaceutical applications

Sorbitol is a widely used medicinal excipient. The medicinal excipients help to protect the drug from impulsive degradation, inactivation and defend patients from undesirable pharmacological or immunological effects. As a part of drug formulation, sorbitol absorbs the surrounding humidity and modifies its crystalline state, which not only prevents the active ingredients but also keeps the hardness of tablets stable. There are seven reported crystalline states of sorbitol [75]. Two crystalline states are in hydrates form while five crystalline states are in anhydrous forms ( $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  and  $\epsilon$ ).  $\gamma$ -Polymorph is the most stable crystalline state which can be obtained by the crystallization of sorbitol [76]. Because of poor absorption in the small intestine and water absorption property, sorbitol can be used as a laxative material. In liquid formulation sorbitol can also be used as a plasticizer to generate gelatin and film [77]. In syrups, it is used to prevent crystallization around the bottles caps. Because of low calorie, sorbitol is also used in sugar free formulation for diabetics. Furthermore, due to protein stabilizing property, it can be used for stabilizing parenteral biological liquids. Sorbitol can also be used as a carrier to increase the dissolution rate of indomethacin [78]. In clinical analysis, sorbitol plays a vital role for analytical marker to detect the liver blood flow. It

can be independently used due to its fast hepatic and kidneys clearance. The plasma flow in liver can be easily estimated by usage of sorbitol, which can be well preserved even in liver disease [79].

### 2.5 Applications of mannitol

Mannitol is the second widely used sweetening and texturing sugar alcohol. It can be directly used in food materials to increase shelf life and taste. Crystalline mannitol is a low hygroscopic material and provides stability to the products in humid conditions. It has half sweetness to sucrose and has very low caloric value (1.6 kcal/g) than sucrose (4 kcal/g). Mannitol is practically insoluble in ketones, ethers and hydrocarbons while sparingly soluble in ethanol. Chemically mannitol is an inert material and mostly used in pharmaceutical formulations. It prevents the active ingredients from moisture absorption, provides excellent compressing properties and inert to active ingredients. Because of negative heat of solution, it provides a sweet cool taste that helps to mask unpleasant taste of many drugs [80]. Mannitol-boric acid complex is used for the preparation of dry electrolytic capacitors. Mannitol can be largely used in the synthesis of surfactants, resins and biofuels [81,82]. In medicine, mannitol is used as a powerful osmotic diuretic. It enhances the urination to prevent renal failure by removing toxic materials from the body [83]. It is also effective for reducing the brain swelling caused by head injury [84]. Hypertonic mannitol enhances the drugs transport across the blood-brain barrier for the treatment of acute brain diseases [85,86]. Mannitol hexanitrate is a common vasodilator which is applied for the treatment of hypertension [87]. It is also vital for the removal of hydroxyl radicals [88].

## 3 Xylitol

Xylitol is a five-carbon chain sugar alcohol having fewer calories compared to sucrose and it has been approved by US department of energy to be one of the top value-added chemicals which can be obtained from biomass [89]. It contains 40% fewer calories than white sugar and it is safe for diabetics. Xylitol is a natural sugar alcohol which is mostly found in plant materials such as vegetables and fruits. It is commonly used as sugar alternatives for the preparation of “sugar-free” edible materials such as mints, chewing gums and other candies. Xylitol is approved by several organizations and countries such as World Health Organization (WHO) [90], the U.S. Food and Drug Administration (FDA) and European Union (EU) [91] as component of food and medicines. Even though xylitol is a more suitable sweetener than sorbitol, but the latter one is more favourable as a sugarless sweetener in food and pharmaceutical industries

due to its low price and ease of manufacturing.

### 3.1 Preparation of xylitol from xylose and hemicellulose

Industrially, xylitol is synthesized by the hydrogenation of pure xylose, while xylose can be achieved through the acidic hydrolysis of hemicellulose biomass such as corn cobs or hardwoods [92]. The first report on the synthesis of xylitol through hydrogenation of xylose over RANEY<sup>®</sup>Ni catalyst was carried out in a three phase slurry reactor which has been published in 2012 [93]. But the major problem of this method was the deactivation of catalytic active sites. Furthermore, supported Pt and Ru catalysts such as Ru/HYZ, Pt/HYZ, Pt/C and Ru/C were also reported for the efficient conversion of xylose into xylitol [94,95], but multistep processes are carried out which start from synthesis of xylose by acid decomposition of hemicellulose biomass followed by catalytic hydrogenation of xylose to obtain xylitol. After the acid decomposition of hemicellulose, the produced xylose needs to be isolated and removed from the mixtures, then an additional catalytic hydrogenation of xylose to xylitol is required at high temperature and H<sub>2</sub> pressure (e.g. 50 atm). This whole chemical process is difficult, costly, energy consuming and unpromising to environment. Only 50%–60% hemicellulose in raw biomass could be converted to xylitol by using this process.

For the consideration of economy and environment, a novel and friendly synthesis route of xylitol has been designed. Instead of multistep process which underwent through separated hydrolysis and hydrogenation steps, the one pot conversion of cellulose/hemicellulose to sugar alcohols by single step has been broadly studied and well acknowledged [96]. In most of the previous reports, the acid-transition metal or bi-functional catalytic systems were used for the hydrolysis and hydrogenation of cellulose to sugar alcohols in presence of high H<sub>2</sub> pressure [96].

Fukuoka *et al.* [97] reported the one pot production of sorbitol using alcohols as H<sub>2</sub> source over simple activated carbons and 0.012% HCl. Inspired by the work of Fukuoka *et al.*, Yi *et al.* [96] settled a one-pot procedure for selective conversion of hemicellulose to xylitol and obtained 81.8% yield of xylitol in 3 h using isopropanol as a hydrogen source instead of high-pressure H<sub>2</sub> over Ru/C catalyst. However, in this process a small amount of acid as additive was essential to convert hemicellulose into xylitol. However, the xylitol yield was only 5.7% without adding any acid additives.

Hernandez-Mejia *et al.* [98] studied the influence of different crystal structures of TiO<sub>2</sub> material supported Ru catalysts on the selective conversion of xylose to xylitol. Like, it was observed that Ru/TiO<sub>2</sub> catalyst designed by supporting Ru metal over rutile titania showed effective hydrogenation and selectivity. However, Ru metal supported on anatase TiO<sub>2</sub> was not proficient for this reaction. The reasons behind this

difference in activity were explained by transmission electron microscope (TEM) analysis. The Ru nanoparticles of 5–7 nm were found to be well dispersed over the surface of rutile-TiO<sub>2</sub>. However, the Ru particles were bulkily agglomerated on anatase-TiO<sub>2</sub> support. This phenomenon can be well explained by highly lattice matching of rutile-TiO<sub>2</sub> and RuO<sub>2</sub> structures, which prevent the mobility of Ru particles during heating treatments. In general, well dispersed metal particles on the surface of supporting materials provide more active sites for hydrogenation, which improves the charge transfer with supporting materials and facilitates the reduction of superficially oxidized Ru particles. On the other hand, the possible formation of Ti<sup>+3</sup> species [99] on anatase-TiO<sub>2</sub> may act as a Lewis base which will divert the reaction pathway.

Liu *et al.* [100] also reported the one-pot conversion of hemicellulose (xylan) into xylitol in biphasic solvent system and obtained 79% xylitol yield in 12 h at 200 °C under 60 bar hydrogen pressure over Ir-ReO<sub>x</sub>/SiO<sub>2</sub> catalyst along with H<sub>2</sub>SO<sub>4</sub>. He studied the effect of acid concentration on the production of xylitol and it was found that the xylitol yield increased with the dosage of acid in a range of 10–30 mg. It was supposed that increasing the acid quantity favors the hydrolysis. However, reduced yield of xylitol was observed by adding more acid which was possibly due to the further hydrogenolysis of xylitol. The performance of Ir-ReO<sub>x</sub>/SiO<sub>2</sub> was also compared with different commercially available precious metal catalysts such as Pt/C, Ru/C, Pd/C and Rh/C in the same reaction environment. However, Ir-ReO<sub>x</sub>/SiO<sub>2</sub> showed higher yield of xylitol than other catalysts (detailed information of different catalytic systems are shown in Table 1). This simple one-pot conversion of hemicellulose process has been recommended as an economical and energy proficient method for commercial manufacturing of xylitol.

Ribeiro and co-workers [105] proposed one-pot conversion of corncob xylan (hemicellulose) into xylitol over Ru/CNT catalyst. The xylitol yield reached to 46.3% in 45 min without using any acid. Catalyst showed sufficient stability and was used for four times without major loss in activity. Since cellulose is the major component of biomass, its presence could possibly influence the xylitol yield by forming other products, its effect on the conversion of xylan and selectivities of product distribution were examined. A 60% yield of xylitol was obtained in 1 h, which indicates that there was no major influence of cellulose presence on reaction process. Furthermore, a combined experiment on cellulose and hemicellulose was also carried out over Ru/CNT catalyst. After a 3 h reaction, increased yields of sorbitol (77%) and xylitol (48%) were obtained. In the case of ball-milling of catalyst together with cellulose and hemicellulose, the selectivities of sorbitol and xylitol were further increased to 81% and 57%, respectively.

Recently, Dietrich *et al.* [106] used commercially available Ru/C catalyst in combination with different heteropoly acids

**Table 1** Different heterogeneous catalytic systems for the synthesis and further conversion of sugar alcohols

Substrate <sup>a)</sup>	Catalyst <sup>b)</sup>	Reaction condition <sup>c)</sup>	Products and yield <sup>d)</sup>	Ref.
Cellulose	16% Ni <sub>2</sub> P/AC	225 °C, 6 MPa, 1.5 h	SOR (48%), PG (8%), 1,2PG (2.2%), MAN (4.7%), XYL (1.7%)	[20]
BMC	16% Ni <sub>2</sub> 6P/AC	230 °C, 5 MPa, 40 min	SOR (62.0%), MAN (4.5%), ERY (1.3%)	[32]
MCC	Pt-SnO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	200 °C, 6 MPa, 0.5 h	SOR+MAN(selectivity 82.8%)	[42]
BMC	Ni/C	210 °C, 5 MPa, 6 h	SOR (57%), MAN (6.8%), PG (1.7%), EG (8%)	[36]
MCC	Ru/[Bmin] <sub>3</sub> PW <sub>12</sub> O <sub>4</sub>	160 °C, 5 MPa, 24 h	SOR (yield.45% Selectivity 70.3)	[101]
MCC	Ni/NCC-ZSM-5	240 °C, 4 MPa, 2.5 h	SOR and MAN (60%)	[37]
Cellulose	1% Rh-5% Ni/MC	245 °C, 6 MPa, 30 min	SOR (51.5%), EG (5.3%), PG (3.5%), ERY (3.4%), MAN (8.3)	[41]
MCC	1% Pt-17% Ni/ZSM-5	240 °C, 4 MPa	SOR & MAN (76.9%), EG (2.3%)	[40]
Cellulose	4% Ru/MCM-48	200 °C, 5 MPa, 6 min	SOR (41.8%), MAN (6.7%)	[43]
D-glucose	Ru:Ni/MCM-48	130–140 °C, 2.5 MPa, 1.5 h	SOR (Selectivity 100%)	[44]
Cellulose	Pt/RGO-433	190 °C, 5 MPa, 24 h	SOR (58.9%), MAN (10.1%)	[45]
Cellobiose	Pt/RGO-433	190 °C, 5 MPa, 3 h	SOR (91.5%)	[45]
Cellulose	0.4% Ru/AC	205 °C, 50 bar, 5 h	SOR (80%), MAN (4.6%)	[46]
Cellobiose	3% RuNPs/Al <sub>2</sub> O <sub>3</sub>	150 °C, 40 bar, 5 h	SOR (80%)	[48]
Sorbitol	P-SO <sub>3</sub> H	140 °C, 0.1 bar, 10 h	ISO (87.9%)	[52]
Sorbitol	ZSM-5(40)	200 °C, 2 h	ISO (80%)	[51]
Sorbitol	Cellulose-SO <sub>3</sub> H	200 °C, 1 h	ISO (67%)	[57]
Sorbitol	Zr-p	210 °C, 2 h	ISO (73%)	[56]
Sorbitol	SA-SiO <sub>2</sub>	120 °C, 10 h, vacuum	ISO (84%)	[55]
Sorbitol	Ni/ZSM-5(Cal:500)	240 °C, 4.0 MPa, 1 h	<i>i</i> -C <sub>6</sub> H <sub>14</sub> and <i>i</i> -C <sub>5</sub> H <sub>12</sub> (32.33%)	[60]
Sorbitol	Pt/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	240 °C, 36 bar	H/C (27%), Oxy./Comp. (29%), CO <sub>2</sub> (35%)	[61]
Sorbitol	Pt/NbOPO <sub>4</sub>	250 °C, 4 MPa, 12 h	HEX (55.9%), PEN (4.8%), ISO (5.3%)	[62]
HEM	Ir-ReO <sub>3</sub> /SiO <sub>2</sub> +HZSM-5+H <sub>2</sub> SO <sub>4</sub>	190 °C, 24 h	<i>n</i> -C <sub>5</sub> H <sub>12</sub> (70%)	[100]
Sorbitol	Pt-Ir-ReO <sub>3</sub> /SiO <sub>2</sub>	0.5 MPa, 453 K, 24 h	Gasoline-ranged products (42%)	[102]
Sorbitol	Ru/C (DBR)	<b>R1:</b> 140 °C; <b>R2:</b> 250 °C, 4 MPa	C <sub>6</sub> H <sub>14</sub> (38.8%), C <sub>5</sub> H <sub>12</sub> (44.1%)	[103]
Sorbitol	Ru/Ca-HT	220 °C, 4 MPa, 4 h	Glycol (46%)	[67]
Sorbitol	Ru/C	200 °C, 4.0 MPa, 1 h	EG (20.8%), PG (27.3%)	[104]
HEM	0.4% Ru/CNT	205 °C, 50 bar, 1 h≤	XYL (60%)	[105]
HEMM	Ru/C+HPA	140 °C, 20 bar, 3 h	XYL (70%–82%)	[106]
HEM	Ir-ReO <sub>3</sub> /SiO <sub>2</sub> +H <sub>2</sub> SO <sub>4</sub>	140 °C, 12 h	XYL (79%)	[100]
Ar-XYL	Ru/USY	160 °C, 5 h	C <sub>5</sub> (90%)	[107]
Arabitol	S-Ru:Ru	240 °C, 10 MPa, 75 min	ERY (10.1%), GLY (10.3%), XYL (6.4%), MAN (7.8%), SOR (6.7%)	[70]
Xylose	5% Ru/C	138 °C, 6 bar, 24 h	C <sub>5</sub> (20%)	[10]

a) HEM: hemicellulose; Ar-XYL: arabinoxylan. b) Cellulose-SO<sub>3</sub>H: cellulose-derived solid acid catalyst; Zr-p: porous zirconium phosphate; Cal:500: calcinated at 500 °C; HPA: hetero poly acid. c) **R1&R2**: duel bed reactor (DBR). d) SOR: Sorbitol; PG: propylene glycol; MAN: mannitol; XYL: xylitol; ERY: erythritol; ISO: isosorbide; EG: ethylene glycol; GLY: glycerol.

for the one pot conversion of hemicellulose to xylitol. Among these acids, phosphotungstic acid, silicotungstic acid and lactic acid can enormously enhance the hydrolysis step. However, phosphomolybdic acid did not show enough efficiency. When phosphotungstic acid or lactic acid was used in combi-

nation with Ru/C in presence of H<sub>2</sub> as reductant, 70% yield of xylitol was obtained. But when isopropyl alcohol was used as the hydrogen source, a higher yield (82%) of xylitol was obtained over phosphotungstic acid and the yield was decreased to 20% when lactic acid was used. This decrease in yield was

possibly due to the occurrence of side esterification reaction. The yield was further improved to 90% by using bifunctional Ru/USY catalyst [107].

## 3.2 Application of xylitol

### 3.2.1 Food and bakery industry

In food industry, xylitol is used to improve shelf life, taste, and color of food products [108]. Similarly, it is also one of the components in sugar free chewing gum, chocolate, hard candies, pastilles and sweets for diabetics. The sugarless pectin jellies are produced from xylitol through hydrogenation of starch hydrolysates. Because of rapid sweetness and good crystallization properties, sugar free chewing gums and coated chewing pellets are extensively synthesized from it. Likewise, in many countries xylitol is one of the ingredients in confectioneries, gum arabic pastilles, ice cream fillings and other sweets as mentioned above. Xylitol also gives a characteristic flavor and color to bakery products. Xylitol was proved to be a good substitute for sugar cakes and can give a pleasant mouth feeling, excellent texture and color [109].

### 3.2.2 Pharmaceutical industry

Xylitol is employed as a sweetener (for diabetic patients) and excipients in pharmaceuticals. Similarly, it is also an important constituent in tonics, cough syrups and vitamin because it can neither ferment nor mold. Furthermore, xylitol is a chemically inert substance, therefore, it neither undergo maillard reactions nor react with other excipients or pharmaceutically active ingredients [110]. The chewing gums containing xylitol have been shown to protect the children's ears from infection [111]. In medicines, xylitol acts as a hardener, sweetener and carrier [112]. Efficient reduction of streptococcus mutants in saliva has been observed using xylitol containing paste [113]. Due to its whole promising effects on dental health, xylitol has also been useful in oral care products, such as mouth rinses [114].

## 4 Erythritol

Erythritol is a C<sub>4</sub> sugar alcohol, mostly found as a food ingredient and it shows similar properties to other sugar alcohols like xylitol, sorbitol, maltitol, mannitol, lactitol and isomalt [115]. Erythritol is well distributed in nature [116], mostly occurs as a metabolite or storage compound in fruits like grapes, melons, pears, seaweed and fungi. The fermented food, such as beer, wines and processed vegetables also possesses a certain amount of erythritol. Because of substantial negative heat, erythritol provides a strong cooling effect when it is dissolved in solution [117]. Erythritol is a low-calorie sweetening agent, it has no bitter aftertaste. To improve the aftertaste it can be combined with intense sweeteners such as aspartame [118].

Currently commercial scale production of erythritol is based on fermentative conversion of glucose upon osmophilic yeast such as *Trichosporon* sp., *Moniliella* sp., *Torula* sp., *Aureobasidium* sp. or *Pseudozyma tsukubaensis*, which are *Trichosporonoides megachiliensis* SN-G<sub>42</sub> yeast [118]. Erythritol can also be isolate from glycerol using *Yarrowia lipolytica* yeast [119].

Although the fermentation process shows a good industrial application for erythritol synthesis, however, it is deemed to be a time-consuming process. As maintenance of carbon balance is difficult during this process. On the other hand, the heterogeneous catalytic fast conversion of biomass based cellulose and carbohydrates into valuable sugar alcohols such as erythritol with high yields is a favorable route.

### 4.1 Synthesis of erythritol from pentose sugars

Since the pentose sugars (arabinose, xylose) are non-digestible biomass based molecules, they would not compete with human food. So pentose sugars are the fascinating alternative precursors for producing C<sub>4</sub>-sugar alcohols (e.g. erythritol). The feedstocks which possess pentose sugars are xylan rich materials such as straw and wood residues while arabinan is abundantly present in citrus or sugar beet pulp [120]. The most efficient route for the synthesis of erythritol from pentose sugars is selective cleavage of C–C bond. In principle, there are two routes for C–C cleavage, including the decarbonylation route which is carried out over homogeneous catalysts and the heterogeneous catalytic cracking of C–C bonds in the presence of hydrogen. In general speaking, the heterogeneous catalysts show poor selectivity towards C–C cleavage [10].

Ru and Rh based catalysts were the prior homogeneous catalytic systems reported for the decarbonylation of sugar with high selectivities (70%–80% isolated yield) [121]. Unfortunately, high boiling solvents were needed for these homogeneous catalytic systems to dissolve both catalysts and sugars. Especially they are sensitive to air and moisture which make them unfavorable for the conversion of biomass. In addition, the separation of products from reaction mixture is also hazardous and energy consuming. To avoid these problems, the conversion of pentose sugar should be carried out over heterogeneous catalysts.

### 4.2 Heterogeneous catalytic systems

Heterogeneous catalytic hydrogenolysis of carbohydrate is a complex process. It is carried out through a series of reactions such as isomerization, (de)hydrogenation, retro-claisen, retro-aldol and decarbonylation reactions (Scheme 6) [10]. To understand the influence of these different reaction pathways on product distributions, it is necessary to explain these reaction pathways first. Since the retro-aldol reaction is carried out through enolates, the carbonyl functional group





geneous catalytic C–C bond cleavage of carbohydrates, however very few attentions have been paid on selective C–C bond cleavage to produce erythritol. Among the few publications, Deutsch *et al.* [70] reported the transformation of several carbohydrates over Ru/C (sulphur modified) catalysts. By studying the structure of resulting products, it was noted that the terminal C–C bond cleavage is dominated by decarbonylation route. It has also been investigated that retro-aldol reactions do not effectively take part in C–C bond cleavage. In violent (205–240 °C/100 bar H<sub>2</sub>) reaction conditions, severe hydrogenolysis can happen to long chain of molecule, which reduces the selectivity and yield of erythritol/threitol.

Fabre *et al.* [128,129] reported the reduction of arabinonic acid to arabitol over various metals (e.g. Pd, Pt, Ru) supported on C, HY and TiO<sub>2</sub>. Although C<sub>4</sub>-alcohols were not their desired products and have not been investigated, it was observed that some amount of tetrityls (erythritol: 0.1%–4.3% and threitol: ~0.1%) have been produced over Ru based catalysts. Higher yields of C<sub>4</sub>-alcohols (erythritol and threitol) were obtained when the reaction conditions were further optimized (140 °C). Under such reaction conditions, C<sub>2</sub> and C<sub>3</sub> products were not formed. Due to the low temperature, the retro-aldol reactions would not be carried out.

Sun *et al.* [130] studied the conversion of xylitol to propylene glycol (PG) and ethylene glycol (EG) under different temperature (160–240 °C) and H<sub>2</sub> pressure (0–100 bar). Different carbon supported catalysts (Pd/C, Pt/C, Ru/C, and Rh/C) and Ru supported on different supporting material (e.g. Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, Mg<sub>2</sub>AlO<sub>x</sub> and ZrO<sub>2</sub>) were investigated. Only 7% yield of C<sub>4</sub>-sugar alcohols (erythritol/threitol) was obtained over Ru/Mg<sub>2</sub>AlO<sub>x</sub> catalyst at 200 °C under 40 bar H<sub>2</sub>. The selectivity towards PG, EG, and C<sub>4</sub>-sugar alcohols was dependent on the supporting materials. It could be concluded that the selectivities towards PG and EG were observed in the following order: C<TiO<sub>2</sub><ZrO<sub>2</sub><Al<sub>2</sub>O<sub>3</sub><Mg<sub>2</sub>AlO<sub>x</sub>. However, Ru/Mg<sub>2</sub>AlO<sub>x</sub> showed the highest selectivity towards C<sub>4</sub>-sugar alcohols.

Van der Klis *et al.* [10] reported the selective terminal C–C scission of C<sub>5</sub>-carbohydrates for the production of C<sub>4</sub>-tetrityls (erythritol and threitol) over 5%Ru/C catalyst. High selectivities (20%–25%) of C<sub>4</sub>-tetrityls were elucidated under relatively mild conditions (138 °C, 6 bar H<sub>2</sub> and 24 h). As previously mentioned [128,129], the low temperature (<180 °C) and hydrogen pressure (<60 bar) was helpful to suppress the retro-aldol reaction and lead to the formation of C<sub>4</sub>-sugar alcohols through selective C–C bond cleavage.

#### 4.4 Applications of erythritol

Erythritol is worldwide consumed as a food sweetener. In US, the daily dosage of erythritol is estimated to be 80 mg/person [131]. Erythritol is a non-cariogenic sweetener and has

been used in many countries. The erythritol ingredient in food stuff was differently labeled in different countries [132,133]. Like in EU and Japan, it is labeled as zero-calorie [132]. The reported data show that the intake of erythritol does not have any adverse effects on humans under the recommended conditions. The present metabolic study shows that erythritol is readily absorbed in human body and without any metabolism, it can be quickly excreted [134].

Moreover, erythritol is present in our diet either endogenously or supplement exogenously. Both clinical and animal toxicological studies proved that consuming more erythritol than the expected daily usage does not have any negative effect. Erythritol is deemed to be a commonly known and safe sweetener [131] based on its available food safety data record and its bulk use.

Erythritol has always been a part of the human food, as it naturally exists in fruits such as melons, pears and grapes, as well as in fermentation-derived foods such as soy sauce, wine, cheese, and mushrooms [135]. Erythritol has been industrially synthesized since 1990 and it is used in beverages and food to deliver sweetness, taste and quality [136]. Generally, erythritol has been used as flavor, humectants, nutritive sweetener, enhancer, formulation aid, stabilizer, thickener, sequester and texturizer. In most occasions, erythritol is preferred as a low-calorie sweetener [131,137]. Erythritol has a high solubilization enthalpy of 23.3 kJ/mol, thus it gives a strong cooling effect when it is ingested [138].

Erythritol is favored over other sugar alcohols for the following advantages: (1) it shows very low or no glycemic response; (2) it can be achieved by renewable biomass with well-established foods chain; (3) it does not cause gastric distress or flatulence [138].

Erythritol can be applied as a bulk sweetener in chewing gum, beverages, confectionery, and bakery products due to its ability to keep low glucose levels in blood by increasing insulin secretion. The structural properties of erythritol are similar to mannitol, a well familiar antioxidant. Yokozaka *et al.* [139] examined the effect of erythritol on oxidative stress and glucose metabolism in diabetic rats. The erythritol showed a beneficial effect in lowering glucose level in serum even at its highest dosage i.e. 15%. Furthermore, its high dosage level does not cause hepatic and renal issues. It is proved that erythritol acts as OH-radical scavenger and inhibitor of diazo compound-induced erythrocyte damage. It was also investigated that endothelial functions remained unaffected and the erythritol was excreted in urine along with other oxidative metabolites. Erythritol acts as an antioxidant and can help to protect against vascular damage caused by hyperglycemia [140]. Whereas, the other sugar alcohols have the clear drawback of causing digestive distress. The scientific reports showed that erythritol has no any laxative effect at specific dosage levels. The main factor of digestive tolerance of erythritol is due to its smaller molecular size. The

small molecular size facilitates its fast absorption in the upper digestive tract [141].

## 5 Conclusions

The conversion of biomass into value-added chemicals and biofuel is a promising technology that can link the traditional (fossils) refinery and renewable sources. The use of catalytic technology will facilitate the hydrolysis and hydrogenation of renewable feedstock. This review has been initiated in the scope of direct conversion of biopolymers like cellulose and hemicellulose to polyols such as sorbitol, mannitol, xylitol, erythritol, and their derivatives, such as isosorbide, glycols, alkanes. Aforementioned sugar alcohols are important chemicals which are extensively utilized in food, pharmaceutical, and chemical industries as moisturizer, sweetener, softener, texturizer, food for diabetic patients etc. Various supported noble and non-noble heterogeneous catalysts have been developed for the conversion of cellulose and hemicellulose into sugar alcohols. Sorbitol can be produced in a large quantity from sugars which can be further converted into valuable chemicals, such as isosorbide, alkanes and glycols, respectively. This process is mostly carried out over different acid and base functionalized porous Ru, Pt and Ni catalysts etc. The catalytic features of these catalysts such as pore size, surface area, and the reaction condition greatly influence both the selectivities and yields of corresponding derivatives. Recent improvements have been observed in selective production of xylitol and erythritol over heterogeneous catalysts. Furthermore, the reported results are encouraging to be applied for large scale preparations. Though, some advances need to be thought to accomplish the global requirements.

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**Conflict of interest** The authors declare that they have no conflict of interest.

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