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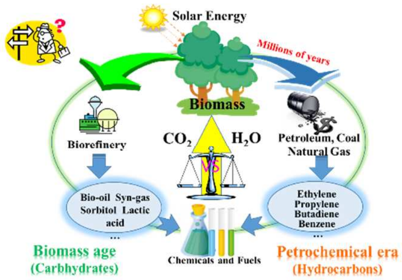

This review summarizes recent advances of biomass upgrading for the polyol production with emphasis on the formation of glycols.

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REVIEW

Recent advances in the production of polyols from lignocellulosic biomass and biomass-derived compounds

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Conversion of renewable, non-edible and resource-abundant lignocellulose to fuels, chemicals and materials has received significant attention for it holds the possibility of carbon neutral technologies as an efficient way to combat global changes. Considering the relatively high oxygen content in cellulose, it is more desirable to be transformed into oxygenated chemicals rather than hydrocarbon fuels in view of the atom efficiency. Among the oxygen-rich chemicals from biomass, polyols, such as ethylene glycol and propylene glycol, are widely used in polymer synthesis, food industry and pharmaceutical manufacture. Hydrolysis, coupled with hydrogenation and hydrogenolysis serves as an effective approach to transform biomass to polyols. This review summarizes recent advances of biomass upgrading reactions for the production of polyols with special emphasis on the formation of glycols.

1. Introduction

The production of chemicals highly depends on non-renewable fossil resources such as petroleum, coal, and natural gas in modern society. However, the decreasing of fossil fuel reserves, along with the growing demand for new energy consumption in the future and the concern on greenhouse gas emissions, is motivating researchers to explore alternative energy that can avoid these issues.[1, 2] The biomass energy, which have been directly acquired *via* combustion to produce heat for thousands of years, has been recalled for its sustainability and enormous reserves (Fig. 1).[3, 4] Cellulose, mainly from agricultural and forestry residues, is one of the world's largest organic raw material resources (nearly 40 billion tones nature renews every year).[5] Different from starch, human's main food source, cellulose cannot be digested by humans and the utilization of cellulose will not impose negative impacts on the food supply. Therefore, cellulose is regarded as a promising resource that can be transformed into fuels and chemicals in the future.[6]

Transformation of biomass to chemicals and fuels is generally achieved by thermal, biological, and chemical methods.[6-8] Thermal techniques such as pyrolysis and gasification can take full advantage of the entire organic substance and transform

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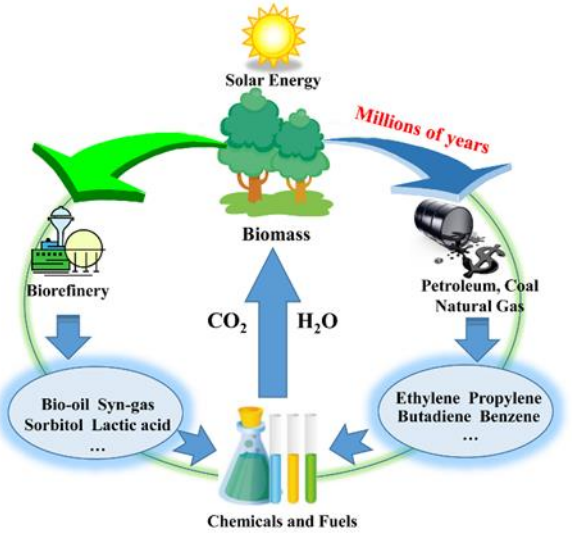


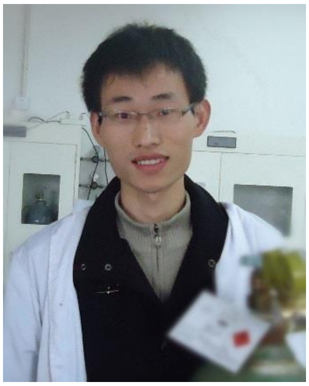
Fig. 1 Carbon cycles in biomass and fossil resource utilization.

biomass into liquid fuel and synthesis gas[7]. Nevertheless, the thermal techniques still suffer from the disadvantages of low selectivity and high energy consumption, which are unacceptable at the present stage. [9] On the other hand, the biological conversions of biomass often unavoidably lose carbon and oxygen, which lead to the low selectivity and low yield of target products. In general, unlike the traditional hydrocarbon raw materials, biomass possesses high oxygen content (~50%).[10, 11] Thus, reasonable routes to promote biomass conversion into value-added chemicals which have analogous carbon skeleton and maintain the oxygen atoms under relatively mild circumstances in liquid phase with a high selectivity are required. [10] In order to transform the polyhydroxy compounds into high value-added chemicals *via* C-C and/or C-O cleavage, selective hydrogenolysis is crucial (Fig. 2).

Polyols, including sorbitol, mannitol, xylitol, ethylene glycol (EG) and propylene glycol (PG) are all important chemicals. Currently, sorbitol and mannitol can be manufactured from hydrogenation of glucose and fructose;[8] Xylitol was prepared by xylose hydrogenation;[9] EG and PG are produced from hydration of ethylene oxide and propylene oxide which are derived from cracking petroleum.[10]

Traditionally, sorbitol, mannitol, xylitol, EG and PG are important materials in the food industry, intermediates in the pharmaceutical industry, monomers in the polymer industry and additives in the cosmetic industry.[6] In the new energy strategy based on biomass, valorization of these platform polyols has also been developed. For example, glycols can be used as the feedstocks of fuel cell to generate electricity[11] and hydrogen[12] can be produced through the aqueous-phase reforming and steam reforming processes, *etc.* Molecular structures and the primary applications of polyols discussed herein were listed in Table 1.

Catalytic upgrading of lignocellulosic biomass for the synthesis of industrial products and fuels has been reviewed recently.[13-21] In this review, we focus specially on the latest advances in transformation of cellulose and biomass-derived compounds into high value-added polyols over heterogeneous catalysts, and particular spotlight is given to the formation of glycols directly from cellulose and from polyhydroxy compounds such as sugars and sugar alcohols.



Shengxi Yao

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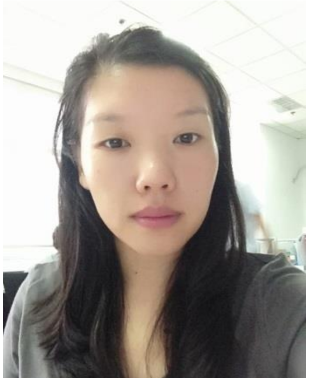

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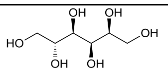
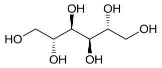
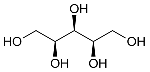
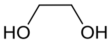
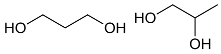
Dr Jing Guan obtained her PhD from Dalian Institute of Chemical Physics, Chinese Academy of Sciences in 2010, and is presently a research associate at QIBEBT, Chinese Academy of Sciences. Her research areas include DFT modeling of reaction mechanisms in heterogeneous catalysis, with the emphasis on the metal-catalyzed conversion of biomass-derived oxygenates to produce value-added chemicals as such polyols and diols.

Xindong Mu

Xindong Mu is a professor of chemical engineering at QIBEBT, Chinese Academy of Sciences, where he leads the Green Chemical Engineering Center. He obtained his PhD from Peking University in 2005, and then worked as a research associate at the University of Tokyo, Japan. He joined QIBEBT in 2008 and was promoted to full professor in 2010. He has filed over 40 patents and published over 50 peer-reviewed papers. His current research interests include green chemistry and engineering with a focus on catalysis, biomass utilization and green materials.

Table 1 Chemical structure and primary applications of polyols

Polyols		Primary applications	Applications
Sorbitol		1, 2, 3, 4, 6, 10, 11, 12, 13, 14	1. Additives in the food industries, 2. Intermediates in the pharmaceutical industries, 3. Monomers in the polymer industries, 4. Additives in the cosmetic industries, 5. Solvent, 6. Sweetening agent, 7. Antifreeze, 8. Coolant, 9. Heat transfer fluids, 10. Synthesis of surfactant, 11. Production of syngas, 12. Production of hydrogen, 13. Fuel cell, 14. Production of glycols
Mannitol		1, 2, 3, 4, 6, 10, 11, 12, 13, 14	
Xylitol		1, 2, 3, 4, 6, 10, 11, 12, 13, 14	
EG		1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13	
PG		1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13	

2. Hydrolytic hydrogenation of cellulose

As mentioned above, lignocellulose is the most abundant form of biomass in nature.[22] However, cellulose is water insoluble for its highly crystalline structure composed of β-1,4-glycosidicbonds.[23, 24] Although a lot of efforts have been focused on the degradation of cellulose by enzymes,[23] mineral acid[25] and supercritical water,[26] drawbacks still exist in these process: the enzymatic saccharification of cellulose suffers from high cost, low reaction rates and succedent low space-time yields and the problems in enzyme recovery; mineral acid hydrolysis suffers from challenges related to waste water disposal, equipment corrosion and the recovery of the acid; the utilization of supercritical water faces a problem of energy consumption.[27]

To date, one-pot chemical transformation of cellulose to polyols over heterogeneous catalysts is one of the most promising routes for the effective utilization of cellulose in more efficient and convenient manners.[28] Several catalytic reaction systems were successfully established through acid catalysed hydrolysis coupled with metal-catalysed hydrogenation/hydrogenolysis.[14] However, challenges still exist in this process. For example, both the substrate and the catalysts are presented in solid state in this reaction, leading to the problems of interaction between catalysts and cellulose. Mass transfer between the substrates and the catalysts is the main barrier in chemical conversion of cellulose.[29] In one-step hydrolytic hydrogenation/hydrogenolysis of cellulose, several independent reactions take place including hydrolysis of cellulose to glucose, hydrogenation of glucose to sorbitol, hydrogenolysis of glucose and sorbitol to low carbon glycols, *etc*. Hydrolysis of cellulose is generally considered as the rate-determining step in this reaction (Fig. 3).[30-32] Product distribution is controlled by the balance between the rates of cellulose hydrolysis and glucose hydrogenation/hydrogenolysis. In this part, we will review recent progress on coupled hydrolytic hydrogenation/hydrogenolysis of cellulose and discuss the process according to the acid used in the hydrolysis step (Scheme 1).

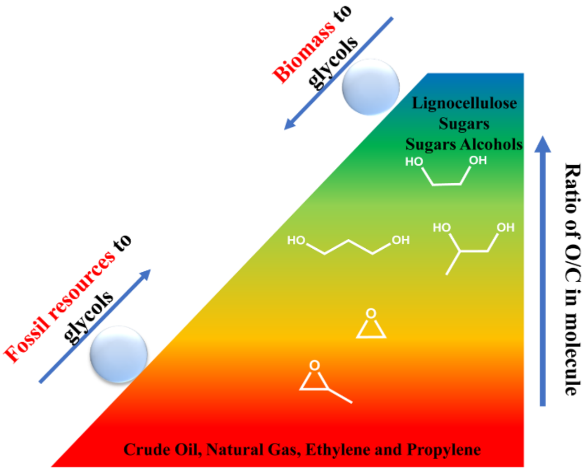
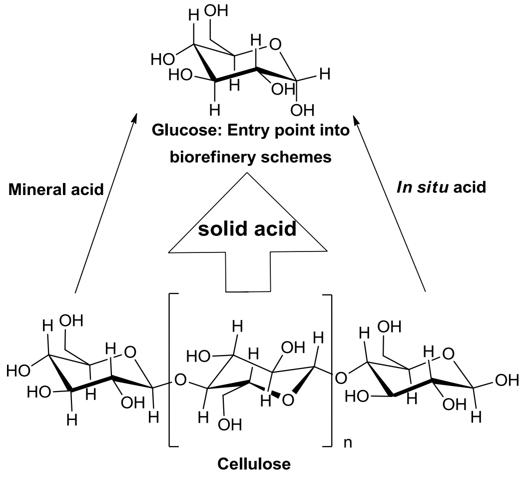


Fig. 2 Comparation of O/C ratios in hydrocarbons, biomass, biomass-derived compounds and commodity polyols.



Scheme 1 Acid promoted hydrolysis of cellulose.

2.1 Acid combined with metal catalysts catalysed hydrolytic hydrogenation/hydrogenolysis of cellulose

Liquid acid is utilized to promote the cellulose hydrolysis to glucose because it is inexpensive and widely applied in industry. In this section, we mainly focus on the application of liquid acid united with the hydrogenation catalyst in the one-pot conversion of cellulose to hexitols and glycols. Table 2 showed the hydrolytic hydrogenation/hydrogenolysis of cellulose over different catalysts promoted by acid. Mineral acids like phosphoric acid and sulfuric acid were introduced into cellulose hydrogenation under the catalysis of supported noble metal cata-

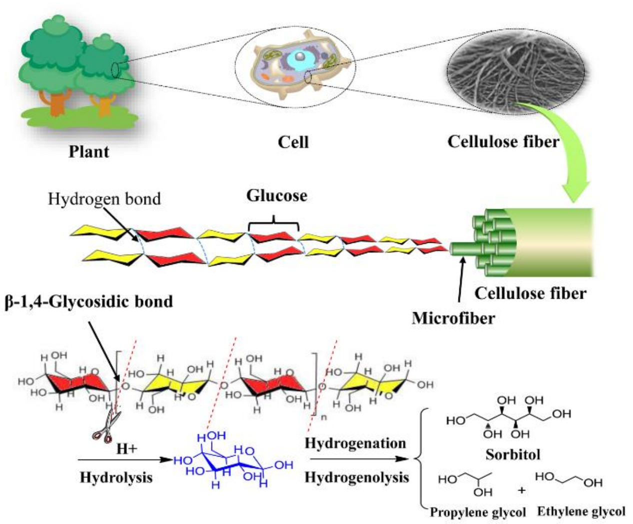


Fig. 3 Typical pathway for the hydrolytic hydrogenation of cellulose.

-lysts based on Pt, Ru and Pd at relatively low temperature and short reaction time.[33] After 5 h's reaction, sugar and sugar alcohols were produced at 60% yield with 72% cellulose conversion at 433 K, 5 MPa H_2.

Sels *et al.*[34] introduced trace amount of mineral acid (ppm grade) into the hydrogenation reaction system with noble metal loaded zeolites acting as hydrogenation catalysts to yield hexitols. The yield of hexitols (sugar alcohol and sorbitan) was as high as 90% under the catalysis of Ru/H-USY promoted by hydrochloric acid (177 ppm) at 463 K, 5.0 MPa H_2. Isosorbide was obtained as the main product when Ru/C and hydrochloric acid were employed to catalyse the hydrogenation of concentrated microcrystalline cellulose under 508 K as demonstrated by Zhao.[35] Hydrochloric acid could accelerate both the cellulose hydrolysis and the dehydration of sorbitol. The balance between catalytic hydrolysis catalysed by hydrochloric acid and the hydrogenation of glucose promoted by Ru/C was ascribed to the high yield of isosorbide.

Apart from mineral acid, heteropoly acid (HPA) was also applied to facilitate the one-pot conversion of cellulose. Sels *et al.*[36]found that the combination of heteropoly acid and Ru supported on carbon could promote the concentrated ball-milled cellulose feed converted into hexitols with notable yield (68% hexitol yield and 99% cellulose conversion) at 463 K, 5.0 MPa H_2 after 1 h reaction. Heteropoly acids such as $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ were selected in their study not only because of their high efficiency in the hydrolysis of cellulose to glucose, but also due to their easy recovery *via* the processes of extraction and recrystallization after reaction. Palkovits *et al.* found that cellulose could be converted into C4-C6 sugar alcohols with a yield of 81% under the catalysis of Ru/C combined with heteropoly acid ($H_4SiW_{12}O_{40}$) at the condition of 433 K, 5 MPa H_2.[37] The main drawback that restricts the utilization of liquid acid in cellulose hydrolysis lies in the recovery of the acid. In order to solve this problem, solid acids were introduced into this reaction.

Compared to liquid acid, solid acid possesses a series of advantages. For example, solid acid is easy to be separated from reaction system and some solid acids have a relatively strong acidity even stronger than H_2SO_4.[38] Therefore, solid acid is an appropriate substitution to liquid acid, and will avoid a great number of problems such as equipment corrosion, neutralization and the waste of water resources that liquid acid has brought into the industrialized application.

Non-stoichiometric caesium salts, CsPW and CsSiW coupled with Ru/C were found to give a much higher yield of hexitols than formerly reported HPAs and Ru/C under a relatively milder reaction condition.[39]CsHPAs exhibited much higher surface acidity and hydrophobicity if the calcination temperature rised from 253 K to 873 K during the synthesis process, leading to much higher activity and selectivity. More importantly, the CsPW salts could be recovered *via* a procedure of recrystallization after reaction, showing its great potential for industrialized application. Ma *et al.*[40] presented that direct conversion of cellulose could be achieved over the catalysis of zirconium phosphates combined with Ru/C. Ball-milled cellulose could be transformed into sorbitol/mannitol at the yield of 81%.Mixed ball-milling of cellulose and solid acid catalysts enhanced the interaction between cellulose and solid acid catalysts and thus promoted the hydrolytic hydrogenation of cellulose.[41] The yield of sugar alcohols could be 90.3% when Zirconium phosphate (ZPA) was employed as the solid acid under the condition of 463 K, 6 MPa H_2 2.5 h.

The combination of MCM-41-n-SO_3H and Ru/C showed high selectivity to alkanediols or γ-valerolactone (GVL) in the hydrolytic hydrogenation of cellulose when both catalysts were added in the reaction at the beginning.[42] However, due to the changes of mesoporous structure and the loss of the acid group of the MCM-41-n-SO_3H, the catalyst deactivated rapidly. The sequential process yielded hexitol and GVL as the main products. Moreover, it is easy to reuse the MCM-41-n-SO_3H because it can be separated *via* the simple process of filtration. Zhang *et al.* employed a phase-transfer catalysts system controlled by temperature in the hydrolytic hydrogenolysis of cellulose.[43] Tungsten acid, a yellow solid and water insoluble at ambient temperature coupled with Ru/C catalysts, was utilized to promote the catalytic conversion of cellulose to EG. This reaction system could be repeated for more than 20 times with no obvious deactivation. Low concentration H_3PO_4 combined with $Ni_{4.63}Cu_1Al_{1.82}Fe_{0.79}$ was utilized in the hydrolytic hydrog-

Table 2 Hydrolytic hydrogenation/hydrogenolysis of cellulose over different catalysts promoted by acid

Starting material	Catalyst	Conditions	Products and yield /%	Ref.
5 wt% cellulose	Ru/C	433 K, 5 MPa H_2, 1 h, H_2SO_4 (2.5 wt%)	SOR (33.2%), SOT (13.6%), XYL (11.3%)	33
10 wt% cellulose-BM	Ru/H-USY	463 K, 5 MPa H_2, 13 h, HCl (177 ppm)	SUA (60%), SOT (33%)	34
2 wt% cellulose	Ru/C	508 K, 6 MPa H_2, 1 h, HCl (0.1 M)	ISO (41.1%)	35
2 wt% cellulose-BM	Ru/C	463 K, 5 MPa H_2, 1 h, $H_4SiW_{12}O_{40}$ (1.22×10^{-2} M)	SUA(68%), SOT (19%)	36
5 wt% cellulose	Ru/C	433 K, 5 MPa H_2, 7 h, $H_4SiW_{12}O_{40}$ (55.1 mM)	C4-C6 (80.6%)	37
2 wt% cellulose	Ru/C	463 K, 5 MPa H_2, 13 h, $Cs_{3.5}SiW$ ($[H^+]$=1.5 mM)	SUA (56%), SOT (14%)	39
2 wt% cellulose-MBM	Ru/C+ ZPA	463 K, 6 MPa H_2, 2.5 h	SUA (90%)	41
1 wt% cellulose	Ru/C+H_2WO_4	518 K, 6 MPa H_2, 0.5 h	EG (54.4%), 1,2-PG (7.3%)	43
1 wt% cellulose- pretreated by 0.06% H_3PO_4	$Ni_{4.63}Cu_1Al_{1.82}Fe_{0.79}$	488 K, 4 MPa H_2, 3 h, H_3PO_4 (0.08 wt%)	SOR (68.07%), MAN (11.96%)	44

[a] SOR: sorbitol, XYL: xylitol, SUA: sugar alcohols, ISO: isosorbide, SOT: sorbitan, BM: ball-milled, MBM: mixed ball milled, ZPA: Zirconium phosphate.

-enation of cellulose to sorbitol.[44] The pretreatment of cellulose with acid in different concentration of H_3PO_4 resulted in the destruction of the cellulose structure. Over the catalysis of $Ni_{4.63}Cu_1Al_{1.82}Fe_{0.79}$, the cellulose pretreated by 0.06 % H_3PO_4 could be transformed to sorbitol and mannitol effectively.

2.2 *In situ* formed acid promoted hydrolytic hydrogenation of cellulose

Eckert[45] *et al*. reported that an environmentally friendly *in situ* formed acid was obtained when the temperature of liquid water was above 473 K. This H^+ ions will disappear when the liquid water cools down to the room temperature, indicating that this is a green process with a capacious prospect in industrial application. *In situ* generated acid promoted catalytic conversion of cellulose over various catalysts were listed in Table 3

The hydrolysis of cellulose catalysed by *in situ* generated reversible protons produced by high temperature liquid water was first employed for the production of sugar alcohols in Liu *et al.*'s research.[32] Ru/C was chosen as the hydrogenation catalyst for its superior performance in glucose hydrogenation. After 30 min, the yield of hexitols was 39.3% at the conversion of 85.5% at 518 K, 6 MPa H_2. Meanwhile, small amount of low carbon glycols such as PG and EG were produced because glucose was more active than the corresponding hexitols under the reaction condition. Once glucose was formed *via* cellulose hydrolysis, there existed two different approaches: if the rate of glucose hydrogenation was greater than that of cellulose hydrolysis, hexitols will be the main products, and on the contrary, glycols like EG and PG will be overwhelming. XRD patterns showed cellulose crystal structure did not change before and after the reaction, revealing that hydrolysis reaction mainly occurred at the surface of the cellulose, which was also confirmed subsequent investigations. [46]

Zhang and co-workers[47] performed the hydrogenation of cellulose under the catalysis of tungsten carbide in order to replace the noble metal catalysts used previously. Tungsten carbide was found to give a higher yield of EG than platinum and ruthenium catalysts at the reaction condition of 518 K, 6 MPa H_2, 30 min. Moreover, the yield of EG increased significantly from 27% to 61% with the promotion of a small amount of nickel. The reason that low molecular weight polyols were obtained as the main product over W_2C/AC catalysts lay in the superior activity of glucose hydrogenolysis and inferior activity of glucose hydrogenation. Furthermore, synergistic effect between nickel and W_2C was another motivation that facilitated the EG yield's remarkable increase. Their further corresponding surface science studies[48] indicated that the higher EG yield was due to weaker bonding between EG and Ni-promoted tungsten carbides. When 3D mesoporous carbon supported tungsten carbide nanoparticles was introduced in this reaction,[49] the selectivity towards EG could be improved further to 72.9%. Zhang's group also developed a series of transition metal-W bimetallic catalysts capable of the production of EG from cellulose in one step.[50] The tungsten component was found to be responsible for the C-C cleavage of glucose, on the other hand, it could efficiently catalyse the hydrogenation of unsaturated intermediates. Thus, the final production distribution could be tuned by changing the weight ratio of transition metal to tungsten. Among the catalysts employed, Ni5-W15/SBA-15 catalysts gave the yield of EG as high as 75% at 518 K, 6.0 MPa H_2. To improve the reusability, the tungsten acid and Ru/C were combined and showed significant improvement in catalyst reusability.[43, 51] In their following studies,[18] they found the homogeneous tungsten bronze generated from the charged tungsten compounds functioned as uniquely active species for the C-C scission of glucose for the formation of glycolaldehyde, which was further hydrogenated to EG catalysed by a hydrogenation active site.

In order to explore a catalyst that can effectively convert cellulose with low-cost, we evaluated Ni based catalysts supported on various supports including hydrothermally stable oxides with varying surface properties (Al_2O_3, kieselguhr, TiO_2, SiO_2, ZnO, ZrO_2 and MgO) in previous investigations.[31] It was found that 20% Ni/ZnO catalyst could convert the cellulose completely and give a 70.4% yield of total 1,2-alkanediols composed of 1,2-PG, EG, 1,2-BDO and 1,2-HDO.

A possible mechanism of the cellulose hydrogenolysis reaction was also concluded by identifying the products formed (Scheme 2). The main drawback of this catalyst lay in its poor hydrothermal stability, which resulted in the decrease of catalytic activity after repeated reaction runs, which was partially ascribed to the leaching of Ni. Further studies are needed to improve the stability and selectivity of current catalysts. We also prepared a series of Ni-Cu/ZnO bimetallic catalysts which were successfully applied to the hydrogenolysis of cellulose for the purpose of producing 1,2-alkanediols as the major products.[52] The mole ratio of Ni and Cu not only dominated the activity, selectivity and product distribution, but also played synergetic roles in the formation of 1,2-alkanediols during the reaction. 2Ni3Cu5ZnO catalyst displayed the best 1,2-alkanediols selectivity (72.5%) with 74% cellulose conversion at 518 K 4 MPa H_2 after 0.5 h reaction.

Palkovits *et al.* [53] conducted the reaction under similar reaction conditions over cheap $CuO/ZnO/Al_2O_3$ catalyst and small alcohols like methanol were obtained abundantly except for glycols and glycerol. By changing the average pore size of the support and the reduction temperature of the $Ni/W/SiO_2$ catalysts, crystalline size of W and the amount of surface acid site could be tuned, resulted in the alteration of the reaction activity.[54] The product distribution was affected by valence state of $Ni/W/SiO_2$ catalysts. Oxidized Ni and W species favored organic acids while the mixture of reduced and oxidized Ni and

Table 3 Hydrolytic hydrogenation/hydrogenolysis of cellulose over different catalysts promoted by *in situ* generated acid

Starting material	Catalyst	Conditions	Products and yield/%	Ref.
2 wt% cellulose	Ru/C	518 K, 6 MPa H_2, 0.5 h	SOR (34.6%), MAN (11.4%), SOT (13.4)	32
1 wt% cellulose	Ni-W_2C/AC	518 K, 6 MPa H_2, 0.5 h	EG (61%), SOR (3.9%), MAN (1.9%)	47
1 wt% cellulose	WC_x/MC	518 K, 6 MPa H_2, 0.5 h	EG (72.9%), SOR (1.2%), MAN (1.4%)	49
1 wt% cellulose	Ni5-W25/SBA-15	518 K, 6 MPa H_2, 0.5 h	EG (72.9%), 1,2-PG (4.1%), SOR (3.1%), MAN (1.3%)	50
1 wt% cellulose	Raney Ni + H_2WO_4	518 K, 6 MPa H_2, 0.5 h	EG (65.4%), 1,2-PG (3.3%), SOR (7.5%), MAN (3.3%)	51
1 wt% cellulose	20%Ni/ZnO	518 K, 6 MPa H_2, 2 h	1,2-PG (34.4%), EG (19.1%), 1,2-BDO (10.1%), 1,2-HDO (4.7%)	31
1 wt% cellulose	2Ni-3Cu-5ZnO	518 K, 4 MPa H_2, 0.5 h	1,2-PG (24.3%), EG (16.9%), 1,2-BDO (7.1%), 1,2-HDO (5.3%)	52
1.6 wt% cellulose	$Ni/W/SiO_2$	518 K, 6 MPa H_2, 1 h	EG (26.8%), SOR (2.3%)	54
5 wt% cellulose	$CuO/ZnO/Al_2O_3$	518 K, 5 MPa H_2, 2 h	MeOH (21%), EG (11.8%)	53

[a] SOR: sorbitol, MAN: mannitol, XYL: xylitol, SUA: sugar alcohols, ISO: isosorbide, SOT: sorbitan, MeOH: methanol.

W species preferred low carbon polyols.

By employing Pt-Mo_2C/C catalyst, hydrogen could be substituted by CO and H_2O in hydrolytic hydrogenation/hydrogenolysis of cellulose in Ma and co-workers' report.[55] Hydrogen species needed in this reaction were produced *via* water-gas shift reaction promoted by Pt-Mo_2C domains present in Pt-Mo_2C/C catalyst. Meanwhile, Pt-C domain existing in this catalyst was responsible for the hydrogenation/hydrogenolysis reactions.

Recent investigations focused on the hydrolytic hydrogenation/ hydrogenolysis of cellulose over bifunctional catalysts combined acid sites and metal active sites in hot compressed water. Such studies incorporated the advantages of solid acid with *in situ* formed acid, as a consequence, cellulose could be upgraded to polyols such as sorbitol, mannitol, EG and PG in a greener process efficiently.

2.3 Bifunctional catalysts

In the reaction of hydrolytic hydrogenation/hydrogenolysis of cellulose catalysed by bifunctional catalysts (solid acid and transition metal), cellulose first undergoes hydrolysis to produce glucose over acidic sites, and glucose is hydrogenated subsequently over the promotion of transition metals. Reaction products mainly include sorbitol, mannitol and some small glycol molecules such as EG and PG formed *via* the reaction of glucose and sorbitol hydrogenolysis. Table 4 demonstrated the catalytic conversion of cellulose over bifunctional catalysts.

Fukuoka and Dhepe[30] pioneered the conversion of cellulose over solid acid supported noble metal catalysts. Cellulose could be directly hydrolytically hydrogenated into sugar alcohols over a bifunctional Pt/Al_2O_3 catalyst at 463 K with around 30% yield of hexitols after 24 h reaction and sorbitol was the dominating product. When promoted by SnOx, as demonstrated by Liu *et al.*,[56] the product composition could be tuned by varying the Sn/Pt atomic ratios in the catalyst. In order to reduce the crystallinity and particle size of cellulose which impeded the conversion of cellulose *via* heterogeneous catalytic transformation, ball-milling was applied in their investigations. By using a catalyst of platinum supported on a carbon black BP200, sorbitol and mannitol were produced at the yield of 70% under the reaction of 463 K, 5.0 MPa H_2, 24 h.[57] They also found that Cl residual on the catalysts induced the side-reactions like the cleavage of C-C and C-O bond, leading to lower yield of sugar alcohols. According to Fukuoka *et al.*[58] amorphous nickel phosphide phase generated from nickel phosphide crystalline with the increasing of the temperature was responsible for the high yield of sorbitol. The leaching of P from the catalysts resulted in poor recyclability. A sorbitol yield of 60% could be obtained under the condition of 503 K, 5 MPa H_2 after 40 min reaction. As demonstrated by Fukuoka *et al.* water tolerant catalysts prepared by Ru supported on mesoporous carbon materials was introduced to promote hydrolysis of cellulose.[59] Ru/CMKs was proved to convert cellulose to glucose efficiently. The support material CMKs catalysed cellulose hydrolysis to oligosaccharides, and Ru was responsible for the conversion of oligosaccharides to glucose. A series of sulfonated silica/carbon nanocomposites for the highly efficient hydrolysis of cellulose to produce glucose were developed by Sels *et al.*[60] Strength of the Brønsted acid density could be tuned by changing carbon content of the sulfonated silica/carbon nanocomposites during preparation steps, thus influence the formation rate of glucose. 50% yield of glucose was obtained at 423 K after 24 h reaction.

In order to harmonize the acid sites and metal sites in the cellulose hydrogenation system to control the product distribution, bifunctional catalysts were needed, which joined the two kinds of active sites together properly. Hence, transition metal like nickel, copper and ruthenium were supported on solid acids such as mesoporous carbon, active carbon, carbon nanofiber pretreated by mineral acid and zeolite like ZSM-5. These bifunctional catalysts can catalyse hydrolytic hydrogenation of cellulose efficiently.

Liu *et al.*[46] found that tungsten trioxide promoted ruthenium catalysts showed outstanding performance in hydrogenolysis of cellulose to yield glycols at 478 K, 6 MPa H_2. Tungsten trioxide was found to promote the hydrolysis of cellulose as well as the C-C bond cleavage of the sugar efficiently. EG was found to be derived from the C-C cleavage of glucose, while PG was produced by degradation of fructose, which was formed by glucose isomerization.

As described above, solid catalysts promoted hydrolytic hydrogenation of cellulose includes acid hydrolysis of cellulose to produce glucose, and the following hydrogenation of glucose to yield hexitols. If the glucose produced from the hydrolysis process could not be involved in the hydrogenation reaction immediately, glucose will undergo degradation, resulted in the decreasing of the yield of hexitols. In order to find a catalyst with an appropriate acid/metal ratio that can optimize the yield of hexitols, Sels *et al.*[61] oxidized the carbon nanofiber with oxidation agents (HNO_3 or 1:1 mixtures of HNO_3/H_2SO_4) to introduce oxygen-containing surface groups. In their investigations, it was found that low density of Brønsted acid sites united with high amount of Ni atom were the key point to maintain the high yield of hexitols. Ni supported at the tip of the carbon nanofiber prepared by catalytic vapour deposition of methane was introduced to promote the hydrogenation of cellulose.[62] The bifunctional catalysts designed in this method improved the accessibility of active metal sites in porous solids, thus giving a high yield of sorbitol (50.3%) at 463 K, 6 MPa H_2 after 24 h.

Dual-functional Nickel phosphide catalysts were also used to promote hydrogenation of cellulose and sorbitol was the main product as demonstrated by Zhang *et al.*[63] The results suggested that hydrolysis of cellulose was promoted by homogeneous phosphoric acid generated by leaching of P from the Nickel phosphide catalysts. As a consequence, this catalyst cannot sustain the hydrothermal reaction condition. Mesoporous carbon supported Ni-noble metal bimetallic catalysts were also introduced in the hydrolytic hydrogenation of cellulose.[64] The mesoporous carbon prepared by nanocasting method using commercial silica fume as hard template not only facilitated the dispersion of metal active sites, but also played important roles in reactant and product adsorption. Excellent performance of this catalyst largely relied on its superior ability to coupling the reaction of cellulose hydrolysis and glucose hydrogenation.

Nitric acid pretreated carbon nanotube (CNT) supported ruthenium catalysts were used in direct hydrogenation of cellulose into sugar alcohol.[65] Catalyst acidity played an important role in hydrolysis of cellulose. The concentration of nitric acid used in CNT pretreatment and Ru particle size all exerted influences on the acid strength of the catalysts. Higher concentration of HNO_3 and larger mean size of Ru particles resulted in higher hydrogenation acidity, thus leading to high yield of sorbitol. The best sorbitol yield was obtained by catalysts with larger mean size of Ru particles and higher acidity (60% sorbitol and 98% cellulose conversion at 458 K, 8 MPa H_2, 3 h). The research group also conducted the hydrolytic hydrogenation

Table 4 Hydrolytic hydrogenation/hydrogenolysis of cellulose over bifunctional catalysts

Starting material	Catalyst	Conditions	Products and yield/%	Ref.
0.8 wt% cellulose	Pt/γ-Al_2O_3	463 K, 5 MPa H_2, 24 h	SOR (25%), MAN (6%)	30
2.5 wt% cellulose	Ru/C + WO_3	478 K, 6 MPa H_2, 0.5 h	EG (51.5%), PG (6.7%), SOR (15%)	46
0.8 wt% cellulose-BM	Pt/BP2000	463 K, 5 MPa H_2, 24 h	SOR (48%), MAN (9%)	57
0.4 wt% cellulose-BM	$N_{12}P_5$	503 K, 5 MPa H_2, 40 min	SOR (62%), MAN (4.5%)	58
0.8 wt% cellulose-BM	Ru/CMK-3	503 K	GLU (27.6%), OLI (14.8%)	59
2 wt% cellulose	3.0 wt% Ni/CNF	483 K, 6 MPa H_2, 24 h	SOR (29.8%), MAN (5%), 1,2-PG (4.3%), EG (4.6%)	61
2 wt% cellulose-BM	7.5 wt% Ni/CNF	463 K, 6 MPa H_2, 24 h	HEX (75.6%)	62
1 wt% cellulose	16% Ni_2P/AC	498 K, 6 MPa H_2, 1.5 h	SOR (48.4%), EG (8.2%), MAN (4.7%), 1,2-PG (2.2%)	63
1 wt% cellulose	16% Ni_2P/SiO_2	498 K, 6 MPa H_2, 1.5 h	SOR (48%), EG (4%), MAN (4.5%), 1,2-PG (1.2%)	63
1 wt% cellulose	16% WP/AC	498 K, 6 MPa H_2, 1.5 h	SOR (1.2%), EG (26.5%), MAN (0.4%), 1,2-PG (2.3%)	63
1 wt% cellulose	1%Ru-5%Ni/MC	518 K, 6 MPa H_2, 0.5 h	EG (3.3%), 1,2-PG (3.0%), MAN (12.6%), SOR (41.6%)	64
1 wt% cellulose	1%Rh-5%Ni/MC	518 K, 6 MPa H_2, 0.5 h	EG (5.3%), 1,2-PG (3.5%), MAN (8.3%), SOR (51.5%)	64
1 wt% cellulose	1%Ir-5%Ni/MC	518 K, 6 MPa H_2, 0.5 h	EG (4.7%), 1,2-PG (3.4%), MAN (9.6%), SOR (47.9%)	64
2 wt% cellulose	Ni/ZSM-5	513 K, 4 MPa H_2, 4 h	HEX (48.6%)	67
3 wt% cellulose	PtNi/ZSM-5	513 K, 4 MPa H_2, 4 h	HEX (76.9%)	69
2.8 wt% cellulose	Ir-BEA	453 K, 1.6 MPa H_2, 24 h	Selectivity SOR (89.2%)	70
2.5 wt% cellulose	3Ni-WO_3/SBA-15	508 K, 6 MPa H_2, 6 h	EG (70.7%), 1,2-PG (5.9%)	71
0.8 wt% cellulose-BM	Ni/KB	483 K, 5 MPa H_2, 6 h	SOR (57%), MAN (6.8%)	72
3.3 wt% cellulose	Ru/SiO_2-SO_3H	423 K, 4 MPa H_2, 10 h	SOR (61.2%), MAN (6.9%), PG (7.2%)	73
0.8 wt% cellulose-BM	Ru/$NbOPO_4$	443 K, 4 MPa H_2, 24 h	SOR (69%)	75
3 wt% cellulose-BM	Ru-Ni/$NbOPO_4$	493 K, 3 MPa H_2, 20 h solvent: methanol	EG (29.6%), EGME (35.5%)	77
0.6 wt% cellulose-BM	Ru-PTA/MIL-100(Cr)	463 K, 2 MPa H_2, 8 h	SOR (57%), MAN (5.3%)	78
0.8 wt% cellulose-BM	Pt/GRO	463 K, 5 MPa H_2, 24 h	SOR (58%), MAN (10%)	79
10 wt% cellulose	CuCr+ $Ca(OH)_2$	518 K, 6 MPa H_2, 5 h	1,2-PG (42.6%), EG (31.6%)	80
5 wt% cellulose (H_2SO_4-impregnated and BM)	Ru/C	433 K, 5 MPa H_2, 1 h	HEX (71.8%)	83

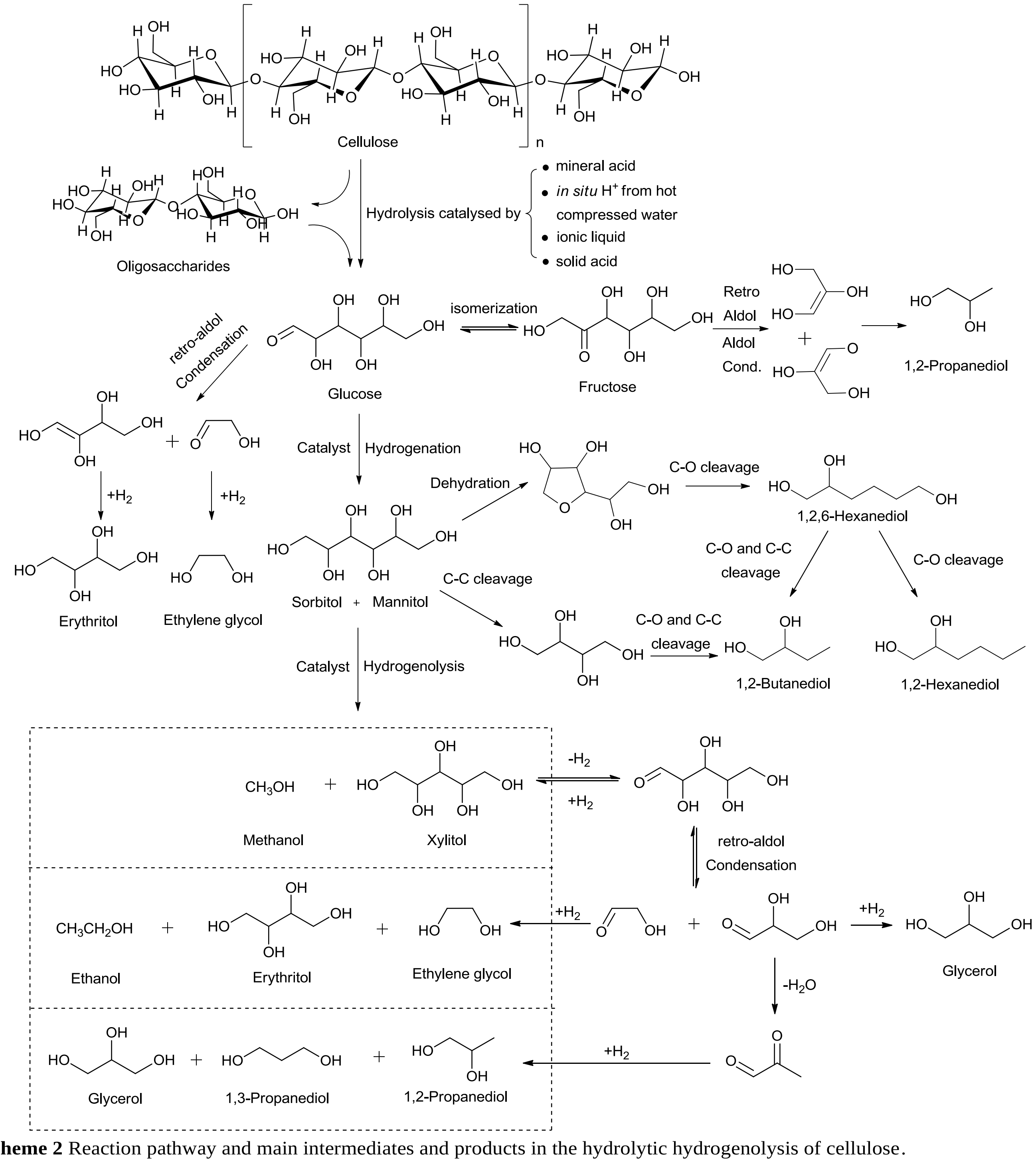
[a] BM: ball-milled, SOR: sorbitol, MAN: mannitol, GLU: glucose, HEX:hexitols, OLI: oligosaccharides, EGME: ethylene glycol monoether.

of ball-milled cellulose to sorbitol over Keggin-type polyoxometalate $Cs_3PW_{12}O_{40}$ supported Ru catalysts in neutral water under mild conditions.[66] Strong intrinsic acidity which was related to the formation of sorbitol, was found to be generated *in situ* from the H_2 rather than $Cs_3PW_{12}O_{40}$.

Zhao *et al.* [67] prepared a series of ZSM-5 zeolite supported Ni catalysts to promote the hydrolytic hydrogenation of microcrystalline cellulose. They found that Ni/ZSM-5 catalysts prepared by impregnation method gave a high yield of hexitols. Ni (1,1,1) crystal face existing in these catalysts was demonstrated as the main active agent in cellulose hydrogenation reaction. The superior activity of glucose hydrogenation and inferior activity of sorbitol hydrogenolysis of these catalysts resulted in the high yield of hexitols. Influence of hydrogenation/dehydrogenation ability of Ni catalysts to the yield of hexitol during cellulose hydrogenation was also investigated.[68] Over Ni/ZSM-5 catalyst, hexitols were produced with a selectivity of over 82%. However, the other Ni catalysts tested tended to produce small molecule glycols instead of hexitols. It was found that high hydrogenation activity and inferior dehydrogenation activity of supported Ni catalysts were the key point to gain high hexitol yield. The lower hexitol yield was attributed to the synergistic effect of Ni active species and acid-base sites, which accelerated the hydrogenolysis of sorbitol. Ni based bimetallic catalysts PtNi/ZSM-5 showed a hexitol yield of 76.9% under the condition of 513 K, 4 MPa H_2 after 4 h and could be reused 4 times.[69] The high dispersion of PtNi alloy particles coupled with the superior ability of hydrogen spillover from the surface of the alloy was reasonable for the enhancement of the hydrogenation activity and the excellent hydrothermal stability of the catalysts. BEA zeolite supported noble metal (Ir, Pd, Ru, Rh) was introduced to promote the conversion of cellulose to glycols.[70] Among the noble metal catalysts selected, Ru/BEA encouraged the catalytic conversion of cellulose with the highest yield (22% conversion of cellulose, 72.8% conversion of glucose). Acidity and the concentrated adsorbed hydrogen of the zeolite (both are high on Ru/BEA) were answerable for the formation of sorbitol. Selectivity to the product was related to the d-band width of the metal constituent which was responsible for the higher selectivity of Ir than Ru. The status of the formation of sorbitol could be ameliorated by adding some additive such as pure nanoscopic hydroxylated SnF_4. Nevertheless, this technique was hard to be shifted into industrialization since the material added was difficult to be recovered.

Wang *et al.*[71] managed the hydrolytic hydrogenolysis of cellulose over Ni-WO_3/SBA-15 catalysts in aqueous phase. There existed a strong electronic interaction between NiO and WO_3, which impacted the reduction of WO_3 and NiO. WO_{3-x} was found to be the active species responsible for the C-C cleavage of cellulose. Over the catalyst of 3%Ni-15%WO_3/SBA-15, EG was produced at the yield of 70.7% when the conversion of cellulose was 100% at 503 K, 6 MPa H_2 after 6 h reaction. Ni catalysts supported on metal oxide and carbons were also introduced to promote hydrolytic hydrogenation of cellulose to hexitols.[72] High water tolerance and no basicity of active carbon and the large Ni particle size made Ni/KB an efficient catalyst for the production of hexitols.

Hydrogenation of cellulose to sorbitol catalysed by Ru/SiO_2-SO_3H bifunctional catalysts was conducted at low temperature.[73] A high sorbitol yield was obtained because Ru nanoparticles and sulfonic groups interacted with each other through electron transfer, preventing sorbitol from further degradation. Sorbitol was produced at a yield of 61.2% at the temperature of 423 K, 4



Scheme 2 Reaction pathway and main intermediates and products in the hydrolytic hydrogenolysis of cellulose.

MPa H_2 after 10 h reaction.

Reactivity of hydrolytic hydrogenation/hydrogenolysis of cellulose was performed over Pt/AlW and AlW in Rataboul *et al.*'s research.[74] The comparison of the performances of Pt/AlW and AlW showed that Pt promoted the conversion of cellulose and changed the product distribution. Pyruvaldehyde was found to be the key intermediate in this reaction with the presence of Lewis acid sites. When AlW was employed as the catalyst, pyruvaldehyde could be transformed into lactic acid. With the promotion of Pt, pyruvaldehyde was hydrogenated to acetol and PG.

Mesoporous niobium phosphate supported ruthenium bifunctional catalysts were employed by Wang *et al.*[75] in catalytic hydrogenation of cellulose to sorbitol $NbOPO_4$ promoted the hydrolysis of cellulose to glucose and Ru nanoparticles catalysed the hydrogenation of glucose to sorbitol. Sorbitol was generated at the yield of 59-69% with the 90% cellulose conversion under the condition of 443 K, 4 MPa H_2, 24 h. A two-step sequential process over the catalysis of

Ru/$NbOPO_4$-pH2 and $NbOPO_4$-pH2 was presented by the same research group for the conversion of cellulose to isosorbide.[76] In this conversion, the hydrolytic hydrogenation of cellulose to sorbitol was promoted by Ru/$NbOPO_4$-pH2, and the dehydration of sorbitol was catalysed by $NbOPO_4$-pH2 to yield isosorbide. The acid amount of solid acid catalyst played a key role in the dehydration of sorbitol. When such reaction was performed in methanol, EG and Ethylene glycol monoether (EGME) were generated as the main products over the Ru/$NbOPO_4$-pH2.[77] Methanol was responsible for this product distribution because the acetalization of methanol and glucose protected the C=O bond of glucose, resulted in the C-C cleavage of methyl glucoside to EG and EGME instead of the glucose hydrogenation. Furthermore, the addition of Ni to the Ru/$NbOPO_4$-pH2 catalyst prevented the degradation of EG and EGME, giving a high yield of EG and EGME. A total yield of 64% to EG and EGME was obtained over Ru-Ni/$NbOPO_4$-pH2 under the condition of 493 K, 3 MPa H_2, 20 h.

Ru-PTA/MIL-100 (Cr) was employed to catalyse the hydrolytic hydrogenation of cellulose because the ratio of acidity to the number of Ru surface atoms of this catalyst could be monitored.[78] The balance between acid promoted hydrolysis and the metal catalysed hydrogenation changed the product distribution. A sorbitol yield of 57 % was produced under the condition of 463 K, 2 MPa H_2, 8 h.

Wu *et al*.[79] reported that Pt/GRO prepared by microwave-assisted EG reduction gave a high yield of sorbitol when it was employed in hydrolytic hydrogenation of cellulose. The graphene oxide was an excellent stabilizer for the Pt nanoparticles which was related to the synergistic effects of the support and the Pt nanoparticles. The hydrogen spillover of the Pt/GRO catalysts was responsible for the improvement of the catalytic activity. The sorbitol yield was 58.9% under the condition of 463 K, 5 MPa H_2, 4 h.

Except for nickel, non-noble metal copper was also employed in the reaction of hydrogenolysis of cellulose. One of the aspects that prevent the industrialization of catalytic hydrogenation of cellulose to glycols is the low feedstock concentration (about 1-3%). It was because once the cellulose degraded into glucose through hydrolysis, the produced glucose must be hydrogenated into corresponding sugar alcohols immediately or else coke-like precipitates will be generated and impede the reaction.

However, Liang *et al*. [80] recently reported that concentrated cellulose (up to 15 wt%) could be converted into 1,2-PG and EG through the reaction of hydrogenolysis with no coke-like precipitates formed over CuCr catalysts promoted by $Ca(OH)_2$. The authors believed that the addition of alkali in the reaction system promoted the C-C cleavage thus hampered the formation of coke-like precipitates. EG and 1,2-PG were obtained with the yields of 42.6% and 31.6% under the reaction condition of 518 K, 6.0 MPa H_2, respectively.

Alkaline pretreatment was utilized in the hydrolytic hydrogenolysis of cellulose by Wang *et al*.,[81] and the pretreatment of cellulose with NaOH enhanced the cleavage of cellulose chains, resulting in the promotion of hydrolysis of cellulose. The main products of the hydrogenolysis of the alkaline pretreated cellulose were EG and PG, which was attributed to the basic conditions alkaline pretreatment rendered.

In order to degrade the robust cellulose, Beltramini *et al*.[82] employed mechanical depolymerisation of cellulose to accelerate the production of water soluble oligomers. With the presence of bi-metallic Ni-Pt/alumina catalyst, high yield of sorbitol and mannitol (90%) was produced under the condition of 473 K, 5 MPa H_2 and 1 h. Mechanocatalytic depolymerization was also introduced by Schüeth *et al.*[83] to convert cellulose into low carbon glycols efficiently. The process was coalesced with Ru/C to promote cellulose hydrogenolysis reaction, and high yield of hexitols (94%) was produced at 423 K, 5 MPa H_2.

2.4 Utilization of ionic liquid

Apart from water, ionic liquid, another green solvent, was also employed in hydrolytic hydrogenation of cellulose. Difficulties in heterogeneous hydrolytic hydrogenation of cellulose lay in the problematic mass transfer of solid catalysts and water insoluble cellulose. However, cellulose can be dissolved in ionic liquid,[84] improving the contact between solid catalysts and cellulose. As a result, hydrolysis of cellulose can be improved when ionic liquid is employed as the solvent. There are some reports on the depolymerization of lignocellulose in ionic liquid.[85-87] Nonetheless, few researches focused on the one-pot transformation of lignocellulose into glycols. The utilization of ionic liquid in hydrolytic hydrogenation/hydrogenolysis of cellulose was shown in Table 5.

Kou and Liu reported the one-pot catalytic conversion of cellulose and cellobiose over metal nanoclusters in ionic liquid.[88] In their research, cellulose could be converted (16% conversion) to hexitols over the promotion of Ru nanoclusters in [Bmim] Cl ionic liquid. Cellulose unfolded in an ionic liquid ([Bmim] Cl) could be converted into hexitols over the catalysis of heterogeneous or homogenous catalysts.[89] When promoted by Ru/C, cellulose could be transformed to glucose, sorbitol and mannitol successfully (cellulose conversion 57%, selectivity of the products: glucose 43%, sorbitol 29%, and mannitol 5%). Sorbitol could be obtained at the selectivity of 74% over the catalysis of HRuCl(CO) $(PPh_3)_3$ at the cellulose conversion of 86% under the condition of 423 K, 3.5 MPa H_2, 24h. Zhu *et al*.[90] reported that ionic liquid-stabilized ruthenium nanoparticle catalyst was employed in hydrogenation of cellulose to hexitols. When ionic liquid ([Bmim] Cl) was utilized in this system, with sodium formate as the hydrogen source, complete cellulose conversion could be obtained with a sorbitol yield of 94% under the condition of 353 K, 5 h. Ru/$[Bmim]_3PW_{12}O_{40}$ was synthe-

Table 5 Utilization of ionic liquid in hydrolytic hydrogenation/hydrogenolysis of lignocellulose

Starting material	Ionic liquid	Catalyst	Conditions	Products and yield/%	Ref.
5 wt% cellulose	[Bmim]Cl	Ru/C	423 K, 3.5 MPa H_2, 24 h 0.17 wt% KOH	Selectivity: GLU (43%), SOR (29%), MAN (5%)	89
5 wt% cellulose	[Bmim]Cl	HRuCl (CO) $(PPh_3)_3$	423 K, 3.5 MPa H_2, 24 h 0.17 wt% KOH	Selectivity: GLU (14%), SOR (74%)	89
Cellulose	[Bmim]Cl	Ru nanoparticles	353 K, sodium formate as hydrogen source, 5 h	SOR (94%)	90
5 wt% cellulose		Ru/$[Bmim]_3PW_{12}O_{40}$	433 K, 5 MPa H_2, 24 h	Selectivity: SOR (70.3%)	91

[a] GLU: glucose, SOR: sorbitol, MAN: mannitol

-sized by dispersion of Ru on ionic liquid ($BmimPF_6$) heteropolyacid ($H_3W_{12}O_{40}\cdot nH_2O$) hybrid as a support, and was introduced into the hydrolytic hydrogenation of cellulose by Ge *et al.*.[91] The catalyst consisted the function of hydrogenation (Ru sites) and hydrolysis (both Lewis and Brønsted acidic sites). Under the condition of 433 K and 5 MPa H_2, microcrystalline cellulose could be converted into sorbitol at the conversion of 63.7% with a selectivity of 70.3% after 24 h reaction. Brønsted acid generated through hydrogen spillover coupled with the supported Ru can promote the hydrolytic hydrogenation of cellulose to glycols.

2.5 Conversion of cellulose raw material to glycols

Gratifying progress has been achieved in the hydrolytic hydrogenation/hydrogenolysis of cellulose up to now. In order to accelerate the process of industrialization of biomass based chemicals and fuels, emphasis of the researchers has been turned to employing real biomass as the feedstock in this reaction. However, the compositions of the real biomass feedstocks exerted notable influences on the catalytic activity, three major components of lignocellulose, namely cellulose, hemicellulose and lignin, tangled together, rendering the separation of these compositions difficult to realize. Besides, the presence of inorganic salts ($CaCO_3$, $NaHCO_3$ and Na_2SO_4) [92]in the lignocellulose is another obstacle, and the presence of these salts shifted the product distribution from sorbitol to by-products. Consequently, investigations on the hydrolytic hydrogenation/hydrogenolysis of raw lignocellulose are worthy to be conducted. Catalytic conversion of raw lignocellulose was demonstrated in Table 6.

Spruce was employed as lignocellulose feedstocks in the hydrogenolysis reaction over Ru/C under the promotion of phosphoric acid and sulfuric acid. Yields of hexitols were 43.3% and 33.1% over Ru/C with the promotion of sulfuric acid and phosphoric acid, respectively. HPA was also utilized in hydrogenolysis of spruce, a yield of 64.9% C4-C6 sugar alcohols was obtained over with the promotion of $H_4[Si(W_3O_{10})_4]$. In our study, hydrogenolysis of cornstalk and corncob was conducted over Ni-Cu-ZnO catalysts.[52] Selectivities of 1,2-alkanediol were 48.5% and 55.5% with cornstalk and corncob as feedstocks, respectively, under the condition of 518 K, 4 MPa H_2. Corn stalks was used as a feedstock for hydrogenolysis reaction to yield EG and 1,2-PG.[93] Cellulosic feedstock with different chemical components and structures were prepared by introducing different pretreatment manners in this research. Results showed that crystallinity of the cellulosic feedstock has limited effects on the formation of glycols in this reaction. Catalytic hydrogenation of cellulose pretreated by ammonia gave a total yield of 48% for both EG and 1,2-PG at 518 K, 6.0 MPa H_2. Raw woody biomass were also employed as a feed stock over supported carbide catalysts, which exhibited high activity in catalytic hydrogenation.[94] Different sources of lignocellulose were introduced as feedstock in this research and it was found that with different chemical component, different catalytic performances were observed over supported carbide catalysts. Compared to supported noble metal catalysts, low price Ni-W_2C/AC showed much higher catalytic activity and gave a much higher glycol yield under the same reaction condition.

Steam explosion and alkali were found to be efficient pretreatment technology in hydrogenolysis of corn stalk.[95] Hemicellulose and lignin could be removed from corn stalk efficiently showing this a valid approach in raw material pretreatment. Corn stalk could be converted into EG (yield 20.38%) and glycerol (yield 52.36%) over Ni-W_2C catalyst after pretreated by steam explosion and alkali.

Kraft pulp from pulp mill was introduced as the feedstock in hydrolytic hydrogenation reaction by Murzin *et al.*[96] to sugars and sugar alcohols over metal supported on H-MCM-48 under the condition of 458 K, 2 MPa H_2. The active sites, acidity and the structure of the mesoporous material have a great influence on the yield of the sugars and sugar alcohols.

Raw Jerusalem artichoke stalk (JAS) was employed by Zhang *et al.*[97] as the feedstock in catalytic conversion promoted by commercial WO_3 and Raney Ni. The water-soluble substances existence in the JAS was found to cause a negative effect on the conversion of hemicellulose. By employing a simple hot water pretreatment, the EG yield could be increased from 29.9% to 37.6% because most of the water-soluble substances could be removed.

Fukuoka *et al.*[92] employed raw silver grass as the feedstock of hydrolytic hydrogenation reaction over the catalysis of carbon supported Pt catalysts to produce polyols. It was found that lignin consisted in raw silver grass diminished the reaction activity of cellulose. With the existence of lignin, small amount of sorbitol (2.8 wt %) and xylitol (7.3 wt %) were obtained. By introducing

Table 6 Hydrolytic hydrogenation/hydrogenolysis of raw lignocellulose over different catalysts

Starting material	Catalyst	Conditions	Products and yield/%	Ref.
1 wt% corn stalks	2% Ni-W_2C	518 K, 6 MPa H_2, 2 h	EG (18.3%), PG (13.9%)	93
1 wt% Birch	4%Ni-30%W_2C/AC	508 K, 6 MPa H_2, 4 h	EG (51.4%), 1,2-PG (14.2%)	94
1 wt% Poplar	4%Ni-30%W_2C/AC	508 K, 6 MPa H_2, 4 h	EG (48.6%), 1,2-PG (12.8%)	94
1 wt% Basswood	4%Ni-30%W_2C/AC	508 K, 6 MPa H_2, 4 h	EG (49.2%), 1,2-PG (11.8%)	94
1 wt% Ashtree	4%Ni-30%W_2C/AC	508 K, 6 MPa H_2, 4 h	EG (52.7%), 1,2-PG (11.9%)	94
1 wt% Beech	4%Ni-30%W_2C/AC	508 K, 6 MPa H_2, 4 h	EG (35.2%), 1,2-PG (11.4%)	94
1 wt% Xylosma	4%Ni-30%W_2C/AC	508 K, 6 MPa H_2, 4 h	EG (36.4%), 1,2-PG (13.7%)	94
5 wt% spruce	Ru/C	433 K, 5 MPa H_2, 1 h H_2SO_4	SOR (36.0%), ISO (7.3%)	33
5 wt% spruce	Ru/C	433 K, 5 MPa H_2, 1 h H_3PO_4	SOR (24.3%), ISO (8.8%)	33
5 wt% spruce	Ru/C	433 K, 5 MPa H_2, 5 h, 5 wt%$H_4[Si(W_3O_{10})_4]$	C4-C6 SUA (64.9%)	37
1 wt% cornstalk	2Ni-3Cu-5ZnO	518 K, 4 MPa H_2, 0.5 h	1,2-PG (20%), EG (15%), 1,2-BDO (4.6%), 1,2-HDO (5.4%)	52
1 wt% corncob	2Ni-3Cu-5ZnO	518 K, 4 MPa H_2, 0.5 h	1,2-PG (24%), EG (17.6%), 1,2-BDO (7.4%), 1,2-HDO (4.3%)	52
0.8 wt% silver grass	Pt/BP2000	463 K, 5 MPa H_2, 24 h	SOR (13%), XYL (14%)	92
1 wt% JAS	WO_3+ Raney Ni	518 K, 6 MPa $H_{2,}$ 2 h	EG (37.6%), 1,2-PG (6.3%)	97

[a] SOR: sorbitol, ISO: isosorbide, SUA: sugar alcohols, XYL: xylitol, JAS: Jerusalem artichoke stalk

weak bases, product distribution can be tuned to EG and PG which was supposed to be generated from decomposition of sugar and sorbitol. Alkali-explosion and neutralization were supposed to be efficient techniques that could increase the yield of sorbitol (13 wt%) and xylitol (14 wt%).

3. Hydrogenation and hydrogenolysis of sugar and sugar alcohols

Hydrogenation/hydrogenolysis of sugar and hydrogenolysis of sugar alcohols are important steps not only in the one-pot hydrolytic hydrogenation/hydrogenolysis of lignocellulose but also in multi-step lignocellulose transformation. Investigations on catalytic hydrogenation/hydrogenolysis of sugar and hydrogenolysis of sugar alcohols are essential to gain insights into the process of glycol production. In this part, we mainly focus on recent advances in hydrogenation/hydrogenolysis of sugar and sugar alcohols over the promotion of supported catalysts. Up to now, researches on developing catalysts utilized in the reaction of sugar and sugar alcohols hydrogenation/hydrogenolysis lie in transition metal catalysts such as nickel, copper and ruthenium catalysts.

3. 1 Reaction mechanism of glucose and sugar alcohols hydrogenolysis

Glucose and sorbitol have similar molecular structure because sorbitol can be produced *via* simple glucose hydrogenation reaction. Hydrogenolysis of these two hydroxyl compounds both need metal catalysts and base promoters under similar reaction condition. Therefore, hydrogenolysis of glucose and sorbitol to glycols might follow a similar reaction mechanism.[14] It is well known that the process of glucose and sorbitol hydrogenolysis contained the cleavage of C-C and C-O bond, as the final products comprised several low carbon polyols. As a consequence, it is necessary to verify the reaction mechanism of glucose and sorbitol hydrogenolysis so as to control the product distribution reasonably.

Sohounloue *et al.* [98] conducted the reaction of sorbitol hydrogenolysis over Ru/SiO_2 catalysts by changing the reaction temperature and aqueous pH. They proposed that C-C bond cleavage in sorbitol hydrogenolysis seems to follow a retro-aldol condensation mechanism in basic medium (Scheme 3 route B). Sorbitol first undergoes dehydrogenation reaction to produce an intermediate product; then an enol-ketone equilibrium could be obtained, resulting in an isomeride; finally this isomeride comes across a retro-aldol reaction with small molecule glycols produced. Andrew *et al.* [99] believed that C-C bond cleavage in hydrogenolysis of sugar (glucose and fructose) also follows the same retro-aldol condensation mechanism. The distribution of reaction products was found to dependent on the competition between the reaction rate of retro-aldol cleavage and sugar hydrogenation. According to the retro-aldol condensation mechanism, hydrogenolysis of glucose and sorbitol needs a structure of β-hydroxyl carbonyl generated from sorbitol dehydrogenation. The formed β-hydroxyl carbonyl undergoes the reaction of retro-aldol condensation forming aldehyde and ketone, which can be hydrogenated to low carbon glycols. In this reaction, metal catalysts promoted the dehydrogenation of sugar alcohols and the hydrogenation of formed intermediate products, while base catalysed the retro-aldol condensation of β-hydroxyl carbonyl.

C-O cleavage mechanism in hydrogenolysis of glucose and sugar alcohols was proposed by Montassier *et al.* [100] They proved the precursor of dehydration reaction was β-hydroxyl carbonyl, the same as retro-aldol condensation mechanism. After the dehydration reaction of β-hydroxyl carbonyl precursor, α,β-unsaturated carbonyl species were generated directly and then hydrogenated to glycols (Scheme 3 route A). In this reaction, metal catalysts promoted the reaction of dehydrogenation and hydrogenation, and base catalysed the dehydration of β-hydroxyl carbonyl precursor. By conducting the reaction of sorbitol hydrogenolysis on supported ruthenium catalysts, Montassier *et al* [101] believed that sorbitol mainly undergoes retro-michael reactions to produce two molecule glycerol by breaking the central C-C bond (Scheme 3 route C). A diacarbonyl species was essential in retro-michael mechanism.

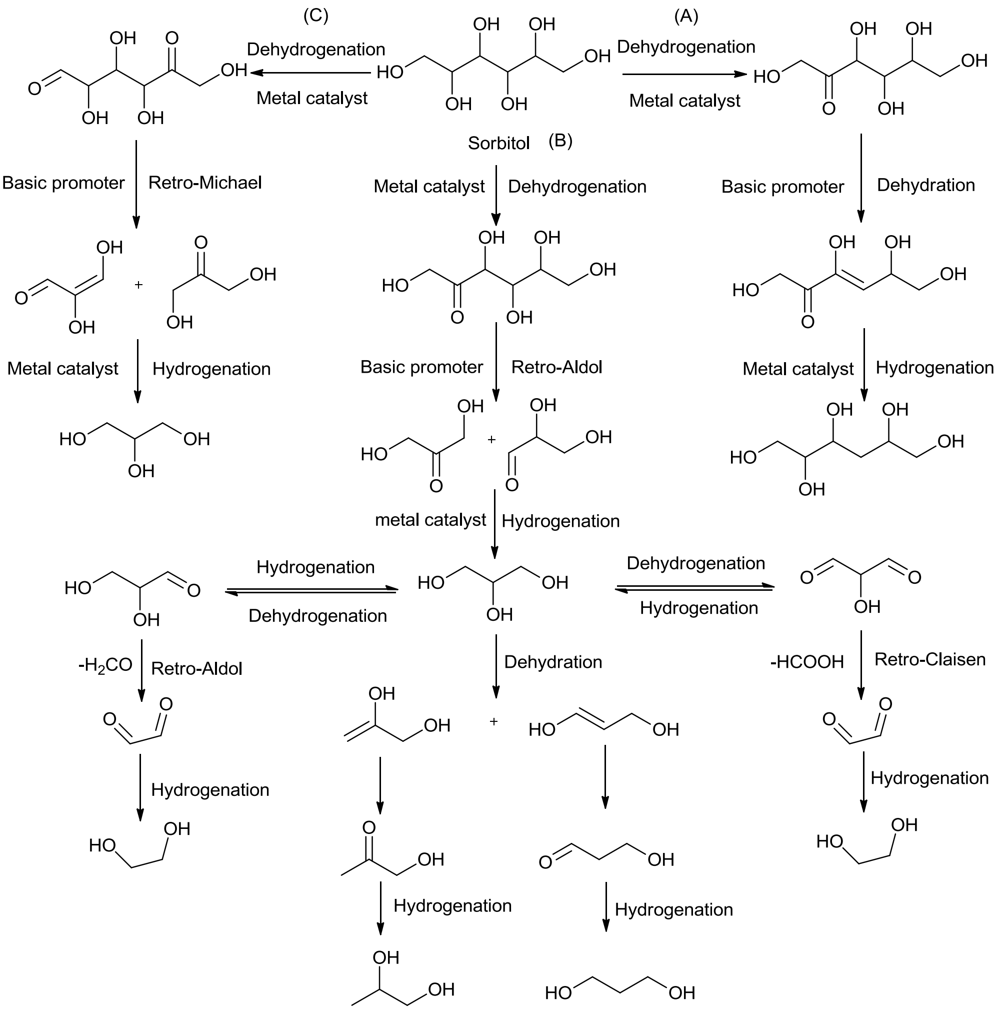
Reaction mechanism of sugar and sugar alcohols hydrogenolysis was deduced using 1,3-diol model compounds as reactants by Wang *et al.*[102] C-C and C-O bond cleavage in sugar and sugar alcohols hydrogenolysis were attributed to retro-aldol mechanism and dehydration of β-hydroxyl carbonyl, respectively. Retro-michael mechanism in sugar and sugar alcohols hydrogenolysis was found to be inappropriate because the dehydrogenation reaction, which is necessary in diacarbonyl species production, is very difficult to occur under the reaction condition. Besides, the precursor of retro-michael reaction was difficult to form because the dehydration reaction of the single carbonyl species was easier to occur than the dehydrogenation reaction. Hydrogenolysis of sugar and sugar alcohols was supposed to follow such mechanism: (1). Dehydrogenation of sugar alcohols to the intermediate product; (2). The intermediate product undergoes two different pathways, a: C-O cleavage reaction occurred *via* dehydration of the intermediate product and hydrogenation to produce glycols. b: C-C cleavage reaction realized through retro-aldol condensation of the intermediate product and the following hydrogenation to produce small molecule glycols.

3.2 Hydrogenation and hydrogenolysis of sugars

Glucose (40 wt%) was hydrogenated into sorbitol over ruthenium catalysts supported on active charcoal pellets in a trickle-bed reactor by Gallezot *et al.*[103] The catalysts were prepared by loading the metal on the supports through cationic exchange or anionic adsorption. The conversion of glucose could be 100%, while the selectivity of sorbitol was 99.2% under the condition of 373 K, 8 MPa H_2. Residence time of the reactant influence the epimerization of sorbitol to mannitol, which finally affected the sorbitol selectivity. Ru/C catalyst was also used by Hydrogenation of glucose was conducted over supported ruthenium catalysts [104] with diverse ruthenium particles under the condition of 393 K and 1.9 MPa H_2 (Table 7). Sorbitol could be produced at relatively high selectivity (87%-96%) under the same reaction condition and catalysts. It was found that the TOF of glucose hydrogenation related to the particle size of ruthenium.

Because of the superior mass transfer ability from micropore to liquid phase and the better desorption ability of sorbitol than the conventional carbon, woven rayon fabric derived active carbon cloths supported ruthenium showed outstanding performance in hydrogenation of glucose to sorbitol (99.5 selectivity at 99.7% conversion under the condition of 373 K, 8 MPa H_2), according to research of Besson et al.[105]

Lin *et al.*[106] conducted the hydrogenation of glucose to sorbitol over Ru supported on MCM-41. Higher sorbitol yield (94%) was obtained over the Ru/MCM-41 catalyst than other



Scheme 3 Reaction mechanism of sorbitol hydrogenolysis (A) C-O bond cleavage proposed by Montassier[100] (B) C-C bond cleavage under Retro-aldol mechanism proposed by Sohounloue and Andrew[98, 99] (C) C-C bond cleavage under Retro-Michael mechanism proposed by Montassier.[101]

catalysts like Ru/C, Ni powder and Pd/C under the condition of 393 K and 3 MPa H_2. The excellent reaction performance was attributed to the higher metal dispersion of Ru/MCM-41.

Zhao *et al.*[107] presented that Ru nanoparticles containing carbon microfibers showed higher activity in glucose hydrogenation than Ru supported on multi-walled carbon nanotubes, alumina microfibers and active carbon. The high activity and stability of this catalyst was attributed to the high degree of Ru dispersion, appropriate particle Ru size and high crystallinity.

Yang *et al.*[108] conducted the hydrogenation of glucose to sorbitol over Ru supported on multi-wall carbon nanotubes prepared by impregnation method. These catalysts showed higher activity in hydrogenation reaction compared with Ru supported on Al_2O_3, SiO_2 and Raney Ni. The superior reaction activity of these catalysts was due to the fine dispersion of Ru on the support which was confirmed by TEM analysis. Kilpio *et al.*

Table 7 Hydrogenation/hydrogenolysis of sugars over different catalysts

Starting materials	Catalysts	Conditions	Main product and yield/%	Ref.
40 wt% GLU	Ru/C	373 K, 8 MPa H_2	SOR (>99%)	103
40 wt% GLU	Pt/ACC	373 K, 8 MPa H_2	SOR (>99.5%)	111
17 wt % GLU	(Ni, Mo and Cu)/ Kieselguhr	423 K, 5 MPa H_2, 2 h	GLY (28%), EG (22%), PG (13%), SOR (4%)	112
1.8 wt% GLU	Ru/C	393 K, 1.9 MPa H_2, 2-3 h	SOR (96%)	104
0.45 wt% GLU	Pt/γ-Al_2O_3+hydrotalcite	363 K, 1.6 MPa H_2, 4 h	SOR (54%), MAN (14%), XYL (4%)	9
1.7 wt% GLU	Ni-W_2C/AC	518 K, 6 MPa H_2, 3 h	EG (36%), 1,2-PG (8%), SOR (9%)	117
5 wt% GLU	$Ni_{2.75}Cu_1Al_{1.49}$	398 K, 3 MPa H_2, 3 h	SOR (65%)	116
10 wt% GLU	Ru/MCM-41	393 K, 3 MPa H_2, 2 h	SOR (80%)	106
25 wt% GLU	Ru/ZSM-5	393 K, 4 MPa H_2, 2 h	SOR (99.2%)	110

[a] SOR: sorbitol, GLY: glycerol, MAN: mannitol, XYL: xylitol, GLU: glucose, FRU: fructose.

[109] performed the hydrogenation of glucose to sorbitol over Ru/C catalyst in a laboratory-scale trickle bed and in a semibatch stirred reactor. Sorbitol was produced at the selectivity of over 90% at the temperature of 363 K - 403 K. The reaction temperature impacted the reaction rate of glucose hydrogenation while the selectivity of the sorbitol did not change when temperature altered.

Hydrogenation of D-glucose over Ru/ZSM-5 prepared by one-step template-free process was evaluated by our research group.[110] Selectivity of D-sorbitol was 99.2% with 99.6% glucose conversion when the hydrogenation reaction was conducted under the condition of 393 K, 4 MPa H_2, 2 h. The superior performance of Ru/ZSM-5 was attributed to the high dispersion of Ru, the strong interaction between Ru and ZSM-5 and the appropriate acidity-basicity balance of the Ru/ZSM-5 surface.

Perrard *et al.*[111] conducted the reaction of glucose hydrogenation over activated carbon cloth supported platinum. A high sorbitol selectivity was obtained because low probability of D-sorbitol epimerization, desorption rate of D-sorbitol from the catalysts was faster than from conventional Pt/C. Dhepe *et al.*[9] conducted the reaction of glucose hydrogenation over the catalysis of $Pt/\gamma\text{-}Al_2O_3$ promoted by hydrotalcite, a basic promoter. Sugar alcohol was obtained at a yield of 68% under the condition of 363 K, 1.6 MPa H_2. Glucose can be transformed into open chain form, which is readily hydrogenated into sorbitol and mannitol by highly dispersed metal particles in the alkaline medium.

Using kieselguhr supported Ni, Mo, Cu catalyst, Saxena *et al.* [112] successfully converted sucrose *via* hydrogenolysis to produce glycerol, EG, PG, and sorbitol. Mo and Cu were chosen to promote the activity of the supported nickel catalysts. By coordinating the amount of Ni, Mo, Cu of the catalysts, the conversion of sucrose and the yield of glycerol could be optimized. Pachulski *et al.*[113] introduced Ni supported on ZrO_2 and/or TiO_2 in hydrogenation of glucose to sorbitol. These catalysts showed outstanding performance in hydrogenation of glucose compared to the Ni/SiO_2 catalysts, which was attributed to the interaction of metal and support. Raney-type Ni (promoted and unprompted) was also employed in hydrogenation of aqueous solution of glucose (10 wt%) at 393 K and 4 MPa H_2 in a three-phase slurry reactor.[114] During the catalytic reaction, the formed gluconic acid resulted in the leaching of Ni, Al and Fe from the surface of the catalysts, making Raney Ni deactivation severely.

Li *et al.*[115] found that Co-B amorphous alloy demonstrated high activity in glucose hydrogenation to sorbitol because the electronic interaction between Co and B alloy and superior hydrogen adsorption ability of Co active sites. Cr and W were both excellent promoters which could enhance the hydrogenation activity of Co-B alloy. Low-valent state Cr^- or W^- promoted polarization of C=O bond making the nucleophilic attack of hydrogen adsorbed on the Co active sites easier. Therefore, the reaction rate of hydrogenation could be enhanced. Ni/Cu/Al hydrotalcites prepared by co-precipitation method were also tested by Liu *et al.*[116] in hydrogenation of glucose to sorbitol. A sorbitol selectivity of 90% was obtained over $Ni_{2.75}Cu_1Al_{1.49}$ catalyst at 398 K and 3 MPa H_2.

Sels *et al.*[117] found that concentrated sugar solution could be converted into low chain glycol EG *via* the reaction of hydrogenolysis. A key intermediate product glycol aldehyde generated by retro-aldol condensation of glucose was identified by researchers, glycol aldehyde was regarded as the precursor of EG. Liang *et al.*[118] performed a two-step hydrogenation of highly concentrated glucose over the Cu-Cr catalysts with base promoters. At the low temperature step, sorbitol and mannitol was easily produced *via* the hydrogenation of glucose. The reaction of retro-aldol condensation occurred when base was added into the reaction system. The formation of coke-like precipitates could be avoided in the presence of base promoters at the high-temperature step. Different base promoters were also introduced in the hydrogenation of glucose, the concentration of OH^-, the metal ionic radius and the electric charge were found to be related to the conversion of glucose. Glucose hydrogenolysis conducted over copper catalysts supported on sulfated spherical carbon was found to yield 1,2-PG as the main product.[119] The selectivity of 1,2-PG can be optimized by tuning the acid sites and the hydrogenolysis sites of the catalysts.

3.3 Hydrogenolysis of sugar alcohols

As described above, sugar alcohols including sorbitol and xylitol can be obtained by hydrogenation of the corresponding sugars under the catalysis of supported Ru, Pt, Ni and other metals. Hydrogenation of sugar to corresponding sugar alcohols could be conducted under pretty mild conditions, while hydrogenolysis of sugar and sugar alcohols requires higher temperature, H_2 pressure and base promoter.[14] Among the sugar alcohols, sorbitol can be produced industrially in large scale by the hydrogenation of glucose over Ni or Ru catalysts. Sorbitol is also an important renewable carbon source and has been considered as one of the 12 top building blocks of biorefinery by United States Department of Energy (US DOE).[6, 120] The main products yielded from hydrogenolysis of sugar alcohols are glycols with short carbon chain like glycerol, EG, 1,2-PG and 1,3-PG which are important chemicals traditionally produced by the petrochemical methods.[10] In this part, we will review recent advances in hydrogenolysis of sugar alcohols to produce glycols. Table 8 exhibited the hydrogenolysis of sugar alcohols over different catalysts.

Gallezot *et al.*[121] demonstrated that sorbitol solution derived from biosustainable resources could be converted into C4-C6 polyols by the reaction of catalytic hydrogenolysis over copper catalysts. CuO-ZnO catalysts gave a 73% yield of C4 polyols under the condition of 453 K, 13 MPa H_2.

Ruthenium nanoparticles supported on carbon nanofiber was prepared and was used in sorbitol hydrogenolysis reaction to produce small molecule glycols.[122] The conversion of sorbitol and the selectivity to the target products over Ru/CNF was found to be superior to Ru supported on commercial activated carbon. Experimental results also indicated that glycerol was the precursor of the PG. Further investigations were also conducted to explore the effect of calcination on sorbitol hydrogenolysis to glycols.[123] Surface oxygen-containing groups (SOCGs) was introduced on the surface of carbon nanofiber *via* calcination. The interaction between Ru particles and sorbitol molecules could be impeded by SOCGs, reducing the conversion of sorbitol. However, unsaturated species were more easily to be hydrogenated to yield glycols with the presence of SOCGs because these species could be restrained around the Ru particle by SOCGs. As a result, selectivities of glycols could be obtained at a higher level.

Effect of different base promoters on hydrogenolysis of sorbitol was investigated by employing different bases [NaOH, KOH, Mg $(OH)_2$, $Ba(OH)_2$ and CaO] in the reaction system.[124] Among the bases utilized, CaO was proved to give the highest glycol selectivity. Ca^{2+} was found to be an important ion in this

Table 8 Hydrogenolysis of sugars alcohols over different catalysts

Starting materials	Catalysts	Conditions	Products and yields/%	Ref
20 wt% SOR	Ru/CNF	493 K, 8 MPa H_2, 4 h+ CaO	EG (19.32%), PG (31.98%), GLY(9.53)	122
10 wt% XYL	Ru/C	473 K, 4 MPa H_2, 1 h + Ca $(OH)_2$	Selectivity: EG (32.4%), PG (24.9%), GLY (9.6%)	125
10 wt% XYL	Pt/C	473 K, 4 MPa H_2, 1 h + Ca $(OH)_2$	Selectivity: EG (25%), PG (23%), GLY (10%)	125
10 wt% XYL	Cu-SiO_2	473 K, 4 MPa H_2, 2 h + Ca $(OH)_2$	Selectivity: EG (19.4%), PG (19.5%), GLY (4.4%)	126
10 wt% XYL	Cu-SiO_2	473 K, 4 MPa H_2, 2 h + Ca $(OH)_2$	Selectivity: EG (19.4%), PG (19.5%), GLY (4.4%)	126
10 wt% XYL	Ni/C	473 K, 4 MPa H_2, 1 h + $Ca(OH)_2$	Selectivity: EG (32.0%), PG (33.7%)	133
30 wt% SOR	Ce-Ni/Al_2O_3	493 K, 7 MPa H_2, 8 h, + $Ca(OH)_2$	EG (17.7%), PG (35.6%), GLY (25%)	127
5 wt% SOR	Ni_2P/AC	473 K, 4 MPa H_2, 0.75 h, + $Ba(OH)_2$	EG (17%), PG (27.7%),	128
20 wt% SOR	Ni-MgO	473 K, 4 MPa H_2, 4 h	Selectivity: EG (26.0%), PG (33.7%), GLY (21.1%)	132
10 wt% SOR	Ni-Re/C	523 K, 1 MPa H_2 N_2, 0.5 h + $Ba(OH)_2$	Selectivity: EG (15.8%), 1,2-PG (31%), GLY (6.8%)	135
15 wt% SOR	Ni-NaY	493 K, 6 MPa H_2, 6 h + $Ca(OH)_2$	Selectivity: EG (7%), 1,2-PG (69%), GLY (4%)	130
25 wt% SOR	Ru/Al_2O_3	493 K, 4 MPa H_2, 4 h	Selectivity: Glycols (19.1%)	134

[a] SOR: sorbitol, XYL: xylitol, GLY: glycerol.

reaction because the complexation of intermediate aldehydes and Ca^{2+} maximize the selectivity of glycols.

Hydrogenolysis of xylitol was conducted over the promotion of catalysts prepared by noble metal dispersed on various supports in the presence of base a promoter by Sun and Liu.[125] The dehydrogenation/hydrogenation activities combined with the surface acid-basicities of the catalysts dominated the final product distribution. The reaction pathway of xylitol hydrogenolysis was proposed to follow the retro-aldol condensation mechanism, xylitol underwent a process of dehydrogenation to xylose on the surface of metal, and then, base promoted retro-aldol condensation of xylose occurred, resulted in two intermediate products, glycolaldehyde and glyceraldehyde, which were hydrogenated to EG and PG, respectively. Copper supported on SiO_2 was also introduced into the reaction of xylitol hydrogenolysis.[126] Yields of EG and PG was 19.4% and 19.5% under the reaction condition of 473 K, 4.0 MPa H_2.

Ce was doped into the Ni/Al_2O_3 catalysts by Yuan *et al.*[127] through different methods in order to promote the catalytic activity in the sorbitol hydrogenolysis. Over the Ce-Ni/Al_2O_3-CP catalyst, glycols were produced at the selectivity of 55-60% at a 90% sorbitol conversion under the condition of 513 K, 7 MPa H_2, 12 h.

Metal phosphides supported on carbon were used to promote the hydrogenolysis of sorbitol, xylitol and glucose to produce EG and PG, Ni_2P was regarded as the active phase which gave the high activity of hydrogenolysis of sorbitol[128] under the reaction condition of 473 K, 4.0 MPa H_2. Yields to EG and PG was 17.0 and 28.5 mol. % and 27.7 and 42.9 mol. % when sorbitol and xylitol were employed as reactant, respectively.

Aqueous-phase hydrodeoxygenation of sorbitol was also conducted by Li and Huber[129] over Pt/SiO_2-Al_2O_3 catalysts. The main reaction pathway was concluded by identification of reaction intermediates. C-C bond cleavage was achieved *via* the retro-aldol condensation and decarbonylation which took place on metal sites. C-O bond cleavage was accomplished through the reaction of dehydration occurred on acid sites.

Nickel and platinum were supported on NaY to catalyse the hydrogenolysis of sorbitol to produce low carbon glycols.[130] 1,2-PG was obtained as the main product over Ni-NaY while glycerol was the principal product when Pt-NaY was utilized. Negligible effect on sorbitol conversion and product selectivity was observed when Pt was doped in Ni-NaY catalyst, however, the addition of base promoter like $Ca(OH)_2$ accelerated the conversion of sorbitol rather than product selectivity.

Besson *et al.*[131] performed the hydrogenolysis of the alkaline aqueous solution of xylitol to EG and PG over the Ru/C catalysts in a trickle-bed reactor. The influence of reaction parameters such as sodium hydroxide concentration, hydrogen pressure and temperature was explored in this research. The reaction results were consisted with the reaction pathway proposed before, and hydrogenolysis of xylitol followed the mechanism of retro-aldol condensation.

In previous researches, the base promoter such as NaOH, $Ca(OH)_2$ *etc*. was inevitably required in hydrogenolysis of sugar alcohols because base promoter was necessary in the C-C cleavage of the dehydrogenation intermediate products. However, the use of alkali brings about problems like difficulties in base recycling and water pollution. We employed MgO, a kind of solid base to support the metal of nickel to promote the hydrogenolysis of sorbitol under mild condition.[132] A high total selectivity (80.8%) of EG, PG and glycerol was obtained at the sorbitol conversion of 67.8% under the condition of 473 K and 4.0 MPa H_2 over the catalysis of Ni/MgO (3:7).

Alkali promoted Ni/C catalysts prepared by physically mix or co-supported method was employed to catalyse the hydrogenolysis of biomass-derived xylitol to produce glycols.[133] Alkali doped in the catalysts efficiently prevented the leaching and sintering of nanoparticles thus showing quite high reaction activity. Selectivity of EG, PG and glycerol was 69.5% while xylitol conversion was nearly 100% at 473 K, 4.0 MPa H_2 after 3 h. Mariscal *et al.*[134] evaluated the hydrogenolysis of sorbitol by employing Ru supported on different oxide supports (Al_2O_3, SiO_2, TiO_2 and ZrO_2) as the catalysts. Ru/Al_2O_3 gave the highest yield of glycols for the high surface acidity and the partially oxidized Ru species it possessed. Hydrogenolysis of sorbitol in the absence of hydrogen was carried out by Xu *et al.*[135] over Ni-Re/C catalyst. An important intermediate, acetol, was identified in sorbitol hydrogenolysis reaction. Re acted as an efficient promoter that could not only prevent the sintering of Ni particles but also accelerate the rate of hydrogen generation on the active sites.

Starting from corn stover derived sugar mixtures from the pretreatment and saccharification process[136] developed in our group, the yield of 1,2-alkanediols was as high as 68.5% over Ni-ZrO_2 catalyst in a 10 L scale of batchwise reaction at 453 K, and 6 MPa H_2 (unpublished results). The reaction can also be conducted over a continuous reactor, exhibiting great prospects in the cellulose conversion to commodity chemicals.

4. Summaries, challenges and prospects

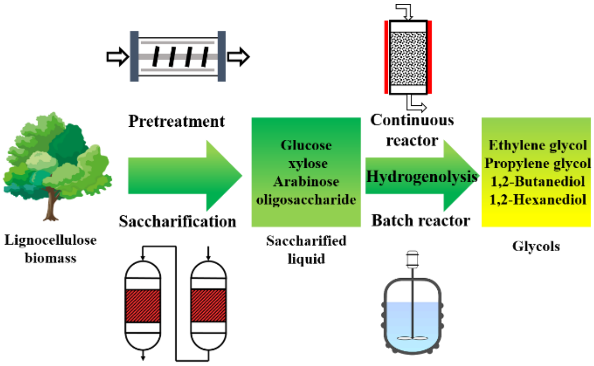


Fig. 4 Proposed route for the conversion of lignocellulosic biomass to glycols.

Biomass is the only renewable carbon resources that can be converted into liquid chemicals and liquid fuels, and the valorization of cellulose and biomass derived compounds holds great potential in solving the current problems such as global warming, food crisis and environmental problems. Recently, global efforts have successfully demonstrated the efficacy of heterogeneously catalytical conversion of cellulose to key primary building blocks of sugar alcohols, and directly to industrially attractive commodity glycols in one step.

Nevertheless, the present development of the catalysts haven't met the level required for commercialization. The components of the lignocellulose and crystalline texture resulted in the robust property and insolubility of lignocellulose in most solvents.[94] The currently available techniques concerning the direct conversion of lignocellulosic biomass usually suffer from the disadvantages of harsh reaction conditions, high energy input, low efficiency, and equipment corrosion. In order to solve the problems of interaction between substrate and catalysts in this process, mechanical degradation method[82, 83] (ball-milling), steam explosion[95], chemical pretreatment[93] (ammonia, H_2O_2, NaOH, *etc.*) and ionic liquid[88, 89, 91] were introduced into this system to facilitate the transformation of lignocellulose into high value-added chemicals. The product distribution of the hydrolytic hydrogenation/hydrogenolysis of lignocellulose was dominated by the coordination of cellulose hydrolysis and glucose hydrogenation/hydrogenolysis. Investigators developed some catalysts that contained various ratios of acid sites to metal sites to harmonize the hydrolysis of lignocellulose and glucose hydrogenation/hydrogenolysis.[50, 61, 65] The yield of sugar alcohols (sorbitol and mannitol) and glycols (EG and PG) can be optimized in this manner.

However, due to the relative low conversion of reactant and selectivity to the products, breakthroughs in catalytic conversion of lignocellulose are still needed.

(1) Investigations on the mechanisms of hydrolytic hydrogenation/hydrogenolysis of lignocellulose, hydrogenation/hydrogenolysis of sugars and the hydrogenolysis of sugar alcohols are still necessary. The influences of the feedstocks (the type and the concentration), the catalysts and the reaction conditions on the product distribution are required.

(2) Rational catalyst design is another challenge confronted in the catalytic conversion of lignocellulose. Bifunctional catalysts have been proved to be efficient in hydrolytic hydrogenation/hydrogenolysis of lignocellulose. The acidity and basicity, the interactions between metal and support, the chemical and mechanical stability and the stability of the catalysts all affected the catalytic activity and the products distribution.

(3) Up to now, reactor utilized in most of the reports are batch reactor. However, continuous reactor is more appropriate in large-scale production. Nonetheless, the main obstacle on this road is still the insolubility of the lignocellulose in most solvents. Starting from saccharified liquid or sugar alcohols, the hydrogenolysis reaction could be very efficient even under quite mild reaction conditions. In this context, effective pretreatment and saccharification techniques should be integrated in the process of transformation of cellulosic biomass to chemicals (Fig. 4), which is also another focus in the biorefinery.

Abbreviations

EG	Ethylene glycol
EGME	Ethylene glycol monoether
1,2-PG	1,2-Propylene glycol
1,2-BDO	1,2-Butanediol
1,2-HDO	1,2-Hexanediol
HPAs	Heteropolyacid
CNT	Carbon nanotube
CNF	Carbon nanofiber
GVL	γ-valerolactone
SOCGs	Surface oxygen-containing groups
GRO	Reduced graphene oxide

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References

1 S. Chu and A. Majumdar, *nature*, 2012, **488**, 294-303.

2 A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cairney, C. A. Eckert, W. J. Frederick, Jr., J. P. Hallett, D. J. Leak, C. L. Liotta, J. R. Mielenz, R. Murphy, R. Templer and T. Tschaplinski, *Science*, 2006, **311**, 484-489.

3 T. P. Vispute, H. Zhang, A. Sanna, R. Xiao and G. W. Huber, *Science*, 2010, **330**, 1222-1227.

4 C. Somerville, H. Youngs, C. Taylor, S. C. Davis and S. P. Long, *Science*, 2010, **329**, 790-792.

5 S. Van De Vyver, J. Geboers, P. A. Jacobs and B. F. Sels, *ChemCatChem*, 2011, **3**, 82-94.

6 P. Gallezot, *Chem. Soc. Rev.*, 2012, **41**, 1538-1558.

7 C. Liu, H. Wang, A. M. Karim, J. Sun and Y. Wang, *Chem. Soc. Rev.*, 2014, DOI: DOI: 10.1039/c3cs60414d.

8 J. Zhang, J. B. Li, S. B. Wu and Y. Liu, *Ind. Eng. Chem. Res.*, 2013, **52**, 11799-11815.

9 A. Tathod, T. Kane, E. S. Sanil and P. L. Dhepe, *J. Mol. Catal. A: Chem.*, 2014, **388**, 90-99.

10 H. Yue, Y. Zhao, X. Ma and J. Gong, *Chem. Soc. Rev.*, 2012, **41**, 4218-4244.

11 J. Xuan, M. K. H. Leung, D. Y. C. Leung and M. Ni, *Renew. Sust. Energ. Rev.*, 2009, **13**, 1301-1313.

12 R. D. Cortright, R. R. Davda and J. A. Dumesic, *Nature*, 2002, **418**, 964-967.

13 M. Besson, P. Gallezot and C. Pinel, *Chem. Rev.*, 2013, **114**, 1827-1870.

14 A. M. Ruppert, K. Weinberg and R. Palkovits, *Angew. Chem. Int. Ed.*, 2012, **51**, 2564-2601.

15 J. C. Serrano-Ruiz, R. Luque and A. Sepulveda-Escribano, *Chem. Soc. Rev.*, 2011, **40**, 5266-5281.

16 Y. G. Zheng, X. L. Chen and Y. C. Shen, *Chem. Rev.*, 2008, **108**, 5253-5277.

17 Y. C. Lin and G. W. Huber, *Energ. Environ. Sci.*, 2009, **2**, 68-80.

18 A. Wang and T. Zhang, *Acc. Chem. Res.*, 2013, **46**, 1377-1386.

19 L. Hu, G. Zhao, W. W. Hao, X. Tang, Y. Sun, L. Lin and S. J. Liu, *RSC Adv.*, 2012, **2**, 11184-11206.

20 C. H. Zhou, J. N. Beltramini, Y. X. Fan and G. Q. Lu, *Chem. Soc. Rev.*, 2008, **37**, 527-549.

21 C. H. Zhou, X. Xia, C. X. Lin, D. S. Tong and J. Beltramini, *Chem. Soc. Rev.*, 2011, **40**, 5588-5617.

22 R. Rinaldi and F. Schuth, *ChemSusChem*, 2009, **2**, 1096-1107.

23 Y. H. Zhang and L. R. Lynd, *Biotechnol Bioeng.*, 2004, **88**, 797-824.

24 D. Yamaguchi, M. Kitano, S. Suganuma, K. Nakajima, H. Kato and M. Hara, *J. Phys. Chem., C.* 2009, **113**, 3181-3188.
25 R. W. Torget, J. S. Kim and Y. Y. Lee, *Ind. Eng. Chem. Res.*, 2000, **39**, 2817-2825.
26 M. Sasaki, Z. Fang, Y. Fukushima, T. Adschiri and K. Arai, *Ind. Eng. Chem. Res.*, 2000, **39**, 2883-2890.
27 P. L. Dhepe and A. Fukuoka, *ChemSusChem*, 2008, **1**, 969-975.
28 M. J. Climent, A. Corma and S. Iborra, *Chem. Rev.*, 2011, **111**, 1072-1133.
29 H. Kobayashi, T. Komanoya, S. K. Guha, K. Hara and A. Fukuoka, *Appl. Catal., A*, 2011, **409**, 13-20.
30 A. Fukuoka and P. L. Dhepe, *Angew. Chem. Int. Ed.*, 2006, **45**, 5161-5163.
31 X. C. Wang, L. Q. Meng, F. Wu, Y. J. Jiang, L. Wang and X. D. Mu, *Green Chem.*, 2012, **14**, 758-765.
32 C. Luo, S. Wang and H. Liu, *Angew. Chem. Int. Ed.*, 2007, **46**, 7636-7639.
33 R. Palkovits, K. Tajvidi, J. Procelewska, R. Rinaldi and A. Ruppert, *Green Chem.*, 2010, **12**, 972-978.
34 J. Geboers, S. Van de Vyver, K. Carpentier, P. Jacobs and B. Sels, *Chem. Commun.*, 2011, **47**, 5590-5592.
35 G. Liang, C. Wu, L. He, J. Ming, H. Cheng, L. Zhuo and F. Zhao, *Green Chem.*, 2011, **13**, 839-842.
36 J. Geboers, S. Van de Vyver, K. Carpentier, K. de Blochouse, P. Jacobs and B. Sels, *Chem. Commun.*, 2010, **46**, 3577-3579.
37 R. Palkovits, K. Tajvidi, A. M. Ruppert and J. Procelewska, *Chem. Commun.*, 2010, **47**, 576-578.
38 T. Okuhara, *Chem. Rev.*,2002, **102**, 3641-3665.
39 B. S. Jan Geboers, S. Van de Vyver, K. Carpentier, P. Jacobs and B. Sels, *Green Chem.*, 2011, **13**, 2167-2174.
40 Q. Y. Liu, Y. H. Liao, T. J. Wang, C. L. Cai, Q. Zhang, N. Tsubaki and L. L. Ma, *Ind. Eng. Chem. Res.*, 2014, **53**, 12655-12664.
41 Y. Liao, Q. Liu, T. Wang, J. Long, Q. Zhang, L. Ma, Y. Liu and Y. Li, *Energ. Fuel.*, 2014. DOI: 10.1021/ef500717p.
42 Z. J. Wu, S. H. Ge, C. X. Ren, M. H. Zhang, A. Yip and C. M. Xu, *Green Chem.*, 2012, **14**, 3336-3343.
43 Z. Tai, J. Zhang, A. Wang, M. Zheng and T. Zhang, *Chem. Commun.*, 2012, **48**, 7052-7054.
44 J. Zhang, S. B. Wu and Y. Liu, *Energ. Fuel.*, 2014, **28**, 4242-4246.
45 T. S. Chamblee, R. R. Weikel, S. A. Nolen, C. L. Liotta and C. A. Eckert, *Green Chem.*, 2004, **6**, 382-386.
46 Y. Liu, C. Luo and H. Liu, *Angew. Chem. Int. Ed.*, 2012, **51**, 3249-3253.
47 N. Ji, T. Zhang, M. Zheng, A. Wang, H. Wang, X. Wang and J. G. Chen, *Angew. Chem. Int. Ed.*, 2008, **47**, 8510-8513.
48 N. Ji, T. Zhang, M. Zheng, A. Wang, H. Wang, X. Wang, Y. Shu, A. L. Stottlemyer and J. G. Chen, *Catal. Today*, 2009, **147**, 77-85.
49 Y. Zhang, A. Wang and T. Zhang, *Chem. Commun.*, 2010, 862-864.
50 M. Y. Zheng, A. Q. Wang, N. Ji, J. F. Pang, X. D. Wang and T. Zhang, *ChemSusChem*, 2010, **3**, 63-66.
51 Z. Tai, J. Zhang, A. Wang, J. Pang, M. Zheng and T. Zhang, *ChemSusChem*, 2013, **6**, 652-658.
52 X. C. Wang, F. Wu, S. X. Yao, Y. J. Jiang, J. Guan and X. D. Mu, *Chem Lett*, 2012, **41**, 476-478.
53 K. Tajvidi, P. J. Hausoul and R. Palkovits, *ChemSusChem*, 2014, **7**, 1311-1317.
54 S. J. You, I. G. Baek and E. D. Park, *Appl. Catal. A.*, 2013, **466**, 161-168.
55 J. Li, L. T. Liu, Y. Liu, M. Z. Li, Y. H. Zhu, H. C. Liu, Y. Kou, J. Z. Zhang, Y. Han and D. Ma, *Energ. Environ. Sci.*, 2014, **7**, 393-398.
56 T. Y. Deng and H. C. Liu, *Green Chem.*, 2013, **15**, 116-124.
57 H. Kobayashi, Y. Ito, T. Komanoya, Y. Hosaka, P. L. Dhepe, K. Kasai, K. Hara and A. Fukuoka, *Green Chem.*, 2011, **13**, 326-333.
58 P. Yang, H. Kobayashi, K. Hara and A. Fukuoka, *ChemSusChem*, 2012, **5**, 920-926.
59 H. Kobayashi, T. Komanoya, K. Hara and A. Fukuoka, *ChemSusChem*, 2010, **3**, 440-443.
60 S. Van de Vyver, L. Peng, J. Geboers, H. Schepers, F. de Clippel, C. J. Gommes, B. Goderis, P. A. Jacobs and B. F. Sels, *Green Chem.*, 2010, **12**, 1560.
61 S. Van de Vyver, J. Geboers, W. Schutyser, M. Dusselier, P. Eloy, E. Dornez, J. W. Seo, C. M. Courtin, E. M. Gaigneaux, P. A. Jacobs and B. F. Sels, *ChemSusChem*, 2012, **5**, 1549-1558.
62 S. Van de Vyver, J. Geboers, M. Dusselier, H. Schepers, T. Vosch, L. Zhang, G. Van Tendeloo, P. A. Jacobs and B. F. Sels, *ChemSusChem*, 2010, **3**, 698-701.
63 L. N. Ding, A. Q. Wang, M. Y. Zheng and T. Zhang, *ChemSusChem*, 2010, **3**, 818-821.
64 J. Pang, A. Wang, M. Zheng, Y. Zhang, Y. Huang, X. Chen and T. Zhang, *Green Chem.*, 2012, **14**, 614-617.
65 W. P. Deng, M. Liu, X. S. Tan, Q. H. Zhang and Y. Wang, *J. Catal.*, 2010, **271**, 22-32.
66 M. Liu, W. Deng, Q. Zhang, Y. Wang and Y. Wang, *Chem. Commun.*, 2011, **47**, 9717-9719.
67 G. Liang, H. Cheng, W. Li, L. He, Y. Yu and F. Zhao, *Green Chem.*, 2012, **14**, 2146-2149.
68 G. Liang, L. He, H. Cheng, W. Li, X. Li, C. Zhang, Y. Yu and F. Zhao, *J. Catal.*,2014, **309**, 468-476.
69 G. Liang, L. He, M. Arai and F. Zhao, *ChemSusChem*, 2014, **7**, 1415-1421.
70 A. Negoi, K. Triantafyllidis, V. I. Parvulescu and S. M. Coman, *Catal. Today.*, 2014, **223**, 122-128.
71 Y. L. Cao, J. W. Wang, M. Q. Kang and Y. L. Zhu, *J. Mol. Catal. A: Chem.*, 2014, **381**, 46-53.
72 H. Kobayashi, Y. Hosaka, K. Hara, B. Feng, Y. Hirosaki and A. Fukuoka, *Green Chem.*, 2014, **16**, 637-644.
73 W. Zhu, H. Yang, J. Chen, C. Chen, L. Guo, H. Gan, X. Zhao and Z. Hou, *Green Chem.*, 2014, **16**, 1534-1542.
74 F. Chambon, F. Rataboul, C. Pinel, A. Cabiac, E. Guillon and N. Essayem, *ChemSusChem*, 2013, **6**, 500-507.
75 J. X. Xi, Y. Zhang, Q. N. Xia, X. H. Liu, J. W. Ren, G. Z. Lu and Y. Q. Wang, *Appl. Catal. A.*, 2013, **459**, 52-58.
76 J. X. Xi, Y. Zhang, D. Q. Ding, Q. N. Xia, J. J. Wang, X. H. Liu, G. Z. Lu and Y. Q. Wang, *Appl. Catal. A.*, 2014, **469**, 108-115.
77 J. Xi, D. Ding, Y. Shao, X. Liu, G. Lu and Y. Wang, *ACS. Sustain. Chem. Eng.*, 2014, DOI: 10.1021/sc500380c.
78 J. Chen, S. Wang, J. Huang, L. Chen, L. Ma and X. Huang, *ChemSusChem*, 2013, **6**, 1545-1555.
79 D. Wang, W. Niu, M. Tan, M. Wu, X. Zheng, Y. Li and N. Tsubaki, *ChemSusChem*, 2014, **7**, 1398-1406.
80 Z. Xiao, S. Jin, M. Pang and C. Liang, *Green Chem.*, 2013, **15**, 891.
81 M. R. Liu, H. Wang, J. Y. Han and Y. F. Niu, *Carbohyd. Polym.*, 2012, **89**, 607-612.
82 A. Shrotri, L. K. Lambert, A. Tanksale and J. Beltramini, *Green Chem.*, 2013, **15**, 2761-2768.
83 J. Hilgert, N. Meine, R. Rinaldi and F. Schuth, *Energ. Environ. Sci.*, 2013, **6**, 92-96.
84 A. Brandt, J. Grasvik, J. P. Hallett and T. Welton, *Green Chem.*, 2013, **15**, 550-583.
85 J. L. Song, H. L. Fan, J. Ma and B. X. Han, *Green Chem.*, 2013, **15**, 2619-2635.
86 T. Vancov, A. S. Alston, T. Brown and S. McIntosh, *Renew. Energ.*, 2012, **45**, 1-6.
87 J. X. Long, X. H. Li, L. F. Wang and N. Zhang, *Sci. China. Chem.*, 2012, **55**, 1500-1508.
88 N. Yan, C. Zhao, C. Luo, P. J. Dyson, H. C. Liu and Y. Kou, *J. Am. Chem. Soc.*, 2006, **128**, 8714-8715.
89 I. A. Ignatyev, C. Van Doorslaer, P. G. Mertens, K. Binnemans and D. E. De Vos, *ChemSusChem*, 2010, **3**, 91-96.
90 Y. Zhu, Z. N. Kong, L. P. Stubbs, H. Lin, S. Shen, E. V. Anslyn and J. A. Maguire, *ChemSusChem*, 2010, **3**, 67-70.
91 X. N. Xie, J. Y. Han, H. Wang, X. L. Zhu, X. Liu, Y. F. Niu, Z. Q. Song and Q. F. Ge, *Catal. Today*, 2014, **233**, 70-76.
92 H. Kobayashi, Y. Yamakoshi, Y. Hosaka, M. Yabushita and A. Fukuoka, *Catal. Today.*, 2014, **226**, 204-209.
93 J. F. Pang, M. Y. Zheng, A. Q. Wang and T. Zhang, *Ind. Eng. Chem. Res.*, 2011, **50**, 6601-6608.
94 C. Z. Li, M. Y. Zheng, A. Q. Wang and T. Zhang, *Energ. Environ. Sci.*, 2012, **5**, 6383-6390.
95 Y. G. Sun, Y. Ma, Z. Wang and J. Yao, *Bioresour. Technol.*, 2014, **158**, 307-312.
96 M. Kaldstrom, N. Kumar, M. Tenho, M. V. Mokeev, Y. E. Moskalenko and D. Y. Murzin, *ACS. Catal.*, 2012, **2**, 1381-1393.
97 L. K. Zhou, J. F. Pang, A. Q. Wang and T. Zhang, *Chin. J. Catal.*,2013, **34**, 2041-2046.

98 D. Sohounloue, C. Montassier and J. Barbier, *Korean J. Chem. Eng.*, 1983, **22**, 391-397.
99 M. A. Andrews and S. A. Klaeren, *J. Am. Chem. Soc.*, 1989, **111**, 4131-4133.
100 C. Montassier, D. Giraud and J. Barbier, *Studies in Surface Science and Catalysis*, 1988, **41**, 165-170.
101 C. Montassier, J. C. Menezo, L. C. Hoang, C. Renaud and J. Barbier, *J. Mol. Catal.*, 1991, **70**, 99-110.
102 K. Y. Wang, M. C. Hawley and T. D. Furney, *Ind. Eng. Chem. Res.*, 1995, **34**, 3766-3770.
103 P. Gallezot, N. Nicolaus, G. Fleche, P. Fuertes and A. Perrard, *J. Catal.*,1998, **180**, 51-55.
104 A. Aho, S. Roggan, O. A. Simakova, T. Salmi and D. Y. Murzin, *Catal. Today*, 2014, DOI: 10.1016/j.cattod.2013.12.031.
105 M. Besson, P. Gallezot, A. Perrard and C. Pinel, *Catal. Today*, 2005, **102**, 160-165.
106 J. Zhang, L. Lin, J. Zhang and J. Shi, *Carbohydr. Res.*, 2011, **346**, 1327-1332.
107 J. Liu, P. Bai and X. S. Zhao, *Phys. Chem. Chem. Phys.*, 2011, **13**, 3758-3763.
108 J. X. Pan, J. H. Li, C. Wang and Z. Y. Yang, React. Kinet. Catal. Lett., 2007, **90**, 233-242.
109 T. Kilpio, A. Aho, D. Murzin and T. Salmi, *Ind. Eng. Chem. Res.*,2013, **52**, 7690-7703.
110 X. C. Guo, X. C. Wang, J. Guan, X. F. Chen, Z. F. Qin, X. D. Mu and M. Xian, *Chin. J. Catal.*, 2014, **35**, 733-740.
111 A. Perrard, P. Gallezot, J.-P. Joly, R. Durand, C. Baljou, B. Coq and P. Trens, *App. Catal. A*, 2007, **331**, 100-104.
112 S. R. V. Utkarsh Saxena, *Ind. Eng. Chem. Res.*, 2005, **44**, 1466-1473.
113 R. Geyer, P. Kraak, A. Pachulski and R. Schodel, *Chem. Ing. Tech.*, 2012, **84**, 513-516.
114 B. W. Hoffer, E. Crezee, F. Devred, P. R. M. Mooijman, W. G. Sloof, P. Kooyman, A. D. van Langeveld, F. Kapteijn and J. A. Moulijn, *Appl. Catal. A*, 2003, **253**, 437-452.
115 H. X. Li, H. Li and M. H. Wang, *Appl. Catal. A*, 2001, **207**, 129-137.
116 J. Zhang, S. B. Wu, Y. Liu and B. Li, *Catal.Commun.*, 2013, **35**, 23-26.
117 R. Ooms, M. Dusselier, J. A. Geboers, B. Op de Beeck, R. Verhaeven, E. Gobechiya, J. A. Martens, A. Redl and B. F. Sels, *Green Chem.*, 2014, **16**, 695-707.
118 Z. H. Xiao, S. H. Jin, G. Y. Sha, C. T. Williams and C. H. Liang, *Ind. Eng. Chem. Res.*, 2014, **53**, 8735-8743.
119 D. Liang, C. W. Liu, S. P. Deng, Y. L. Zhu and C. X. Lv, *Catalysis Commun.*, 2014, **54**, 108-113.
120 J. J. Bozell and a. G. R. Petersen, *Green Chem.*, 2010, **12**, 539-554.
121 B. Blanc, A. Bourrel, P. Gallezot, T. Haas and P. Taylor, *Green Chem.*, 2000, **2**, 89-91.
122 L. Zhao, J. H. Zhou, Z. J. Sui and X. G. Zhou, *Chem. Eng. Sci.*, 2010, **65**, 30-35.
123 L. Zhao, J. H. Zhou, H. Chen, M. G. Zhang, Z. J. Sui and X. G. Zhou, *Korean J. Chem. Eng.*, 2010, **27**, 1412-1418.
124 J. H. Zhou, G. C. Liu, Z. J. Sui, X. G. Zhou and W. K. Yuan, *Chin. J. Catal.*,2014, **35**, 692-702.
125 J. Sun and H. Liu, *Green Chem.*, 2011, **13**, 135-142.
126 Z. Huang, J. Chen, Y. Jia, H. Liu, C. Xia and H. Liu, *Appl. Catal., B*, 2014, **147**, 377-386.
127 L. Ye, X. Duan, H. Lin and Y. Yuan, *Catal. Today*, 2012, **183**, 65-71.
128 T. Soták, T. Schmidt and M. Hronec, *Appl. Catal., A*, 2013, **459**, 26-33.
129 N. Li and G. W. Huber, *J. Catal.*, 2010, **270**, 48-59.
130 M. Banu, S. Sivasanker, T. M. Sankaranarayanan and P. Venuvanalingam, *Catal. Commun.*, 2011, **12**, 673-677.
131 F. Auneau, M. Berchu, G. Aubert, C. Pinel, M. Besson, D. Todaro, M. Bernardi, T. Ponsetti and R. Di Felice, *Catal. Today*, 2014, **234**, 100-106.
132 X. G. Chen, X. C. Wang, S. X. Yao and X. D. Mu, *Catal. Commun.*, 2013, **39**, 86-89.
133 J. Y. Sun and H. C. Liu, *Catal. Today*, 2014, **234**, 75-82.
134 I. M. Leo, M. L. Granados, J. L. G. Fierro and R. Mariscal, *Chin. J. Catal.*, 2014, **35**, 614-621.
135 J. Zhang, F. Lu, W. Yu, J. Chen, S. Chen, J. Gao and J. Xu, *Catal. Today*, 2014, DOI: 10.1016/j.cattod.2014.03.021
136 C. Liu, E. van der Heide, H. S. Wang, B. Li, G. Yu and X. D. Mu, *Biotechnol Biofuels*, 2013, **6**, DOI: 10.1186/1754-6834-6-97 *http://www.biotechnologyforbiofuels.com/content/6/1/97.*