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**NANYANG
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**BIOMASS CONVERSION AND UPGRADING OVER
CARBON CATALYST**

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SCHOOL OF CHEMICAL AND BIOMEDICAL
ENGINEERING

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Abstract

Biomass conversion and upgrading are promising solutions for energy shortage and environment problems. Located in Southeast Asia, Singapore is surrounded by abundant biomass resource in its neighboring countries. However, most of the biomass feedstock is underutilization.

Cellulose, which represents the most abundant biomass resource, has been examined over noble metal supported carbon catalyst as an example of biomass conversion. As a Johnson Matthey (JM) supported program, we examined cellulose hydrogenation over Pt/AC produced from JM by the trial-and-error method. After tuning the reaction conditions, a sorbitol yield up to 25% is obtained. We also proposed a novel and effective catalyst optimization method which can further improve the sorbitol yield to 50% by further reducing the Pt/AC in ethylene glycol. This catalytic performance improvement is attributed to the effect of particle size according to XRD and TEM results. CV scans of the Pt/AC indicate that the decline of platinum's oxidation and reduction activity after EG treatment may suppress the side reactions during cellulose hydrogenation, hence improve sorbitol yield.

Ruthenium has been proved as an ideal catalyst in biomass conversion, especially for cellulose hydrogenation. However, studies of such reactions are extremely time-consuming due to the numerous side reactions and the complexity of interactions among reaction parameters. In this work, we introduced multivariate analysis method for the study of cellulose hydrogenation. The effect of temperature, hydrogen pressure, catalyst amount and ruthenium loading were comprehensively explored based on a response surface design

(RSD). Among all the 26 hydrogenation reactions, the highest sorbitol yield of 71.9% was obtained. The reaction data was then used to produce a regression model which shows strong statistical significance and high accuracy. Though this model, we evaluated the effectiveness of all the reaction parameters. It was found that ruthenium loading and temperature were the two main driving forces for sorbitol yield. High sorbitol yield could only be obtained while ruthenium loading and temperature were well tuned. The synergistic effects among reaction parameters were well presented with the help of contour plots and surface plots generated from the model. Lastly, a prediction formula according to the reaction data was constructed to predict the sorbitol yield under other reaction conditions.

Sorbitol, which is the main product of cellulose hydrogenation, has been examined over sulfonated carbon catalysts as an example of biomass upgrading. The sulfonated carbon catalysts show high catalytic activity towards the synthesis of isosorbide from sorbitol, with a yield up to 60% with negligible performance loss for five consecutive runs. The sulfuric groups are identified as the main active sites for sorbitol dehydration. The physical and chemical properties of the catalysts are evaluated by advanced and extensive characterization techniques, such as XRD, TEM, SEM, BET, FTIR, EA, EDAX, TGA and Raman spectroscopy.

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List of Abbreviations

1,2-PG	1,2-propanediol
AC	Active carbon
APR	Aqueous-phase reforming
Aq C	Soluble carbon content
ATR-IR	Attenuated total reflection infrared
BET	Brunauer-Emmett-Teller
BmimCl	1-buty-3-methylimidazolium chloride
CCD	Central composite design
CNT	Carbon nanotube
CrI	crystallinity index
CV	Cyclic voltammetry
DFF	2,5-diformylfuran
DP	degree of polymerization
EA	Elemental Analysis
EDAX	Energy-dispersive X-ray spectroscopy
EG	Ethylene glycol
FDA	2,5-furandicarboxylic acid
FTIR	Fourier-transform infrared spectroscopy
FTIR	Fourier Transition Infrared Spectroscopy
GC-MS	Gas chromatography–mass spectrometry
GHG	Greenhouse gas
GVL	gamma-Valerolactone
HMF	5-hydroxymethylfurfural

HPLC	High performance liquid column
HUSY	H form of ultra-stable Y zeolite
JM	Johnson Matthey
RSD	Response surface design
SCW	Supercritical water
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscopy
TGA	Thermal gravimetric analysis
TOC	Total organic carbon
TON	Turnover numbers
XRD	X-Rays Diffraction

Chapter 1 Background and Philosophy

1.1 Background

Energy is the driving force of our society[1]. As our society grows rapidly, the demand for energy surges up in the same way[2]. Currently, fossil fuel produces more than three-quarter of the total energy we consumed[3]. However, fossil fuel is not renewable, as it takes millions of years to evolve but now depletes out at a much faster rate[4, 5]. It is estimated that the current reserves of oil can only supply our need for less than 40 years[3]. Moreover, our environment has been heavily pressured for the unprecedented use of fossil fuels. As a result, environmental issues such as global warming, air pollution, and climate changes leave us in a danger and unpredictable situation against our long-term development[6-8]. Therefore, it is urgently needed for the research and development of renewable green energy such as solar energy, geothermal energy, tide energy, wind energy, nuclear energy etc.[9-11].

Biomass is surprisingly one of the promising options. As the natural carrier of solar energy, plants and biological microorganisms from land to sea reserve about 130×10^{12} watt of the radiation energy through photosynthesis[12]. Annual production of lignin and cellulose is estimated to be 16 billion tons, which is more than ten times of annual oil production[13]. Moreover, the consumption of biomass produces much less emission of greenhouse gas (GHG) than fossil fuels, since those CO_2 released from biomass energy equals to the CO_2 captured during their photosynthesis process.

We have a long history of utilizing biomass. The food our ancestors harvested, the wood they used to warm up and the timber they used to build

houses and a variety of tools all come from the world of biomass[14, 15]. Traditional medicine and flagrant sediment are also examples of utilizing biomass. Since the late 19th century, industrial revolution spread around the world and increased the needs of biomass such as rubber and lubricant. Biomass could be classified as edible biomass and non-edible biomass. The former includes agriculture products such as corn, wheat, potato which contain a high amount of starch or vegetable oils. Conversion of edible biomass to glucose or other valuable chemicals has been established industrially by companies like Roquette and Cognis, who could process megatons of edible biomass every year. This edible biomass process produces valuable products, yet inevitably raises some moral issues. Since many developing countries are still facing food shortage, it is widely considered controversial to produce energy or chemical from a food resource. That is why studies on non-edible feedstock like woody plants, agriculture residues energy grass crop, and municipal waste become increasingly popular nowadays.

Thermal, chemical, and biochemical processes are widely used for conversion of biomass into energy. In specific, there are combustion, gasification, pyrolysis, hydrolysis fermentation, anaerobic digestion, and biological hydrogen production methods. Direct combustion as the most straightforward method has been applied in some power plants with the net power cycle efficiencies from 23% to 25%[16]. Gasification can be viewed as a partial combustion of biomass with low oxygen fed, which produces a mixture of carbon monoxide, water, carbon dioxide, char, tar and hydrogen[17]. Pyrolysis is a subclass of gasification where the operating temperature is much lower (450°C to 600°C)[18-20]. The main

product of this method is a liquid bio-oil which can be used as fuel in power stations. Anaerobic digestion as a biochemical method exists widely in almost all biological material under decomposing process. In a conventional industrial fermentation setup, the biomass is usually stored in a fermentation tank together with specific bacteria. Then the biomass will be converted to organic acid or alcohol, which will be further converted to methane with carbon dioxide as a byproduct. Upon removing of carbon dioxide, the biogas of the fermentation process could be used in internal combustion engines, micro-turbines, or fuel cells.

Our study focuses on the catalytic conversion of biomass into value-added chemicals through chemical reactions. Typically, the non-edible biomass or plant biomass contains cellulose, hemicellulose, and lignin. Cellulose, which is the most abundant biomass, consists of a long linear chain of D-glucose unit, while hemicellulose possesses random and branched structure amorphously formed by xylose, glucose, mannose, and other sugar monomers. Hence it is feasible to depolymerize these feedstocks to produce valuable chemicals such as glucose, xylose, or other sugar monomers as a platform chemical for industrial applications. For example, fructose as the isomer of glucose could be dehydrated to produce 5-hydroxymethylfurfural (HMF). HMF could be used to produce dimethylfuran, levulinic acid, 2,5-furandicarboxylic acid (FDA), 2,5-diformylfuran (DFF), dihydroxymethylfuran or 5-hydroxy-4-keto-2-pentenoic acid which have extensive applications[13, 21-23]. Conversion of cellulose to produce sorbitol, which followed by upgrading sorbitol to isosorbide is another

example of value-added process. During this process, a very valuable medicine precursor isosorbide nitrate could be prepared from such low-cost feedstock.

1.2 Aims and outline of this dissertation

This PhD study aims to investigate the conversion and upgrading of biomass into value-added chemicals. The hydrogenation of cellulose and dehydration of sorbitol are two main reactions in this study. Reaction conditions are thoroughly examined to determine the activity and selectivity of the catalysts. Various characterization techniques are also applied to study the structure and chemical properties of the catalysts.

We have specific aims as listed below:

1. Examine and optimize the noble metal supported active carbon catalyst from our sponsor JM for the hydrogenation of cellulose to sorbitol.
2. Investigate and explore the relationship between reaction performance and reaction parameters using the multivariate analysis method.
3. Design and prepare solid acid carbon catalyst for the upgrading of sorbitol to isosorbide.

The catalysts characterization is performed by using a series of characterization techniques, e.g., transmission electron microscopy (TEM), field emission scanning electron microscope (FESEM) and X-ray diffraction (XRD), thermal gravimetric analysis (TGA), Fourier transmission infrared spectroscopy (FTIR), and inductively coupled plasma (ICP). These results will be described in detail in Chapter 3.

Platinum catalyst from Johnson Matthey (JM) has been examined for two different cellulose substrates (crystalline cellulose and milled cellulose) on

hydrogenation reaction. Effects of cellulose pretreatment and other reaction variables have been assessed by using the trial-and-error method. Optimization of reaction condition for cellulose conversion and possible side reactions are discussed. Based on the discussion, a catalyst optimization method has been used to increase the reaction performance. Finally, Characterization such as XRD, TEM, BET and CV have been conducted to study performance improvement. These results are presented in Chapter 4.

Studies about cellulose hydrogenation, especially how reaction factors affect the reaction independently and collectively, remains at an early stage. To better understand the relationship between reaction performance and reaction variables, cellulose hydrogenation over ruthenium catalyst has been conducted using a multivariate analysis method by a widely-used statistic software JMP from SAS (Version 10) which provides many useful pre-set designs of experiment (DoE) and powerful visualized tools. Ruthenium supported active carbon catalysts were prepared and used to explore the effect of variables for reactions based on a 2-level response surface design. A regression model has been built according to the reaction data. The individual and synergistic effect of variables are evaluated. Finally, a prediction formula has been generated to predict sorbitol yield. These results are discussed in Chapter 5.

Sorbitol, as the main product of cellulose hydrogenation, is an important platform chemical. Here synthesis of isosorbide via sorbitol dehydration is studied as an example of biomass upgrading. Carbon-based solid acid is widely applied as the catalyst for dehydration reaction[24]. In this study, we prepared carbon acid catalyst by sulfonation of active carbon and carbon nanotubes. The

as-synthesized carbon catalysts possess advantages in such reaction for superior reaction performance, easy separation, and excellent recyclability. The morphology, structure, active site and chemical composition of the carbon catalysts have been fully examined by characterization methods, such as XRD, TEM, SEM, BET, FTIR, EA, EDAX, TGA and Raman spectroscopy. The effect of reaction temperature, reaction time and catalyst amount have been studied and optimized. These results are presented in Chapter 6.

Based on our result, we suggest some important future studies which can either help us better understand the mechanism of the biomass conversion process or further improve the application of product from the process. We also emphasize the needs of studies from a more industrial perspective to examine the current result we have obtained. Those discussions are presented in Chapter 7.

Chapter 2 Literature Review

The review of literature begins with an introduction of the basic structure and composition of plant biomass, followed by various approaches that are studied to break down biomass to useful chemicals. Then, the multivariate analysis methods are addressed. In the fourth section of this chapter we present some key research works on the upgrading of sorbitol, a major product from biomass conversion. Finally, in the last section the application of carbon catalyst is discussed.

2.1 Chemical composition and structure of plant biomass

Plant biomass, especially non-edible biomass, has great potential for production of biofuels and chemicals in a green way. However, the production efficiency is usually affected by the source, species and conditions of the biomass feedstock. Therefore, a deeper understanding of the structure and chemical composition of plant biomass is crucial. Plant body consists of three vegetative organs: root, stem, and leaf. Under each organ, various plant tissues are made of different types of cell for different functions. One of the critical components of a plant cell is cell wall. There are two cell walls: primary cell wall and secondary cell wall. The primary cell wall is the outer and thinnest layer of the cell wall, which allows the cell to expand and elongate. Secondary cell wall, which is inside of protoplast, will later undergo lignification to enhance the mechanical property of the plant.

Cellulose, hemicellulose and lignin are the three major structural components that build the cell wall. In particular, cellulose is the most abundant organic polymer on earth. It is estimated that the annual production of cellulose

is 1.5×10^{12} ton [25]. Typically, cellulose accounts for 40-50% of the weight of the dry plant cell wall. Cellulose is formed by many anhydrate glucose unit connected with β -1, 4 glycolic bonds with DP (degree of polymerization) ranging from 1000 to 15000[26], which can be determined by modified BCA method[27]. As a macromolecule, cellulose is stabilized by inter and intra hydrogen bonds as well as van der Waals forces. Several cellulose chains pack together to form cellulose elementary fibril[28]. It is widely accepted that in most embryophyte there are 36 chains within the cellulose elementary fibril[29-31]. All those chains form a hexagonal shape of size of 3 nm $\times$ 5 nm, of which 18 are surface chains, 12 are transition chains and 6 are core chains[29]. Among the hexagonal surfaces, two are hydrophobic, the other four are hydrophilic. Usually, several cellulose elementary fibrils will aggregate through the hydrophilic faces to form microfibril[31]. The orientation and arrangement of those microfibril vary by the cell type. In the primary wall, the microfibrils are usually disordered, while in the secondary wall the microfibril are parallel in layers with different orientation[32].

Hemicelluloses are usually branched or nonbranched polymer made of a wide variety of sugar units such as xylose, mannose, galactose, rhamnose, and arabinose as well as some sugar acid or non-carbohydrate subunits. Hemicellulose is a kind of smaller polymer compared to cellulose with DP ranging from 50 to 200 and can be classified to xylans, mannans, xyloglucans, and cereal β -glucans depending on its composition[33, 34]. Unlike cellulose which is insoluble and inert to depolymerization, most hemicellulose is soluble and easy to be hydrolyzed[35, 36]. In the cell wall, hemicellulose serves as the bridge between cellulose fibril and lignin[37].

Unlike cellulose and hemicellulose, there is no specific composition of lignin. As the second most abundant biomass, lignin is a kind of polymer which is made of different aromatic alcohols such as guaiacyl (G), sinapyl (S), and p-hydroxyphenyl (H) units[38]. Due to its hydrophobic property, it is considered to seal the pore of cell wall for plant vessels and tracheid promoting better water transportation[39]. It also serves as mechanical support for plant and protects the plant against natural microbial attack. Strong aromatic vibration at 1600 cm^{-1} of lignin is usually taken as a semi-quantified method in Raman scattering microscopy[40-43].

2.2 Hydrolysis, hydrogenation, hydrogenolysis and APR of biomass

Since cellulose is made of anhydrate glucose unit, it is of great interest among industry and academic to set up a feasible top-down approach to produce value-added chemicals or platform chemicals[44]. Even though the conversion of polysaccharides, starch, polyurethane, or triglycerides have been well established with an output of more than 133 megatons per year[45-48], commercial methods for cellulose conversion is still at an early stage. The difficulty of breaking down cellulose's stable structure, which we have mentioned above, is the main obstacle. Studies of biomass conversion have different focuses, which can be grouped solely by reactions such as hydrolysis, hydrogenation, hydrogenolysis and aqueous-phase reforming (APR).

2.2.1 Hydrolysis

A comparison study of cooking cellulose and starch hydrothermally indicates that the transition of cellulose from crystalline status to amorphous status at 320°C and 25MPa promotes the water-cellulose interaction and

increases the hydrolysis process which resembles the gelatinization of starch[49]. Mechanism study of cellulose hydrolysis in dilute acid suggests that the breakage of hydrogen bonding at a specific temperature and acid concentration causes the disorder of the cellulose crystalline structure, which facilitates the penetration of acid molecules[50]. A more recent study explains the hydrolysis process further using in situ attenuated total reflection infrared (ATR-IR), which reveals the breakage of the glycosidic bond observed by their distinctive C-O vibrational stretches and formation of smaller cellulose before the formation of glucose monomer[51]. Interestingly, the hydrolysis reaction may be an autocatalytic reaction, as an evidence of hydrolysis of difructose anhydride suggests that adding fructose promotes the overall hydrolysis performance[52]. Paolo Carniti et al. explored the hydrolysis of three disaccharides sucrose, maltose and cellobiose, which is connected by α -1, β -2 glycosidic bond, α -1,4 glycosidic bond, and β -1,4 glycosidic bond, respectively. Their results indicate that the order of reactivity of the three disaccharides is sucrose >> maltose > cellobiose due to the better stability of the 1,4-glycosidic bond over the 1,2-glycosidic bond[53]. γ -Valerolactone (GVL) as a biomass derivative promoting the solubilization of biomass could promote the production of soluble carbohydrates from biomass feedstock with dilute acid[54]. It was also found that GVL reduced the apparent activation energy for biomass hydrolysis[55].

Cellobiose, which is constructed by the β -1,4-glycosidic bond of two glucose units, is commonly considered as the model molecule of cellulose and widely used in the study of the mechanism of biomass hydrolysis. It is reported that the decomposition of cellobiose is also accelerated by adding metal sulfates

in supercritical water (SCW) such as CuSO_4 , FeSO_4 or MgSO_4 [56]. A study of the effect of the atmosphere on cellobiose hydrolysis reveals that oxidizing setup, which weakens the β -1,4 glycosidic bond, is superior over inert or reducing setup[57].

Solid acid catalyst stands out in cellulose hydrolysis for easy separation and recyclability. Organic-inorganic hybrid mesoporous silica catalysts binding with butylcarboxylic acid, arenesulfonic acid, and propylsulfonic acid functional groups are found to efficiently catalyze the cellobiose hydrolysis in which the apparent activation energies are similar to that of homogeneous organic acids[58]. Ayumu Onda et al. reported the hydrolysis of glucose from cellulose over a series of solid acid catalyst such as H-form zeolite catalysts, $\gamma\text{-Al}_2\text{O}_3$, H-ZSM5(45), Amberlyst 15, sulfated zirconia and sulfonated active carbon, among which they found that sulfonated active carbon exhibits the most excellent activity[59]. Similar surface modification method was applied to graphene-based amorphous carbon. The bearing of SO_3H serves as the Brønsted acid sites, whereas the COOH and OH groups serve as effective adsorption site[60]. The surface acidity modification was further applied in the synthesis of magnetic solid catalyst $\text{Fe}_3\text{O}_4\text{-SBA-SO}_3\text{H}$, which facilitates the separation and recycle of catalyst from products[61]. Similar synthesis strategy was adopted in the preparation of silica-protected cobalt spinel ferrite nanoparticles decorated with acid groups, among which alkyl sulfonic acid nanoparticle is able to achieve 78% conversion of cellobiose at 175°C for 1 hour[62]. The effectiveness of sulfonation is related to the sulfonation temperature, as CMK-3 sulfonated at 250°C shows higher hydrolysis activity than CMK-3 sulfonated at 200°C or 150°C [63]. Sulfonated

chloromethyl polystyrene resin, which resembles cellulase with a cellulose binding group and catalytic group, was reported to significantly reduce the apparent activation energies of the hydrolysis reaction and achieve up to a 93% yield of glucose from cellulose[64].

Interestingly, non-sulfonation modification can also be used to promote the hydrolysis reaction. CMK-3 can work with noble metal in cellulose hydrolysis reaction. Ru/CMK-3 as water tolerant and reusable catalyst hydrolyzed cellulose to glucose with high yield and TONs, as the CMK-3 helps to break down cellulose to oligosaccharides and Ru enhances the final conversion of oligosaccharides to glucose[65]. Active carbon K26 after a simple activation method was reported to achieve a glucose yield up to 88% from cellulose with the assistance of trace amount of HCl[66]. Sulfated zirconia is found to modify efficiently SBA-15, which could produce glucose from cellobiose with a 60% yield in 90 minutes at 160°C[67]. High loading tungsten oxide is able to improve the surface acidity and structural stability of zirconia oxide and promote better performance in cellobiose hydrolysis[68].

Hydrolysis of cellulose and cellobiose via enzyme also receives great attentions. β -glucosidase from *Sclerotinia sclerotiorum* is able to produce about a 33% of glucose from cellobiose in 9 hours[69]. However, enzymatic methods for biomass conversion are facing many challenges. Activity loss of the β -glucosidase has been observed in the presence of soil minerals, i.e. montmorillonite, kaolinite and goethite[70]. Other inhibitors of cellulose enzymatic hydrolysis include xylooligomers, xylose and xylan, which compete with cellulose for the hydrolysis reaction[71].

2.2.2 Hydrogenation

Back to the 1930s, researching had been conducted on cellulose hydrolysis by mineral acid[72]. However, recycling of the acid, corrosion of the equipment and product separation were some critical issues preventing the upscale of this homogenous conversion method. Fukuoka et al. first reported direct conversion of cellulose to sugar alcohol in 2006 by using heterogeneous catalytic system[73]. The yield of the main product sugar alcohol reaches up to 31%. Instead of using mineral acid, they proved the feasibility of solid catalyst in biomass conversion. Precious metal platinum and ruthenium were supported on γ -Al₂O₃ and zeolite (HUSY) by wet impregnation method. A typical reaction took place with a mixture of a certain amount of crystalline cellulose, catalyst and water, with constant stirring at 463K for 24 hours after pressurization with hydrogen to about 50bar in a stainless-steel autoclave. It is shown that without the impregnation of metal, the supports alone could only produce less than 4% glucose. Based on the result, they proposed a mechanism for supported metal catalyst for cellulose conversion, according to which hydrogen is first split in situ on metal surface, then combines with intrinsic acid sites of the support surface and then promotes the cellulose hydrolysis reaction. The glucose is then readily reduced to sorbitol under high pressure hydrogen. Those primary works inspire worldwide interest in producing value-added chemicals directly from biomass feedstock. However, there still leaves much work to be finished. For example, the overall sorbitol yield and selectivity are not very high. Moreover, there are lots of side reactions along with the main reaction. A big picture of the total reactions and parameters that control those main reactions and side reactions is urgently needed.

As discussed, it is believed that the hydrogenation of cellulose usually undergoes two steps, the hydrolysis step[27, 50, 51, 55, 59, 61, 65, 71, 74-76] and hydrogenation step[65, 77-79]. In detail, cellulose macromolecule will be hydrolyzed to produce oligosaccharide, which will later be further hydrolyzed to trisaccharide or disaccharide and eventually to glucose[80]. The hydrolysis of cellulose or oligosaccharide which are considered as the rate-determined step, are significantly affected by the acid concentration or acid sites on the support[81]. Many reports of cellulose hydrogenation with the assistance of diluted acid or heteropoly acid are published. Palkovits et al. reported that cellulose hydrogenation produces sorbitol with 84% selectivity and 72% conversion under 160 °C under 5 MPa H₂ over 5wt% Ru/C catalyst with the assistance of 2.5wt% sulfuric acid[82]. Similarly, Geboers et al. reported a full yield of hexitols from milled cellulose using H₄SiW₁₂O₄₀ heteropoly acid as hydrolysis assistance over Ru supported active carbon catalyst at 190 °C under 9.5 MPa H₂[83].

Even though adding additional acid dramatically improves the overall performance of cellulose conversion, it apparently, at the same time, adds up the cost and brings many other issues. Hence, many studies have focused on increasing the acidity of the support as an alternative to accelerate the hydrolysis step. A variety of acid supports such as Al₂O₃, ZSM-5, MCM-41[84], AC-SO₃H, Zr-SBA-15 have been widely examined[73, 85-88]. Some supports provide Brønsted acid sites, while some afford Lewis acid sites. Han et al. reported a yield of hexitols of 65% over a 10%wt Ru/AC-SO₃H catalyst. It is believed that the -SO₃ increases the surface acidity and improves the overall cellulose conversion.

However, in their experiment, leaching of $-\text{SO}_3$ function group was also observed during catalyst recycle[88].

Pre-treatment such as ball milling of cellulose reported by Fukuoka[85], promotes the yield of sorbitol up to 53%. Crystalline and amorphous parts both exist in cellulose structure. It was observed that after the mechanical milling, the crystallinity index (CrI) of cellulose decreased from 81% to 14% after 4-day milling. The morphology change was confirmed by XRD patterns and images directly from the microscope. The positive effect of ball milling was also proved in the hydrolysis of cellulose, in which the crystallinity index decrease was observed in CP/MAS NMR[89]. Later, a mix milling in which the solid catalyst and the reactant cellulose were mixed, showing better performance than the single milling method. Quantitative studies indicate that the mix milling pre-treatment promotes the solid-solid reactions for the production of soluble oligomers from insoluble cellulose, whose rate constant is 13-time larger than those in the single milling[90]. In addition to mechanical milling, many other pre-treatment methods are also effective in cellulose conversion by decreasing the crystalline index, lowering degree of polymerization, increasing the surface area or weakening the fiber strength of cellulose[91]. Biomass will swell in alkalis such as sodium hydroxide, potassium hydroxide or calcium hydroxide, which can increase the surface area of cellulose[35]. Heating cellulose with dilute sulfuric acid ($0.1\text{--}0.2\text{ mol/m}^3$) can reduce the crystalline index of cellulose[92]. The crystallinity index of cellulose after acid treatment decreased from 84% to 33%[93], which raised sorbitol yield to 69% for cellulose hydrogenation reaction.

Ionic liquid as a new solvent is receiving attention worldwide for its low melting, thermal stability and vapor pressure[94, 95]. Recently, ionic liquids have been applied to biomass conversion by which cellulose could be well dissolved and regenerated[96, 97]. Ionic liquid is found to selectively catalyze the conversion of cellulose to levulinic acid[98]. Acidities of the ionic liquid $[\text{C}_3\text{SO}_3\text{Hmim}]^+$ is highly dependent on the anions with the acidity decrease as the order of $\text{HSO}_4^- > \text{CH}_3\text{SO}_3^- > 1\text{-NS} > \text{H}_2\text{PO}_4^-$. Zhu et al. employed a 1-buty-3-methylimidazolium chloride (BmimCl) together with ruthenium nanoparticles and raised the yield of sorbitol up to 85% at a temperature around 80°C[99]. A similar method was also employed by Zhang, who achieved a 97.2% yield of mixture product containing glucose, cellobiose and HMF [100]. They indicate that the pore size, acid amount, water amount and the timing for adding water could influence the overall catalytic performance. Adding ionic liquid such as BmimCl into resin catalyst Nafion NR50 enhances the hydrolysis of cellobiose by transferring protons from the resin into reaction solution via ion-exchange, which reaches a maximum when the amount of BmimCl equals to the protons of the resin[101]. A similar strategy was adopted for the hydrolysis of cellulose and even wood, which could be dissolved in BmimCl with the presence of large pores resin, e.g. Amberlyst 15DRY[102]. A further examination of the catalytic system suggests that the acid strength, impurity content and temperature had a profound influence on the hydrolysis reaction[103].

2.2.3 Hydrogenolysis

Hydrogenation of cellulose via noble metal catalyst are receiving worldwide attention for promising conversion of biomass, at the same time, hydrogenolysis

of cellulose for production of ethylene glycol (EG) over tungsten-related catalytic system raises as another hot topic. Various catalytic systems containing tungsten components and reducing catalyst are designed to realize the production of diols from cellulose and other biomass feedstock. Zhang et al. first discovered the direct conversion of cellulose to EG via Ni-W₂C/AC catalytic system[104]. The tungsten component plays the role of degradation of cellulose whereas transition metal facilitates the hydrogenation of the reaction intermediates[105]. However, the W₂C component was reported as unstable in a later report, which suggests a post-impregnation of nickel instead of co-impregnation used in the earlier work. The tungsten component in the post-impregnation method goes through a redispersion process, which contributes to a higher EG yield[106]. A new mesoporous carbon made of commercial silica template, which improves the dispersion of tungsten carbide and transport of the reactant, reaction intermediate and reaction product, shows better EG yield than regular active carbon, even without the impregnation of nickel nanoparticle[107]. Tungsten acid (H₂WO₄) was found as an active co-catalyst of Ru/C or Raney nickel for cellulose hydrogenolysis as they are dissolved in hot water during reaction for the hydrolysis of cellulose and cleavage of C-C bond and are precipitated after the reaction for recovery[108, 109]. It was further pointed out that different tungsten component follows the order of H₄SiW₁₂O₄₀ < H₃PW₁₂O₄₀ < WO₃ < H₂WO₄ for promoting the EG yield[109]. A systematic examination of AC, W-supported AC, nickel-supported AC, a mixture of Ni/AC + W/AC, and two Ni/W/AC catalysts prepared in different approach indicate the importance of virgin metallic status of the nickel and tungsten for the effective production of EG from cellulose[110].

Studies of glucose hydrogenolysis in a fed-batch reactor using a bifunctional nickel tungsten carbide catalysis provide convincing explanation on the ethylene forming mechanism, as the intermediate of various side reaction are well captured due to low catalysts contacting time[111]. The EG yield in this study could reach up to 66% with volume productivities of $300 \text{ g}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$ after the optimization of conditions such as temperature, pressure and glucose addition rate.

Propanediol have also been reported as the primary product for cellulose hydrogenolysis. Rataboul et al. discovered the catalytic effect of Pt/AlW (platinum supported on tungstated alumina) on the production of propanediol from cellulose. In their research, the formation of pyruvaldehyde is identified as the key intermediate, while the presence of platinum is responsible for the conversion of pyruvaldehyde to propanediol, without which the reaction intermediate will be converted to lactic acid[112]. Studies of tungsten trioxides loaded on different supports with different WO_3 densities suggest that WO_3 crystallites is attributed to the hydrolysis of cellulose and selective cleavage of C-C bonds, whereas dispersed WO_3 mainly acts as the solid acid in cellulose hydrolysis. The main product shifts from EG to propanediol via $\text{WO}_3\text{-Ru/AC}$, which indicates the isomerization effect of active carbon on glucose to fructose[113]. The isomerization of glucose to fructose as the vital step for propanediol production could also be realized over the Lewis acid site of alumina oxides[114].

The bifunction catalytic system could also be applied to raw biomass feedstock such as corn stalk and birch. However, lignin content [115] and

inorganic impurities[116] are found to inhibit the production of the diols. Application of the proper pre-treatment of the raw biomass is crucial, as treatment with 1,4-butanediol, NaOH, H₂O₂, and ammonia significantly improve the yield of EG and 1,2-PG compared to less effective treatment with ethanol, hot water or supercritical carbon dioxides[117]. Even though tungsten series catalyst dominates the studies of diols production from cellulose, other catalytic systems such as MOF-Ru/C catalyst[118], La-Ni catalyst[119] and Cu/CaO-Al₂O₃[120] catalyst have recently been proved to be equally effective for diols production with various advantages.

The production of diols from cellulose is believed to follow a new reaction mechanism, which could be simply grouped into three steps. Firstly, cellulose is hydrolysed to produce glucose, which may share similarity with cellulose hydrogenation reaction. In the second step, the glucose goes through retro-aldol reaction and forms reaction intermediates glycolaldehyde. In the last step, those secondary reaction intermediates are reduced to ethylene glycol. Balancing of each step is viewed as the key for high production of the diols[121, 122]. Nevertheless, the actual reaction pathway and mechanism could be much more complicated with numerous potential reaction intermediates[123].

2.2.4 Aqueous-phase reforming

Despite being considered as a complicated multistep and high energy demanding process at this moment, biomass enzymatic fermentation, gasification, and pyrolysis are widely studied technologies to provide alternative options to replace the depleting fossil and fuel resources[124-131]. For example, 2 to 4 grams of hydrogen can be produced from 100 grams of biomass feedstock mixed

with 2-3% sodium carboxymethylcellulose (CMC) via cellulose gasification in supercritical water [132]. However, one limitation of this method is that it requires a high temperature of 500 °C which is difficult to achieve. Alternatively, aqueous-phase reforming (APR) as a relatively new approach is receiving widespread attention for energy production from biomass since APR of sugar or alcohol could be performed under low temperature (227°C) over platinum-based catalyst. Hydrogen and gaseous alkanes are the primary products, whose selectivity depend on the source of reforming feedstock[133]. As a versatile method, APR could also be tailored to produce heavier alkanes from C4 to C5 by tuning of reaction conditions and using additional hydrogen as a co-feeding source[134]. The APR process of sorbitol can be divided into two steps, dehydration of sorbitol on acid catalyst and hydrogenation of the intermediate over the noble metal catalysts. Repeating and controlling the two steps can produce alkene with a carbon number ranging from C1 to C6, whereas liquid alkane of C7 to C15 can be produced by adding an upstream aldol condensation step[135]. Controlling the cleavage of C-C bonds and C-O bonds is the key for product tuning, during which isosorbide, 1,2,6-hexanetriol, 1,2-Hexanediol, hexanol, 1-Hydroxy-2-pentanone, Butanol, 1,2-Propanediol are identified as the intermediates[136]. Kinect modelling of sorbitol is also adopted to study the APR process base on a proposed pathways of sorbitol transformation. Satisfying fitting was obtained for C3 and C6 component while others needed to be improved[137].

2.3 Application of JMP in multivariate analysis

Although a large body of literature has concentrated on cellulose conversion, very few of it focuses on the optimization of the process comprehensively. To do so, it is critical to investigate the effect of each parameter on the overall performance. In another word, how the factors work on the response. Considering the complexity of cellulose conversion reaction, it will be a great challenge using the traditional “trial-and-error” method to analyze all the factors. Usually, in such method, the researcher can only change one factor at a time while keeping all other factors in constant to evaluate the effect of the single factor. This method is based on the assumption that the effect of the varied factor will be the same when other factors are set to a different value. This assumption could be invalid when some of the factors are not independent of each other. For example, under a certain condition, the yield of sorbitol increases as temperature increases. However, the effect of the temperature could be different when the amount of catalyst has been changed. In this case, the change of catalyst amount will make a difference on the way temperature affects the sorbitol yield. Therefore, the optimisation of temperature effect may be invalid when other conditions change [138]. It will also be a big challenge when using the “trial-and-error” method to analyse synergistic effects among factors as well as determine the weight of each factor. Moreover, the run for examining the factors increases exponentially when the number of factors increases. For example, the number for a full factorial examination of 2-factor experiment will be 9, which will increase to 243 when the number of the factor increases to 5. Given that there may be as much as five factors in cellulose conversion reactions and the factors may correlate with each

other, it is neither practical nor efficient to use the “trial-and-error” to do condition optimization.

One of the popular alternatives is to use statistical software. Statistical software makes it much easier to analyze multiple factors of complex reactions especially when there are many factors. Statistical software like JMP from SAS provides a set of useful designs of experiment (DoE) for users to do comprehensive condition screening. A variety of DoE such as screening design, response surface design, full factorial design, space filling design and augment design could be chosen depending on the specific engineering problems. The response surface design (RSD) is the most popular DoE for condition optimisation. RSD can help to locate a maximum or minimum response, if it exists, within the screen range.

Currently, the statistical software had been applied among various research area. As shown in biomedicine, JMP is used for modelling published data of microsatellite marker, such as microsatellite parameters, and population parameters[139]. Step-down model linear regression and standard least squares fit models are used in the data analysis, which implies that microsatellite diversity is related to endemism and motif structure. In another study, Norbert Becker et al. reported the application of JMP to analyze the effect of metallic copper spray for mosquitoes control[140]. By comparing different copper dosages, pH of water, exposure time and mosquito mortality rates, they found metallic copper spray helped to control mosquitoes at low costs. Thomas J. Ebert et al. analyzed four different *nasal cannulae* designs and its effect on oxygen delivery and accurate end-tidal CO₂ detection using statistical software JMP[141].

The statistical method also finds its application in environment engineering and food science. In a study, with the help of JMP, scholars discovered an association between growth parameters, the photosynthetic pigment and the removal of heavy metals and initial Cd^{2+} and initial Ni^{2+} concentrations in the study of water pollution [142]. Another example of was reported by S. Demim et al. who studied not only the cation concentration but also the incubation period and fronds number on those heavy metal removal[143]. JMP is also used to analyze the effect of oxygen percentage, fermentation temperature, wort concentration and yeast pitching rate during beer fermentation process[144].

The statistics software is also usually used for optimization of synthesis, catalytic and industrial process in a broad area. Hutchens et al. employed a statistical approach to evaluate the effects of culture conditions for *gluconacetobater hansenii* to determine the optimum cellulose growth conditions, [145]. Brian Edwards et al. reported the analysis of monomer concentration, photoinitiator concentration and UV exposure time on coating yield of three novel phosphorus-based flame retardant monomers using JMP[146]. K. Subramani et al. found that the coating containing multiwall carbon nanotube influenced osteoblast proliferation, differentiation, and matrix mineralization while coated to titanium substrates on MC3T3-E1 osteoblasts with a statistical significance of $p < 0.05$ [147]. Sujit et al. reported a multivariate analysis using response surface methodology to optimize the reaction condition for p-nitroacetophenone (p-NAP) reduction reaction[148]. RSD was also applied to the optimization of conversion of methane to liquid fuels over copper catalyst[149]. Response Surface Methodology (RSM) was selected to analyze direct methanol

fuel cell (DMFC)'s power density regarding temperature, methanol concentration, air flow rate, methanol flow rate and air relative humidity[150]. Optimization of condition was obtained through the modelling, which was proved to be in good agreement with actual experiment results. Yang et al. reported the use of JMP, in vanadium substituted mesoporous molecular sieves (V-MCM-41) synthesis, to study how the structure, pore size and vanadium content are affected by the synthesis variables such as alkyl chain length, pH and surfactant[151]. Ferreira et al. used the multivariate model to optimise the sample preparation and compound separation for chromatography[152]. Experimental design and statistical analysis using JMP are proved to be an effective and systematic method for precision and robustness evaluation of HPLC analysis[153]. JMP could also be used to improve HPLC method by optimising chromatographic condition such as the gradient program, the concentration of the mobile phase, the temperature of column, the flow rate and the evaporative light scattering detector parameters[154]. Multivariate models are also widely applied in the semiconductor industry for etching process[155].

2.4 Upgrading of platform chemicals to value-added chemicals

The potential applications of biomass via proper upgrading extend from FMCG (Fast-moving consumer goods) industry to aerospace industry, influencing area like food supply, environment, communication, housing, recreation, health, hygiene and transportation[156-162]. For example, glucose, which is the intermediate platform molecules derived from cellulose hydrolysis, could be used to produce fumaric acid. Fumaric acid can be used as secondary intermediates to produce tetrahydrofuran (THF), 1,4-butanediol, or γ -

butyrolactone. Those tertiary intermediates can later be used as plasticisers, and serve as intermediates towards the application in food packaging, beverage bottles or beverage cans coating in food supply industry[163].

Platform chemicals, which have been included in the “Top 10 chemicals” by US Department of Energy in 2004[164], are discussed in following section.

1)5-Hydroxymethylfurfural (HMF). HMF has been examined extensively as promising platform chemicals. Fructose could be used to produce HMF[165] with high yield and conversion[166-169]. Homogeneous and heterogeneous catalysts showing acidity could be used to dehydrate fructose solution partially to HMF[170, 171]. Recent research reveals that the dehydration reactions could be facilitated by introducing extra solvent or liquid acid. Methyl isobutyl ketone (MIBK) as an extracting solvent[172] was found to raise the HMF yield to 74% for a fructose solution. Introducing liquid acids such as HCl or sulfuric acid could also improve the overall conversion and HMF yield[173-175]. Apart from dissolving fructose in water, sizable efforts have been devoted to conducting the reaction in DMSO solvent. It is believed that DMSO as a solvent could cut off the formation of byproducts in such reactions effectively[169].

As a popular platform chemical, selective oxidation of HMF produced 2,5-diformylfuran (2,5-DFF) or 2,5-furandicarboxylic acid (2,5-FDCA). Pt/ZrO₂ catalyst was reported to yield 98% of 2,5-FDCA under constant oxygen flow[176]. Moreau reported an 86% yield of 2,5-DFF from HMF by air oxidation in toluene and MIBK mixture solvent over supported V₂O₅/TiO₂ catalyst [177]. In return, 2,5-DFF is widely applied in the synthesis of diamine, Schiff bases and other products[178, 179]. In addition to oxidation method, hydrogenation of

HMF has been extensively discussed as well. For instance, supported metal catalyst could reduce HMF to 2,5-bis(hydroxymethyl)furan (2,5-BHMF)[180-185], which, in turn, found its application in the production of polyurethane foam.

2) Xylose. As mentioned before, xylose and other sugars are the building blocks of hemicellulose. Being 5C unit which could be further converted to furfural, furan, furfurylic acid, or furoic acid, xylose is a very important platform chemical. It was reported furfural could be produced from agricultural and forestry waste[186-196]. Furfural yield of 72% could be accomplished over zeolite embedded siliceous TUD-1 mesoporous matrix[197, 198]. Xylitol can be produced from xylose, xylans or raw biomass feedstock[199-202], which plays an important role in cosmetic, pharmaceutical industry and food additive industry. For hydrogenation of furfural to furfurylic alcohol, Pt-Sn catalyst was reported to achieve a 98% selectivity at optimized condition[203].

Figure 2.1 Upgrading of HMF to 2,5-diformylfuran, 2,5-furandicarboxylic acid and 2,5-bis(hydroxymethyl)furan.

3) Sorbitol. Annual production of sorbitol is estimated to be 700,000 tonnes by hydrogenation of glucose over Raney nickel catalyst[204, 205]. However, leaching of nickel is a common problem in the catalytic system. On the contrary, Ru/C, which is nearly free of leaching, has attracted many attentions for glucose hydrogenation. In a trickle-bed reactor, a 99.5% yield of sorbitol could be obtained with negligible catalyst leaching when using Ru/C instead of Raney nickel[206]. Starting from starch, a well-designed reaction combining hydrolysis and hydrogenation steps could have a 95% yield of sorbitol by Ru-HY catalyst. Sorbitol is important additives in food, cosmetic and pharmaceutical industries. A double dehydration reaction of sorbitol will produce higher valuable chemical isosorbide, which could be used in personal care products or forming dimethylisosorbide, isosorbide esters and other polymers.

Figure 2.2 Upgrading of sorbitol to value-added chemical isosorbide.

4) Isosorbide. Known as 1,4:3,6-dianhydrohexitols, isosorbide has two isomers, isomannide and isoidide, depending on the position of the two hydroxyl

groups. While those isomers are mainly produced from their own precursors, they can also be synthesized via the isomerization between each other over nickel catalyst[207]. The starting materials for isomannide and isoidide are fructose and idose, respectively. Compared with glucose, fructose and idose are not ready-made and more expensive[208]. Owing to its high stability and its two hydroxyl groups, isosorbide is considered as a versatile platform chemical in area like medicine, surfactant, fuel additive and polymer[209-218]. Isosorbide mononitrate is commonly used for the treatment of heart disease[219]. Ditetrahydrofuran can be synthesized by functionalization of isomannide via an intermediate dichloro derivative[220, 221]. In industry, isosorbide diester has been used to replace phthalates to produce polyvinyl chloride[222]. The etherification of isosorbide is a popular topic, which greatly expands the applications of isosorbide. One of the common etherification methods is the Williamson method which uses organohalides as substituents[223, 224]. Telomerization method using 1,3-butadiene to produce isosorbide O-C₈ is another effective option for isosorbide etherification[225].

Figure 2.3 Isosorbide and its isomers (from left to right: isosorbide, isomannide, isoidide).

Isosorbide has an advantage as a special fuel or a fuel additive since the energy per molecules can be tailored by using substituents to replace hydroxyl group with methyl group and nitrate[226]. Isosorbide has been widely studied in polymer science as a renewable bio resource[227-230]. Unsaturated polyesters and unsaturated polyesters resins have been synthesized with green monomer such as 1,3-propanediol, isosorbide and itaconic acid[231]. The polymers show good thermal stability, while the resins show highly hydrophobic nature. Makoto Kato et al. reported the preparation of several co-polycarbonates starting with isosorbide, bisphenol A and diphenylcarbonate over various catalyst[232]. The storage and tensile moduli results indicate that isosorbide helps to increase the strength of the polymer. Isosorbide has also been used for the synthesis of biodegradable polyesters, whose glass transition temperature is greatly increased by the adding of isosorbide[233].

Similarly, isomannide and isoidide have been investigated for polymer synthesis via solvent-free enzymatic catalysis[234]. Similar enhancement of the glass transition temperature is observed. While cross-linked with polyisocyanates for preparation of solvent-borne coatings, those biomass-based polyesters help to increase the hardness of the coating materials.

2.5 Application of carbon catalyst

Supported carbon-based catalysts have gained wide attention in biomass conversion due to its stability, high surface area, and recyclability[235]. Popular carbon materials include activated carbon, carbon nanotube, biomass-based carbon catalyst.

Active carbon (or activated carbon) includes a broad range of carbonaceous materials with high degree of porosity and high surface area. Application of active carbon could be dated back to the 1500BC when Egyptians used charcoal for medicinal purposes[236, 237]. Active carbon prepared from vegetable origins first entered sugar refining industries in 1900's[238]. Later in the World War I, they were applied in gas masks against hazardous gases. It is currently the most affordable and commercialized carbon material. Commonly seen in our daily life, active carbon is used as a purifier for removal of undesirable odor, color and taste for its high adsorption ability[239, 240]. In electric chemistry active carbon is used as double layer capacitor[241, 242]. It is also used to treat poisonings and overdoses in medical practice. Moreover, Active carbon is outstanding support for heterogeneous catalyst[243].

Regarding the component of active carbon, carbon is the dominant element accounting for 85% to 95%, and the oxygen constitutes the second largest element which ranges from 1 to 20% depending on processing method and starting materials. The other elements such as hydrogen, nitrogen, sulfur are usually less than 2% in total., The surface area of active carbon ranges from 800 to 1500 m²/g, and its pore volume from 0.2 to 0.6 cm³g⁻¹.

Active carbon is mainly produced by timber, bamboo, or coal are the primary sources, though any carbonaceous material can be used to produce active carbon. In the preparation of active carbon, the sources materials go through two steps, carbonization and activation. During the first step, most of the noncarbon element are eliminated as volatile products such as CO₂, CO, NO₂, SO₂, while the remaining carbon elements are piled to form stacks of carbon sheets in

random manner. Before activation, however, the pores that form during the carbonization process are filled with tarry matter or other decomposition products. Hence, the char product will go through higher temperature treatment between 950 to 1000°C to eliminate various carbonaceous compounds and disorganized carbon. Traditionally, charcoal as the precursor for active carbon preparation is heated in high-temperature furnace for surface modification. After those two steps, active carbon is endowed with a vast number of pores with random shapes and size, which contribute to its large surface area.

Active carbons have certain microcrystalline structure, called turbostratic[244]. Because of the presence of O and H atoms, and vacant lattice sites, the microcrystalline layers of active carbon are less ordered. In addition, the interlayer spacing of active carbon is larger than the one in graphite. Active carbon can be classified as graphitizing carbons and non-graphitizing carbons based on their graphitizing ability[245]. The porous structure of active carbon derived from removing the tar and disorder carbon is found to be related to the degree of burn-off during activation[246]. When the burn-off is less than 50%, microporous structure is produced. When the burn-off is larger than 75%, active carbons will show a macroporous structure. A widely accepted classification of the pores proposed by Dubinin[247] is based on the distance between walls of pores. Thus, the pores can be grouped as micropores, mesopores, and macropores with the effective radius for each type being less than 2nm, 2 to 50 nm and 50 to 200 nm, respectively. Regarding the shape of active carbon, studies indicated that slit-shaped, V-shaped and ink-bottle shape, capillaries shape are all possible[248].

In addition to the crystalline structure and pore structure, the chemical structure of the carbon surface also plays a significant role in its chemical reactivity. One of the most crucial surface groups are the C-O groups, which significantly influence the surface properties such as wettability, polarity, and acidity. There exist three types of C-O surface groups, acidic, basic and neutral. The acid surface groups are formed when carbons go through treatment up to 400°C or reaction with oxidation reactant at room temperature. It is believed that those acidic surface groups are mainly carboxylic, lactone, and phenolic groups. The basic surface groups are formed at a high temperature up to 1000°C in a vacuum or inert atmosphere. Pyrone structure or chromene structure[249, 250], within which oxygen atoms are sitting in a heterocyclic ring with an activated = CH₂ group[251], are believed as the main structure in basic oxygen surface group. Lastly, the neutral surface C-O groups are formed during the irreversible chemisorption of oxygen.

Modifications of active carbons such as nitrogenation, halogenation, sulfurization and impregnation further extend its applications. A significant amount of C-N surface groups can be introduced to active carbon via reactions with dimethylamine or ammonia[252]. Those nitrogen-doped carbon materials receive wide attention in photocatalyst study[253]. Sulfurization by heating carbons with sulfuric acid[254] or elementary sulfur[255] can introduce sulfur content as high as 50%, which is a widely applied modification method in studies of dehydration reactions[212, 256, 257]. Various metals and metal oxides can be loaded on active carbon for different applications. For example, Fukuoka et al.

examined the supported precious metal active carbon for the conversion of cellulose[73, 258-262].

Carbon nanotubes are one of the unique carbon materials. Discovered by Kroto et al. in 1985[263], CNTs have been widely studied and applied in many fields. CNTs are formed by rolling graphene sheet to a cylinder, which can be tens of micrometers in length while as thin as 0.7 nm in diameters[264]. CNTs can be classified as single wall carbon nanotube, double wall carbon nanotube and multi-wall nanotube based on the layers of graphene sheets. Determined by the direction of graphene rolling, CNTs can be created in several different structures such as armchair CNTs, zigzag CNTs, and chiral CNTs. Owing to its special structure and arrangement of carbon atoms, CNTs show very special electronic, mechanical, and thermal properties. Carbon atoms in CNTs are bonded to each other via sp^2 molecular orbitals, which gives the fourth electron the ability to move along the carbon frames. Depending on the chirality, diameters, length and defects, CNTs can be either conducting or semi-conducting materials[265-273]. When the graphene sheets are rolled up in the axial direction, CNTs reveal a strong mechanical property[274]. It was measured that the Young's modulus of CNTs can be as high as 950 GPa, while the tensile strength as high as 63 GPa[275]. Both theoretical calculations[276-279] and experimental works[268, 280-286] have been conducted to measure Young's modulus of CNTs. It was found that the diameter was proportional to CNTs' mechanical strength[287-290]. The thermal conductivity has been measured to be 3000W/K for individual MWNTs[291] and 2000 W/K for SWNTs[292]. It was also found

that the thermal properties are contingent on defects, diameter, and length of CNTs as well as the impurity contents[293-295].

The first attempt of multi-wall CNTs synthesis was reported by Iijima in 1991 using an arc-evaporation method[296]. Since then CNTs have been synthesized via arc discharge, laser ablation and chemical vapor deposition methods. For arc discharge technique, an electric arc is generated between two graphite electrodes distanced 1 mm under inert and low-pressure gas atmosphere [297]. When a direct current of 50 to 120 A is induced by 30 V potential, a high-temperature ($>3000^{\circ}\text{C}$) plasma will then be generated within the space between the two graphite electrodes [297], which may also contain catalysts [298]. Under constant heating, the carbon on graphite electrodes are gradually consumed, which then go through vaporization and condensation to grow as CNTs [297]. Laser-ablation method is similar to arc discharge. Instead of using large current, a laser source is employed to produce high temperature on carbon sources. Similarly, the carbon consumed is then fast cooled down under helium or argon atmosphere to produces CNTs [299]. CVD method for CNTs production was discovered in 1996[300, 301]. Instead of using solid carbon as CNTs precursor, gaseous hydrocarbon such as methane, ethylene and acetylene, are used under relatively lower temperature 700°C to 900°C for CNTs production[301]. Gaseous precursor mentioned above will be cracked into hydrogen and carbon by transition metal catalysts, such as Fe, Ni and Co[302]. Carbon will be dissolved into the metal particles until it reaches its solubility limit, then the excessive carbon will precipitate to form a crystallized cylindrical network[303]. Arc discharge and laser ablation methods can produce CNTs with high quality

compared to the CVD method. However, the cost of arc discharge and laser ablation are much higher than the CVD method.

Like active carbon, a variety of methods is available for CNTs' surface functionalization. Oxidation of CNTs to create surface functional groups such as ketone, phenol, carboxyl can help to increase the hydrophilicity and wettability of CNTs[304]. Usually, the CNTs oxidation is performed by using aqueous nitric acid[305-310]. Doping heteroatom like N is an efficient approach to adjust the structural and electronic properties of CNTs[311]. To do so, nitrogen precursors such as ammonia[312] or organic amine[313] were introduced into CNTs synthesis apparatus together with hydrocarbon. Sulfonation of CNTs shows advantages in esterification, dehydration and condensation reactions as a recyclable solid acid catalyst. Sulfonation can be achieved by emerging CNTs into $\text{SO}_3/\text{H}_2\text{SO}_4$ vapor for two days at 60°C [314] or by reaction with ammonia sulfates[315, 316]. CNTs and functionalized CNTs as catalysis have been extensively studied for its special mechanical, electrical and thermal properties. As revealed../ in heterogeneous catalysis, CNTs have been used for various reactions such hydrogenation[317-321], hydrogenolysis[322-324], carbon monoxide and hydrogen conversion[325-330], dehydrogenation[331, 332] and oxidation reactions[333-338].

Chapter 3 Techniques of Characterization, Synthesis, and Catalytic Reactions

Analyses of catalyst and reaction now enter the stage of atom level with various characterization approaches. With the help of advanced characterization equipment, a comprehensive understanding of structure, morphology, chemical composition, physical and chemical properties of the catalysts is obtained and enables the proper design of catalyst. As an essential part of this PhD work, various characterization techniques will be introduced in this chapter along with an elaboration of the preparation of catalysts and the reactions they involved.

3.1 Characterization techniques

3.1.1 Characterization of catalyst morphologies and structures

Field emission scanning electron microscopy (FESEM) provides direct observation of catalysts' morphology such as shape, size and chemical composition in a broad scale from several hundred nanometers to several hundred micrometers. The images of catalyst in our study were obtained by FESEM of model JOEL JSM 6701F. Specifically, the samples were placed in a holder fixed with an adhesive carbon double-sided tape deposited with atomic Pt via sputtering for a minute. To examine the morphology of supported noble metal, we apply transmission electron microscope (TEM), which can provide size and shape information of nanoparticle in the scale of several nanometers to several hundred nanometers. Our TEM results were obtained through JEOL JEM-2010, at 200 kV. Before characterization, samples were dispersed in ethanol after sonication for several minutes, then dropped and dried on carbon-coated copper grids.

The surface area, pore volume, pore size and pore size distribution are essential properties of the catalyst, which can be evaluated by studies on nitrogen physical-adsorption. Here, we apply Brunauer-Emmett-Teller (BET) to study the BET surface area of various supports such as active carbon, CNT, and sulfonated carbon catalyst while using Barrett-Joyner-Halenda (BJH) approach to study pore size. In detail, nitrogen adsorption-desorption isotherms had been carried out at 77 K on Micromeritics ASAP 2020 cooled by liquid nitrogen. The supports were first degassed at 200 °C overnight until the residual pressure was less than 10^{-4} Torr. Baratron pressure transducer had been employed for low-pressure (0.001-10 Torr) measurements. Pore size and pore size distributions were determined by analyzing the desorption branch of isotherms.

X-ray diffraction (XRD) is widely used to determine the crystallinity, particle size, structural strain and chemical composition by reading electron density caused by a beam of incident X ray[339]. XRD result can be used to evaluate the effectiveness of the milling effect on the cellulose's crystallinity index which is affected by the amount of amorphous cellulose and crystalline cellulose. It can also be used to determine the size of loaded precious metal by comparing their designated peak height. Based on the XDR results, the particle size was calculated by using Scherrer's equation[340]. Powder X-ray diffraction patterns were measured from 10 to 90° (2 θ) with a resolution of 0.02° using a Bruker Advance 8 X-ray diffractometer via a Ni filtered Cu K α radiation ($\lambda=0.154\text{nm}$), operated at 40 kV and 40 mA.

3.1.2 Characterization of catalyst active sites

The inductively coupled plasma (ICP) was used to calculate the loading percentage of the precious metal on supported carbon catalyst. Samples were first dissolved in nitric acid after heating in the microwave for around 2 minutes. The metal loadings were determined using external mixture standard over a Perkin-Elmer Dual-view Optima 5300 DV ICP-OES (Optical Emission Spectrometry) system. In a typical method, the axial time was set for 3 seconds, radial time 3 seconds and the number of integration for 3. During the measurement, the temperature was set at 30°C, radio frequency (RF) at 1.1KWm and pump flow at 1.0ml/min.

Fourier-transform infrared spectroscopy (FTIR) was applied to detect the functional groups of the catalyst. Those function groups include ketone groups, hydroxylic groups, and carboxylic groups. Besides those intrinsic function groups of carbon catalyst, we also introduced sulfuric acid groups to various carbon-based catalysts, such as active carbon and carbon nanotubes. FTIR can be used to evaluate the effectiveness of the sulfonation treatment for sorbitol dehydration reactions. In this PhD study, the FTIR results were obtained on Digilab FTS 3100 FTIR with a 4 cm⁻¹ resolution for the wavenumber ranging from 400 to 4000 cm⁻¹ using dehydrate KBr as blank.

Raman spectroscopy, which yields similar but complementary information to FTIR, is usually used to identify molecule by its fingerprint signal. Raman is especially useful in the characterization of carbon materials such as active carbon, chocoral, carbon black and carbon nanotubes to examine the proportion of graphitic to disordered carbon. A typical Raman result of carbon material shows

a D band around 1330 cm^{-1} and G band around 1600 cm^{-1} , which are attributed to amorphous carbon and graphite carbon respectively[341-343]. Hence, the intensity ratio of I(D)/I(G) is an important indicator of the crystallinity index of carbon[344]. In this study, Raman characterization of carbon catalyst was conducted at the excitation of 633 nm on a Renishaw 1000 Raman spectrometer.

3.1.3 Characterization of chemical properties of catalysts

Elemental Analysis is widely used to evaluate the mass percentage of carbon, hydrogen, nitrogen and sulfur of a given samples. With those knowledges, we will be able to determine the presence of certain functional groups, the structure and purity of materials. In this PhD work, several carbon solid acid catalysts are prepared by sulfonation method. Element analysis was conducted to investigate the presence of sulfuric acid group after the treatment. Here, this part of characterization was carried out by a Vario EL III CHNS Elemental Analyzer.

Thermal gravimetric analysis (TGA) is employed to study the thermal stability of catalyst in a broad temperature range. It is also applied to investigate the organic and inorganic content of supported catalyst, which helps to understand the structure of the catalysts. Thermal stability of sulfonated carbon catalysts was examined in chapter 6 to evaluate the recyclability of the catalysts. In this research, the TGA test was obtained on an SDT Q600 instrument and alundum pans under air atmosphere.

3.2 Catalyst preparation and synthesis methodologies

3.2.1 Material

Microcrystalline Cellulose (>99%, Sigma-Aldrich), Active carbon (type 18, Johnson Matthey), Active carbon (type 622, Johnson Matthey), Ruthenium

trichloride $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (Sigma-Aldrich), Potassium chloroplatinate K_2PtCl_6 (>99.9%, Sigma-Aldrich), Palladium(II) chloride PdCl_2 (>99%, Aldrich), ethanol (>96%, Fluka), cellobiose (>99.8%, Sigma-Aldrich), glucose (>99.9% Sigma-Aldrich), sorbitol (>99.8%, Sigma-Aldrich), xylitol (>99.9%, Sigma-Aldrich), erythritol (>99.8%, Sigma-Aldrich), glycerol (>99.8%, Sigma-Aldrich), ethylene glycol (>99.8%, Sigma-Aldrich), 1,2-propanediol (>99.8%, Sigma-Aldrich), methanol (>99.8%, Sigma-Aldrich), isosorbide (>99.8%, Sigma-Aldrich), CNT (>95%, Cnano), concentrated nitric acid (69%, Sigma-Aldrich), Chlorosulfonic acid ClSO_3H (99.9%, Sigma-Aldrich), Sulfuric acid H_2SO_4 (99.9%, Sigma-Aldrich), concentrated nitric acid HNO_3 (69%, Sigma-Aldrich).

3.2.2 Preparation of Ru supported on active carbon catalyst

Ru nanoparticle supported active carbon catalyst was prepared according to a modified adsorption-reduction method[345]. According to this method, Ruthenium trichloride as Ru precursor was first dissolved in ethanol solvent (99.9%). The Ru^{3+} concentration was kept as 1 mg/ml for all the ruthenium catalyst synthesis. For the synthesis of 5% of Ru supported active carbon catalyst, 10 ml of Ru/ethanol was added to 200 mg active carbon, which had been evenly dispersed in 10 ml ethanol. The mixture was then sonicated for 10 minutes before transferring to a rotary evaporator. The pressure was set to be 0.3 bar, and temperature at 40°C. After 2 hours, the catalyst was transferred to a tube furnace and reduced under pure hydrogen flow. The furnace was heated up to 300°C from room temperature in 1 hour and kept at 300°C for another 2 hours. Platinum supported active carbon catalyst, 0.1% Ru/AC, 0.5% Ru/AC and 1% Ru/AC, were prepared in similar manner.

3.2.3 Ethylene glycol reduction of Pt/AC

Platinum supported active carbon catalysts received from Johnson Matthey (JM) were optimized via a further reduction method for better hydrogenation reaction performance. The optimization was conducted in following procedure: 1 gram of fresh platinum catalyst and 15 ml of ethylene glycol were well mixed after ultrasonication for 30 minutes in a 20-ml glass liner, which was then transferred to a 50 ml Parr reactor. The reactor was then pressurized with 60bar pure hydrogen and heated up to designate temperature with constant stirring for 15 hours. After cooling down, the mixture was filtered and washed with excessive DI water. The optimized Pt/AC-EG-220°C or Pt/AC-EG-200°C was obtained after dried in vacuum overnight.

3.2.4 Preparation of sulfonation active carbon and CNT

The sulfonated active carbon (AC-SO₃) was prepared by sulfonation of active carbon with chlorosulfuric acid in chloroform[254]. In detail, 500 mg of active carbon was added into 25 ml of chloroform followed by ultrasonication for 30 minutes. Next, 5 ml of chlorosulfuric acid was added to the dispersed active carbon chloroform mixture carefully, with constant stirring and ice bath. Then the round-bottomed flask containing the active carbon and chlorosulfuric acid was equipped with a cold-water condenser and heated at 70°C for 4 hours. After 4 hours, the suspension was cooled to room temperature and diluted with 75 ml chloroform in an ice bath, which was filtered and washed with excess ethanol and water until the pH of the filtrate became neutral. The sample was dried in an oven at 110°C overnight and designated as AC-SO₃. CNT-SO₃ was prepared in a similar manner.

3.3 Catalytic reactions

3.3.1 Hydrogenation of cellulose to sorbitol

The hydrogenation of cellulose to sorbitol was performed in a 50 ml Parr reactor. In a typical reaction, required amount of cellulose and noble metal catalyst were added to a glass liner together with DI water. After sealed up, pure hydrogen was first purged five times before it was pressurized to the desired pressure. The reactor was heated by a heat jacket to the desired temperature with an impeller stirring mechanically. After the reaction, the heat jacket was removed, and the reactor was cooled in an ice bath. Normally, 1 ml of reaction sample was filtered using 0.25 μm membrane for analysis on HPLC, and the rest was filtered and washed with DI water, then dried and weight for calculation of conversion.

Figure 2.4 Proposed reaction pathway of cellulose hydrogenation via glucose intermediate for the production of sorbitol.

Cellulose conversion and sorbitol yield were calculated as below:

Cellulose converted = weight of initial loading – weight of dried solid residue

$$\text{Conversion (\%)} = \frac{\text{Cellulose converted}}{\text{weight of cellulose feed}} \times 100\%$$

$$\text{Yield (\%)} = \frac{\text{moles of carbon in the product}}{\text{moles of carbon of loaded cellulose}} \times 100\%$$

3.3.2 Dehydration of sorbitol to isosorbide

The dehydration of sorbitol to isosorbide was performed in a rotary evaporator. In a typical reaction, 500 mg of sorbitol was added to a 25ml round-bottle flask, together with 50 mg catalyst. The flask was then attached to a vacuum pump and depressurized to be 0.8 bar and heated to a designated temperature with constant rotary. After the reaction, the flask was cooled to room temperature in an ice bath. Then 50 ml of DI was added to the flask, which was ultrasonicated until all the products were dissolved. After that, 1 ml of reaction sample was filtered using 0.25 μm membrane for analysis using HPLC.

Figure 2.5 Proposed reaction pathway of sorbitol dehydration via 1,4-sorbitan for production of isosorbide.

Conversion of sorbitol and yield of isosorbide and other product were calculated as below:

$$\text{Conversion (\%)} = 100 - \frac{\text{mol of sorbitol remaind}}{\text{mol of sorbitol fed}} \times 100$$

$$\text{Yield (\%)} = \frac{\text{mol of the product}}{\text{mol of sorbitol fed}} \times 100$$

3.3.3 Analytical method

The liquid sample after the reaction was analyzed by Agilent 1100 High performance liquid column (HPLC), equipped with a Bio-rad Aminex HPX-87H column, which was 300mm long and 7.8mm in diameter. We used 0.005 mol aqueous sulfuric acid as the mobile phase. The column temperature was set to be 60°C, and its flow rate was at 0.6 ml/min as constant. Injection volume was 10 μ l with needle wash, while refractive index detector was configured to be 30°C.

As a supplement, two HP-CP8713 GC columns were installed in an Agilent GC-FID 5890 and an Agilent GC-MS 5890 respectively. This GC column is 30 meters long, 0.25 mm in diameter and 0.25 μ m for pore size. The injector of both GC system was set to be 250 °C, with a 30:1 split ratio. Helium as carry gas ran at a constant flow of 0.8 ml/min. The initial oven temperature was 40 °C, which was held for 5mins then heated up to 100 °C at 7.5 °C/mins. It was held for another 15 mins, then heated up again to 230 °C at 15°C/min and being held for 10mins. Flame ionization detector was set as 300 °C, with an air flow of 400 ml/min, H₂ fuel flow of 30 ml/min and helium make-up flow of 25 ml/min.

Another GC column TDX01 was set up in another GC for the analysis of gaseous products such as CO, CO₂, methane and other small alkanes. The inlet was set at 120°C with total gas flow of 29.0ml/min. The oven was set at 30°C and being held for 3 mins, then heated up to 190°C at 10 °C/min. The gas products were detected using TCD (thermal conductivity detector) at 200°C, with 40 ml/min reference flow and 5.5 ml/min make up flow.

Total organic carbon (TOC) analyzer was introduced to evaluate the conversion from the perspective of soluble carbon products in water. We used

Shimadzu TOC-VCSH with autosampler ASI-V. The reaction product solution was diluted to 10-100 ppm then being transferred to the specialized 24 mL vials. The machine would inject 50 μ l sample into the analyzer to do the measurement. The sample went through wild combustion at 953K and all the carbon content was then raised as carbon dioxide. By using a Non-dispersive infrared detector, the amount of carbon dioxide was measured and then the carbon concentration of the samples was calculated.

Chapter 4 Cellulose hydrogenation via Pt/AC and its further optimization

4.1 Introduction

Fukuoka et al. first reported direct conversion of cellulose to sugar alcohol in 2006 by using noble metal catalyst[73]. The yield of the main product, sugar alcohol, was up to 31%. Instead of using mineral acid, they proved the feasibility of solid catalyst in biomass conversion. Precious metal platinum and ruthenium were supported on γ -Al₂O₃, H form of ultra-stable Y zeolite (HUSY) by wet impregnation method. The reactions took place in a high-pressure reactor with constant stirring at 463K for 24 h. Later, they found that decreasing the cellulose crystallinity could significantly improve the reaction performance[85].

Figure 4.1 Cellulose hydrogenation to sorbitol and side reactions.

As we can see from the reaction scheme above (figure 4.1), cellulose hydrogenation is a complicated reaction. Cellulose can go through hydrolysis to

produce the reaction intermediate glucose, or other random by-products under the thermal conditions. Glucose can undergo hydrogenation to produce sorbitol as our target product or pass through other reactions such as isomerization, oxidation or retro-aldol reactions to create other by-products. Sorbitol as a very stable chemical can also go further hydrogenolysis to produce smaller polyols such as xylitol, erythritol, glycerol and ethylene glycol.

In this chapter, we start with the performance test of platinum supported active carbon catalyst from JM (Pt/AC) to study how different factors affect the reactions, followed by the optimization of the catalyst.

4.2 Reaction time course study for crystalline cellulose and milled cellulose

Crystalline cellulose is very stable due to its hydrogen bond rich structure. As a result, reactions must be conducted in long reaction time for achieving good conversion. As shown in Table 4.1, only 22.1% of cellulose is converted for 1-hour reaction, and only 4.4% of sorbitol is produced. Extending reaction time to 8 hours, we can observe a much higher conversion of 76.2% with 19.5 % yield of sorbitol. We also find that a reaction time of 16 hours and above is required to obtain full conversion of cellulose. But the yield of sugar alcohol decreases in a long-time reaction, which indicates that sorbitol and other polyols may be converted to other smaller byproducts. Moreover, a higher yield of gaseous product is observed when reaction prolonged. For example, nearly none of carbon dioxides is observed for 1-hour reaction. But carbon dioxides yield increases to 2.1% for 8-hour reaction and further increases to 4.1% for 16 hours reaction.

Table 4.1 Reaction time course study for crystalline cellulose (0.5g crystalline cellulose, 225°C, 60bar hydrogen, 25ml of DI water and 0.2g Pt/AC).

Time (h)	Conversion (%) ^a	Aq C (%) ^b	Yield (%) ^c			
			Sorbitol	1,2-PG	CO ₂	Other Gas ^d
1	22.1	19.6	4.4	0.0	0.0	0.0
2	45.1	37.7	9.3	1.7	1.1	0.1
4	68.0	58.0	17.6	1.9	1.5	0.2
8	76.2	63.2	19.5	4.0	2.1	0.3
16	97.4	82.7	5.7	7.3	4.1	1.0

[a] The conversion was calculated by the weight difference of cellulose before and after the reaction.

[b] Aq C indicates carbon balance by TOC.

[c] The yield of products was calculated using the equation: yield (%) = (mol of carbon in the products)/ (mol of carbon in cellulose) ×100%.

[d] Other gases include carbon monoxide, methane, and propylene.

When Fukuoka et al. reported their discovery on cellulose hydrogenation, their best result of sorbitol yield was about 30% and reactions were conducted at 190°C for 24 hours[73]. As we have discussed in Chapter 2, cellulose has a lot of inter and intra hydrogen bonds, which make it inactive for reactions. It is noteworthy that amorphous cellulose has fewer hydrogen bonds (5.3 per glucose unit) than crystalline cellulose[346] (8 hydrogen bonds per glucose unit). Because the hydrogen bond is reduced in amorphous cellulose, reaction for cellulose containing more amorphous cellulose will encounter less obstacle. Inspired by Fukuoka et al.[85], we conducted similar cellulose ball milling treatment for the crystalline cellulose. As we can observe from XRD result in Figure 4.2, crystalline cellulose has a unique sharp peak around 23°, which

indicates that this sample has very high crystallinity. After balling milling treatment, it reveals that the unique peak of cellulose has dramatically decreased, which suggests that the amount of crystalline cellulose has decreased, while amorphous cellulose increased.

Figure 4.2 XRD patterns of crystalline cellulose and milled cellulose.

Comparison of reactions using crystalline and milled cellulose under the same reaction conditions is presented in Figure 4.3. The milled cellulose has better reaction performance than crystalline cellulose in terms of conversion and sorbitol yield. Reactions were conducted in the same conditions, namely 0.5g of cellulose (either crystalline cellulose or milled cellulose), 0.2g of Pt/AC, 60bar of hydrogen and 25 ml of water as solvent. According to Table 4.2, cellulose conversion increases from 22.1% to 74.2% for milled cellulose for 1-hour reaction, and sorbitol yield increases from 4.36% to 12. 6%. Almost all milled cellulose has been converted within 2 hours at 225°C. In contrast, only less than

half of crystalline cellulose is converted. These findings demonstrate that milling of cellulose is an efficient way to improve reaction performance. However, further increasing reaction time from 2 hours to 4 hours leads to a slight decrease of sorbitol. In a similar study of glucose hydrogenation to sorbitol, it was also observed that reaction with excessive runtime will result in lower sorbitol yield [347]. Glucose produced from cellulose hydrogenation is also likely to undergo isomerization to form fructose[348].

Table 4.2 Reaction time course study for milled cellulose (0.5g milled cellulose, 225°C, 60bar hydrogen, 25ml of DI water and 0.2g Pt/AC).

Time (h)	Conversion (%)	Yield (%)				
		Sorbitol	Xylitol	Erythritol	EG	1,2-PG
0.5	30.7	2.5	1.2	0.1	0.2	0.9
1	74.2	12.6	2.8	1.7	0.4	2.6
2	99.2	25.1	4.1	1.2	0.5	6.7
4	102.2	24.3	5.6	8.1	3.8	8.3

Figure 4.3 Comparison of crystalline and milled cellulose for hydrogenation reaction over Pt/AC.

4.3 Reaction condition screen for cellulose hydrogenation

4.3.1 Effect of temperature

Temperature is one of the key variables for biomass conversion. The effect of temperature on milled cellulose hydrogenation is presented in Table 4.3. As shown in the table, conversion of cellulose is highly related to the reaction temperature. As temperature increases from 190 °C to 225 °C, cellulose conversion increases dramatically from 19.8% to almost 100%. Following this trend, the yield of sorbitol increases from 2.1% to 25.1% when the temperature rises from 190°C to 225°C. However, when further increase temperature from 225°C to 250°C, a decline of sorbitol yield to 11.0% and a rise of smaller polyols such as EG and 1,2-PG are observed. The results indicate the need of conducting cellulose conversion under high temperature to overcome its structural stability. However, over raising the temperature will lead to the decomposition of sorbitol and decreases its selectivity to 11%. Thus, it is important to carefully tune the reaction temperature for the balancing of conversion and selectivity.

Table 4.3 Effect of temperature on cellulose hydrogenation (0.5g milled cellulose, 60bar hydrogen, 25ml DI water and 0.2g Pt/AC for 2 hours).

Temperature (°C)	Conversion (%)	Yield (%)				
		Sorbitol	Xylitol	Erythritol	EG	1,2-PG
190	19.8	2.1	1.1	1.4	0.1	0.1
205	63.2	13.2	1.3	1.9	0.3	3.2
225	99.2	25.1	4.0	1.2	0.5	6.7
250	99.5	11.0	3.6	1.7	3.1	7.0

4.3.2 Effect of catalyst amount

Effect of catalyst amount on cellulose hydrogenation over Pt/AC is presented in Table 4.4. As a bifunctional catalyst, change of the amount of catalyst leads to changes in platinum amount and AC amount. To simplify the effect of catalyst amount, controlled experiments were also conducted. For example, we examined a reaction with 10 mg catalyst. A control experiment with similar amount of platinum but different amount of support AC (10 mg of Pt/AC and 30 mg of AC) was also conducted as a comparison.

As shown in Table 4.4, increasing catalyst amount from 10 mg to 40 mg improves the conversion from 80.5% to 99.5% and sorbitol yield from 12.3% to 25.14%. However, it is hard to tell whether the improvement is caused by Pt or AC since both vary. Through the comparison with controlled groups, it is found that the cellulose conversion and sorbitol yield significantly increase as the amount of AC increase, even when the Pt is kept the same (10 mg Pt/AC compared with 10 mg Pt/AC and 30 mg AC, or 20 mg Pt/AC compared with 20mg Pt/AC and 20mg AC). The results indicate that it is the increase of AC amount that promotes the cellulose conversion and sorbitol yield.

A plausible explanation is that the cellulose hydrogenation as a two-step reaction closely depends on the first step of the hydrolysis of cellulose to glucose, which is the rate-limiting step[349]. AC is mainly responsible for the hydrolysis step for its rich surface acid functional groups. The increase of AC facilitates the hydrolysis of cellulose. As a result, more glucose will be available for hydrogenation reaction to produce sorbitol. Hence both conversion and sorbitol yield increases.

It was also found that the maximum sorbitol yield of 32.2% is obtained for the combination of 20 mg Pt/AC and 20 mg AC. Further increasing the amount of Pt/AC to 30 mg and 40 mg results in less yield of sorbitol, which indicates that platinum is also attributed side reactions which reduces sorbitol selectivity. In a word, it is crucial to balance the ratio of AC and supported platinum to achieve favorable hydrolysis and hydrogenation reaction to minimize side reactions.

Table 4.4 Effect of catalyst amount on cellulose hydrogenation (0.5g milled cellulose, 225°C, 60bar for 2h in 25ml water).

Pt/AC (mg)	AC (mg)	Conversion (%)	Yield (%)				
			Sorbitol	Xylitol	Erythritol	EG	1,2-PG
10	0	80.5	12.3	1.3	1.6	0.9	3.5
10	30	98.7	29.3	1.5	1.4	0.5	5.6
20	0	85.2	18.6	1.3	1.9	0.3	3.2
20	20	99.6	32.2	4.8	1.5	0.9	7.2
30	0	92.3	23.1	3.9	1.0	0.4	4.5
30	10	99.6	28.6	3.9	1.1	0.4	5.2
40	0	99.5	25.1	4.1	1.2	0.5	6.7

4.3.3 Effect of hydrogen pressure

Hydrogen pressure as another crucial variable is examined and its effect is described in Table 4.6. Our result indicates that the hydrogen pressure does not affect cellulose conversion and it only has limited impact on sorbitol yield. Conversions of cellulose are almost the same for reactions with different hydrogen pressure, while sorbitol yield slightly increases from 18.2 % to 22.4 % when hydrogen pressure increases from 40bar to 50bar. Small increases from 22.4 % to 25.1% and 26.12% are observed for pressure increasing from 50bar to 60bar and 70bar, respectively.

Hydrogen as a non-polar gas has very low solubility in water. Hydrogen

concentration can be roughly estimated according to Henry's Law:

$$K_H = \frac{P}{C}$$

In this formula, K_H stands for Hydrogen concentration, P is the H_2 pressure in the reactor, and C represents the concentration of the hydrogen in water. Since the K_H does not vary much across a broad range of temperature[350], here $K_H = 1300 \text{ bar}\cdot\text{l/mol}$ is used to calculate the hydrogen concentration under different conditions as listed in Table 4.5.

Table 4.5 Hydrogen solubility.

H_2 pressure	$H_2(\text{mmol})$ amount in 10 ml water			
	353K	363K	373K	498K
30	0.25	0.25	0.25	0.31
40	0.33	0.34	0.34	0.41
50	0.41	0.42	0.42	0.51
60	0.49	0.51	0.51	0.62
70	0.57	0.59	0.59	0.72

The dissolved hydrogen in water depends on the hydrogen pressure, but it seems 40bar of hydrogen is sufficient for the reactions. The stoichiometric hydrogen required for total hydrogenation of cellulose is about the same as mol of the anhydrate glucose unit, which is about 0.54 mmol. Given that hydrolysis of cellulose is a slow reaction, the hydrogen dissolved in water is more than adequate for the reactions. What's more, our results contradict Fukuoka's assumptions that the hydrogen splits over the platinum surface and participates in the hydrolysis of cellulose, because higher conversion is not observed under higher hydrogen pressure.

Table 4.6 Effect of H₂ Pressure on cellulose hydrogenation (0.5g milled cellulose, 0.2g Pt/AC, 225°C, for 2h in 25ml water).

H ₂ Pressure (bar)	Conversion (%)	Yield (%)				
		Sorbitol	Xylitol	Erythritol	EG	1,2-PG
40	96.7	18.2	1.1	1.5	0.2	3.1
50	98.2	22.4	1.3	2.0	0.4	3.2
60	99.2	25.1	4.1	1.2	0.5	6.7
70	99.5	26.1	4.0	1.7	0.4	6.9

4.4 Optimization of JM Pt/AC via ethylene glycol reduction

In our previous experiments, the performance of the sorbitol yield over Pt/AC for milled cellulose conversion is only about 30%. To improve the sorbitol yield of platinum catalyst, we further reduced the fresh catalyst by using ethylene glycol as solvent media, under 200°C and 220°C, with 60bar of hydrogen for 15h. Surprisingly, Pt/AC after the further reduction outperforms the fresh one. As shown in Table 4.8, the yield of sorbitol is almost doubled from 25.1% to 50% for milled cellulose. When using cellobiose as reaction substrate, an increase of sorbitol yield is also observed for platinum catalyst after further reduction. The yield of sorbitol increases from 49.6% to 62.1% for platinum catalyst after reduction at 200°C, and further increases to 73.5% for platinum catalyst after reduction at 220°C.

Table 4.7 Effect of EG reduction on cellulose and cellobiose hydrogenation (0.5g reactant, 225°C, 60bar, 2 hours, 0.2g catalyst, 25ml DI water).

substrate	catalyst	conversion(%)	yield(%)			
			sorbitol	erythritol	1,2-PG	EG
milled cellulose	Pt/AC	99.2	25.1	1.2	6.7	0.5
	Pt/AC EG200°C	98.5	35.2	1.1	1.3	3.2
	Pt/AC EG220°C	97.9	49.3	2.1	1.1	5.7
cellobiose	Pt/AC	99.5	49.6	0	0.8	1.5
	Pt/AC EG200°C	99.5	62.1	0.2	0.7	1.1
	Pt/AC EG220°C	99.6	73.5	0.9	0.9	1.7

To explain the performance improvement, characterizations of the catalysts were performed by Raman spectroscopy, XRD, TEM, SEM, BET and CV. As seen from Table 4.10, the BET surfaces of the platinum catalysts decreases slightly from 793.7 m²/g to 682.8 m²/g and 685.7 m²/g after further reduction at 200°C and 220°C, respectively. The decline of BET surface area may be

attributed to the collapse of some pores or channels during the further reduction process. However, the pore volume and pore size almost remain unchanged. The N_2 adsorption isotherms of the three catalysts are presented in Figure 4.4. It is observed that all the three materials exhibit similar nitrogen adsorption and desorption properties of active carbon with well-developed microporosity[324]. The BET results exclude the textual effect on performance enhance of the EG reduction method on Pt/AC.

Table 4.8 Textual properties of fresh Pt/AC and Pt/AC with further reduction.

catalyst	BET Surface Area(m^2/g)	Pore Volume(cm^3/g)	Pore size(nm)
fresh Pt/AC	793.7	0.47	5.4
Pt/AC EG 200°C	682.8	0.46	5.6
Pt/AC EG 220°C	685.7	0.45	5.6

Figure 4.4 N₂ adsorption isotherms of the fresh Pt/AC and Pt/AC with further reduction.

Raman spectroscopy of fresh Pt/AC, Pt/AC (EG 200°C) and Pt/AC (EG220°C) is displayed in Figure 4.5. The Raman spectra were collected with an excitation λ of 633 nm. The D band situated at 1325 cm^{-1} is attributed to amorphous carbon, while the G band centred at 1598 cm^{-1} is considered as the graphite-oriented carbon[351]. The ratio of the intensity of the two peaks $I(D)/I(G)$ roughly indicates the degree of structural disorder of the carbon material. The ratio of peak intensity of D band to G band of the fresh Pt/AC is 2.2, which slightly increases to 2.39 and 2.4 for Pt/AC (EG 200°C) and Pt/AC (EG220°C). The results of Raman spectrum indicate that there was no significant change of the support (active carbon) before and after the ethylene glycol reduction treatment in terms of carbon crystallinity.

Figure 4.5 Raman spectra of fresh Pt/AC, Pt/AC further reduced in EG at 200°C and 220°C.

XRD patterns (refer to Figure 4.6), reveal that the peak intensity of platinum in Pt/AC with further reduction was much larger than the ones in fresh Pt/AC, especially for Pt (111), Pt (200) and Pt (220)[352]. This intensity difference indicates that the particle size of the Pt/AC after post-treatment is larger than the fresh one. It is worth to mention that the catalysts were reduced in a quartz vial. It is possible that some of the quartz powder would be scratched down and mixed into the catalyst, which explained the sharp peak around 26 degree[353, 354]. The SEM images presented in Figure 4.7 (a and b) provide little morphology information about the EG reduction. In the contrary, the TEM images reveal that the particle size of platinum for Pt/AC with further reduction are much larger than the fresh ones. It is believed that platinum particle will aggregate under high temperature, since the fresh Pt/AC are reduced at 225°C for 15 hours. Therefore,

we could confirm that our further reduction method increases the particle size of platinum.

Figure 4.6 XRD patterns of fresh Pt/AC from JM, and Pt/AC after post-treatment.

Figure 4.7 SEM and TEM of Pt/AC. (a) SEM of fresh Pt/AC from JM. (b) SEM of Pt/A (EG220°C). (c)TEM of fresh Pt/AC from JM. (d) TEM of Pt/A (EG220°C).

Effect of particle size has been widely reported among the research of C=O hydrogenation on various topics. Noritatsu et al. found that sorbitol yield would increase as the Pt nanoparticle supported on reduced graphene oxides increases from 2.0 nm to 3.6 nm[355]. However, they failed to provide any further explanation for this finding. In another study, Wang et al. reported that the larger ruthenium particle favors the cleavage of the β -1,4-glycosidic bond during cellobiose hydrogenation, while the smaller ruthenium particle favors the reducing of cellobiose to isomaltitol[93]. Higher sorbitol selectivity is also favored over platinum catalyst with larger particle size in the glucose hydrogenation. Moreover, it is suggested that sorbitol production via C=O bond hydrogenation is favored over Pt (111) facets, which are at higher density on larger Pt particles[348]. Despite various hypotheses are proposed to explain the size-effect, the actual governing mechanism remains unclear. Therefore, CV scanning was performed to examine the electronic properties of the Pt catalyst

before and after EG reduction. According to Figure 4.8, the hydrogen adsorption peak at -1.3 V of Pt/AC (EG) becomes smaller compared to fresh Pt/AC. Hydrogen adsorption and desorption peak indicate the catalysts' ability to couple and decouple hydrogen on the surface. Hydrogen couple and decouple on the precious metal surface is believed to be the key to many side reactions such as hydrogenolysis and dehydrogenation. This may partially explain the increase of sorbitol yield over Pt/AC further reduced in EG.

It is also found in Figure 4.9 and 4.10 that the platinum oxidation peak shifts from 0.40 V to 0.41V and 0.42 V as the Pt/AC go through EG reduction under 200°C and 220°C, while the platinum oxide reduction peak shifts to left from 0.38 V to 0.35 V and 0.32 V. Such shifting indicates the activity of Pt/AC(EG) for reduction and oxidation reactions decreases as higher voltage is required for its oxidation and lower voltage is required for its oxide's reduction. Many side reactions of cellulose hydrogenation such as hydrogenolysis and dehydrogenation proceed through oxidation or reduction over the platinum surface via electron transaction. Further reducing Pt/AC with EG narrows the path of various reactions including main reaction and side reactions. The narrowed pathway blocks some of the side reactions which require lower platinum oxidation voltage or higher platinum oxide reduction voltage. As a result, sorbitol yield increases as fewer by-products are produced.

It is believed in catalytic science that metal catalysts with smaller particle size are more desired than the ones with larger particle size. The smaller the particle size, the larger the surface area, which means more reaction active sites. However, our study indicates that larger particle size favors the performance. In

other words, in cellulose hydrogenation reaction, tuning of active sites which reduces side reactions rather than increases the active sites appears to be the key to improve the sorbitol yield.

Figure 4.8 Cyclic voltammograms (CVs) of Pt/AC, Pt/AC (EG 200°C) and Pt/AC (EG 220°C) in 0.5M H₂SO₄ electrolyte solution with a scan rate of 20mV·s.

Figure 4.9 Platinum oxide reduced peak of Pt/AC, Pt/AC (EG 200°C) and Pt/AC (EG 220°C) in 0.5M H₂SO₄ electrolyte solution with a scan rate of 20mV·s.

Figure 4.10 Platinum oxidized peak of Pt/AC, Pt/AC (EG 200°C) and Pt/AC (EG 220°C) in 0.5M H₂SO₄ electrolyte solution with a scan rate of 20mV·s.

4.5 Insight into the reaction pathway of cellulose hydrogenation

Combining the results of our study and reports by other scholars [73, 105, 120, 347, 348, 356-358], the reaction pathway and potential side reactions are described in Figure 4.11. The cellulose hydrogenation mainly consists of two steps. In the first step, cellulose is hydrolyzed into sugars or polysaccharide with the assistance of acid sites on the support. A small percentage of cellobiose may be reduced to isomaltitol before they are hydrolyzed to glucose. Since sugar is not stable under such condition, it may further react with other materials through hydrogenation, oxidation, dehydration, retro aldol and dehydrogenation. In the second step, most of the sugar will be reduced to sorbitol as the main product. Some of the glucose will isomerize to fructose, which may be further dehydrated to HMF (5-(Hydroxymethyl)furfural) or produce glyceraldehyde under retro-aldol reactions. Glyceraldehyde will later be reduced to 1,2-propanediol. Even though sorbitol is more stable than sugars, part of them tends to undergo further hydrogenolysis reaction to produce smaller polyols such as xylitol or through dehydration reactions to produce by-products such as sorbitan and isosorbide.

As a complex reaction, factors such as reaction time, reaction temperature, catalyst amount, and hydrogen pressure interplay with each other and produce a well-mixed product. Different factors favor different reactions. For example, hydration reactions depend more on temperature and acidity of the support. Reduction and oxidation rely on the amount of precious metal, while hydrogen pressure favors hydrogenation reactions and suppresses oxidation reactions. Longer reaction time favors conversion while results in poor product selectivity as more side reactions such as hydrogenolysis and dehydration will be involved.

The activity of the supported platinum relies on its particle size. The Smaller the particle size, the higher the activity towards side reactions, which will may overtake the main hydrogenation reactions. The key to attain a high level of cellulose conversion while keep the selectivity high relies on the tuning of the factors and catalyst.

Figure 4.11 Proposed reaction pathway of cellulose conversion.

4.6 Summary

In this chapter, platinum catalyst from JM has been examined for two different cellulose substrates (crystalline cellulose and milled cellulose) in hydrogenation reactions. Cellulose exhibits high structural stability due to its rich inner hydrogen bonds. Milling as a simple mechanical method can greatly reduce cellulose crystallinity and produce amorphous cellulose, which, in turn, favors the hydration reactions. Various reaction factors have been evaluated by the trial-and-error method. Among those factors, temperature and reaction time have a significant effect on cellulose conversion and sorbitol yield. Hydrogen pressure has limited impact on the overall conversion. The ratio of Pt/Ac and AC exert a significant influence on sorbitol yield. After tuning of those factors, a 32% of sorbitol yield of is achieved.

A simple reducing method using ethylene glycol significantly improves the sorbitol yield from 25% to 50%. Characterization such as XRD, TEM, BET and CV were conducted to investigate the performance improvement. As revealed in the results, the EG reduction process increases the platinum particle size, which, in turn, weakens its hydrogen adsorption ability and activity in oxidation and reduction reactions, while improves the sorbitol selectivity by suppressing many side reactions.

Optimization of reaction conditions for cellulose conversion is like dancing on the eggs[121]. Many side reactions appear which lead to a low yield of sorbitol and low carbon balance. Achieving high conversion and high sorbitol yield at the same time can be achieved through carefully tuning the reaction conditions and optimizing the catalysts.

Chapter 5 Multivariate analysis of cellulose hydrogenation over Ruthenium catalyst

5.1 Introduction

Despite our effort spent on examining the Pt catalyst from JM, the optimized sorbitol yield could only reach about 50%. Ruthenium as another active precious metal reveals high performance in cellulose hydrogenation reactions. Precious metal including Ru, Ir, Pd and Ru supported on BEA zeolite were evaluated for cellulose hydrogenation reactions, and ruthenium catalyst was found to have the highest catalytic activity[323]. Early in 1998, Pierre Gallezot et al. found that ruthenium catalyst with low loading percentage (1.6% to 1.8%) displays superior catalytic performance on glucose hydrogenation[206]. In their study, nearly 100% yield of sorbitol is achieved over Ru/C catalyst with an initial specific activity of $1.1 \text{ mol h}^{-1} \text{ g}^{-1}$ for 40% glucose aqueous solution in a trickle bed reactor. The authors also suggest that the selectivity is highly dependent on the residence time, since the longer residence time favors the epimerization of sorbitol to mannitol. In addition, compared with platinum catalyst on cellulose hydrogenation[73], ruthenium catalyst supported on active carbon is proved to have better catalytic performance as the total yield of hexitols increases to 39%[243]. Similarly, Wang Ye and co-workers' research on ruthenium catalyst on several different supports also demonstrated that Ru/CNT is the most efficient catalyst for conversion of cellulose to sorbitol in water[322]. The comparisons of different supports and different treatments for CNT in the same study also indicate that the acidity of the support is a critical factor for sorbitol selectivity. Pre-treatment of cellulose in phosphate acid significantly reduced cellulose crystallinity and dramatically

improve the sorbitol yield. In their experiments, a sorbitol yield of 36% can be obtained for commercial cellulose with 85% crystallinity, while a 69% yield of sorbitol was observed for cellulose with 33% crystallinity after phosphate acid treatment. In another study using cellobiose hydrogenation as the model reaction, it was revealed that the mean size of the ruthenium particle is crucial for catalytic performance[93]. The authors proposed that smaller ruthenium particle size favors the intermediate reaction of reduction of cellobiose to 3-b-D-glucopyranosyl-D-glucitol, but hinders the hydrolysis of the reaction intermediate, which leads to a lower sorbitol selectivity. However, they failed to provide further explanation on why the size of nanoparticle favors such reactions. Other researchers also pointed out that Ruthenium catalyst coupled with heteropoly acids outperform the combination of mineral acid[83], as the presence of heteropoly acid such as $\text{H}_3\text{PW}_{12}\text{O}_{40}$ could effectively accelerate the hydrolysis of cellulose to glucose. Besides, the presence of ruthenium particle on carbon support is also found to promote the cellulose hydrolysis[65], as the yield of glucose increases from 20.5% to 34.2%. In Lucília Sousa Ribeiro et al.'s study, they investigated the direct conversion of cellulose to sorbitol over ruthenium catalyst and compared the effect of the supports. As revealed in their study, even though ruthenium supported CNT achieves the highest sorbitol yield, it exhibits little advantage than the other kinds of supports. Such results lead to their conclusion that no significant correlation of support textural properties and reaction activities was found[324].

Despite the excellent reaction results achieved by Ru-based catalyst, the mechanism behind the reaction remains unclear, especially how reaction

variables interplay with each other and affect the sorbitol yield. Very few studies have investigated the reaction from the industrial point of view. Moreover, most of the studies of cellulose hydrogenation were carried out in a trial and error method, namely varying one factor at a time while fixing all other factors and evaluate how the changing factor affects the response. Such setting is not only time-consuming and costly, but also fails to evaluate the impact of multiple factors at the same time. On top of that, the trial and error method may be problematic in interpreting the factors and response relations when the synergistic effect exists among the factors. In other words, the variation of a factor may also influence the way the other factors affect the response.

To overcome these issues, this study aims to examine the cellulose hydrogenation over ruthenium catalyst using a multivariate analysis method by JMP (version 10) from SAS. Statistical software like JMP provides many useful pre-set designs of experiment (DoE) which help to meet the needs of different experiment scenarios. Users are also provided with various regression models for studies with different emphasizes. JMP also comes with powerful visual plot tools which allow the user to interpret the data from multiple dimensions. JMP can easily model a certain experiment setting and generate prediction formula to predict the response without conducting the actual experiments.

Using statistic analyzing approach, we explored the effects of temperature, hydrogen pressure, catalyst amount and ruthenium loading on sorbitol yield of cellulose conversion based on ruthenium supported active carbon catalyst with three different loading percentages (0.25%, 0.5% and 1.0% respectively). We will also investigate the synergistic effect among those factors. The overall effect

of the variables will be summarized in a single experience-base prediction formula for further application.

5.2 Statistical design of cellulose hydrogenation

Unlike the trial and error method, multivariate analysis method requires a proper design of experiment which can help to analyze multiple factors (temperature, pressure, metal loading, cellulose amount, catalyst amount) concurrently for the sake of saving time and resources. Sorbitol yield is treated as the response which we try to maximize through the sets of reactions. The range of the factors is described in Table 5.1.

Table 5.1 The experiment factors and response of cellulose hydrogenation over ruthenium catalyst.

Factor	Range
temperature T (°C)	190-210
hydrogen pressure P (bar)	30-50
cellulose amount W1 (mg)	80-120
catalyst amount W2 (mg)	30-50
Ru loading R (%)	0.1-1
Response	
sorbitol yield Y (%)	

Many designs of experiment are available according to a specific goal and research question, e.g., screening design is good at locating the most effective factor among all the factors. Other DoE includes mixture design, choice design, space filling design and non-linear design. In this work, as we are interested in how factors influence the response and how to maximize the response, response surface design (RSD) which is useful to locate a maximum or minimum response was employed. RSD includes full factorial design, central composite design (CCD) and box-behnken design. In the full factorial design, every setting of each

factor appears with every setting of every other factor. In a 2-level setup, the required run of experiments is 2^k , which increases exponentially when the factor number goes beyond 5. As a first-order model, the full factorial design is not sufficient for the analysis of intercorrelated factors. The Box-Behnken design is an independent second order design without an embedded factorial or fractional factorial design. In this design, the treatment combinations are at the midpoints of edges of the process space. This design is suitable for experiments which require 3 levels of factors. However, it has limited capability for orthogonal blocking compared to the central composite design. We selected the central composite design (CCD) for our analysis since we only need 2 level of factors and those factors may interact with each other. A typical central composite design includes a center point, several axial points and fractional factorial points as shown in Figure 5.1.

- 1: central point
- 2: axial point
- 3: fractional factorial point

Figure 5.1 Central, axial and fractional factorial points in CCD.

A set of reaction runs, based on the embedded CCD, was generated as presented in Table 5.2, which covers a broad range of experiment conditions available within our capability. A unique pattern was designated to each run to reflect its position in CCD. For example, ‘-’ indicates fractional factorial points setting at the lower level, while ‘+’ represents fractional factorial points locating at the higher level. The axial points were marked with ‘a’ (indicating the lower value) or ‘A’ (indicating the higher value). The axial value was set to be one on the face with two center points, whose pattern was marked as ‘0’. Center points serves as a boss point as an option to lower the prediction variance at the center of the design. Since excessive amount of center points will lead to the loss of mathematical optimality, only two center points were used to improve the predictability of the model.

Table 5.2 DoE for cellulose hydrogenation over ruthenium catalyst.

Pattern	Run	temperature	H ₂ pressure	catalyst amount	Ru loading	sorbitol yield
-----	1	190	30	30	0.25	2.29
----+	2	190	30	30	1.00	44.05
---+-	3	190	30	50	0.25	4.45
---++	4	190	30	50	1.00	27.42
a000	5	190	40	40	0.50	52.1
-+---	6	190	50	30	0.25	4.85
-++-	7	190	50	30	1.00	46.97
-++-	8	190	50	50	0.25	6.9
-+++	9	190	50	50	1.00	32.26
0a00	10	200	30	40	0.50	65.8
00a0	11	200	40	30	0.50	71.93
000a	12	200	40	40	0.25	2.2
0	13	200	40	40	0.50	69.69
0	14	200	40	40	0.50	69.69
000A	15	200	40	40	1.00	36.85
00A0	16	200	40	50	0.50	58.75
0A00	17	200	50	40	0.50	66.08
+---	18	210	30	30	0.25	2.2
++--	19	210	30	30	1.00	49.5
++--	20	210	30	50	0.25	3.5
++--	21	210	30	50	1.00	21.75
A000	22	210	40	40	0.50	56.6
++--	23	210	50	30	0.25	3.7
++--	24	210	50	30	1.00	46.15
++--	25	210	50	50	0.25	3.9
++++	26	210	50	50	1.00	19.2

As the variables were set in different scales, for example, the temperature was set from 190°C to 210°C, while the ruthenium loading was set from 0.25% to 1%, direct comparison of the effects of those variables will be biased. To equalize the weight of the variables, all the variables (temperature, hydrogen pressure, catalyst amount and ruthenium loading) had been standardized by the following formula:

$$x_{standardized} = \frac{x_i - (x_{max} + x_{min})/2}{(x_{max} - x_{min})/2}$$

Table 5.3 Normalized DOE for cellulose hydrogenation over ruthenium catalyst.

Pattern	run	temperature	H2 pressure	catalyst amount	Ru loading	sorbitol yield
-----	1	-1	-1	-1	-1	2.29
----+	2	-1	-1	-1	1	44.05
---+-	3	-1	-1	1	-1	4.45
---++	4	-1	-1	1	1	27.42
a000	5	-1	0	0	-0.333	52.1
-+---	6	-1	1	-1	-1	4.85
-++-	7	-1	1	-1	1	46.97
-++-	8	-1	1	1	-1	6.9
-+++	9	-1	1	1	1	32.26
0a00	10	0	-1	0	-0.333	65.8
00a0	11	0	0	-1	-0.333	71.93
000a	12	0	0	0	-1	2.2
0	13	0	0	0	-0.333	69.69
0	14	0	0	0	-0.333	69.69
000A	15	0	0	0	1	36.85
00A0	16	0	0	1	-0.333	58.75
0A00	17	0	1	0	-0.333	66.08
+----	18	1	-1	-1	-1	2.2
+---+	19	1	-1	-1	1	49.5
+--+-	20	1	-1	1	-1	3.5
+----	21	1	-1	1	1	21.75
A000	22	1	0	0	-0.333	56.6
++---	23	1	1	-1	-1	3.7
++--	24	1	1	-1	1	46.15
+++-	25	1	1	1	-1	3.9
++++	26	1	1	1	1	19.2

Figure 5.2 Normal quantile plot of temperature, hydrogen pressure, catalyst amount and Ru loading.

The normality of the variables is of great importance in multivariate analysis for better interpretation of the results. If the variables are not normally distributed or highly skewed, the coefficient of the variables may be overestimated or underestimated. Normality can be assessed by the normal quantile plot, which is also known as quantile-quantile plot or Q-Q plot. According to Figure 5.2, all the variables are well distributed along the diagonal line, which demonstrates the normality of the variables.

5.3 Regression model of cellulose hydrogenation

According to the DoE and sorbitol yield results in Table 5.3, we ran the simulation script using standard least square with an emphasis on effect screening. The model was generated and described in Table 5.4 with the estimated value for intercept, and coefficient, standard error (SE), t ratio and p value for each variable.

In Table 5.4, the column of estimate indicates the effect of each variable on sorbitol yield when other factors remain unchanged. The positive value means an increase of the factor will lead to an increase of sorbitol yield, while a negative value indicates otherwise. Since these variables are standardized, the magnitude of the effect can be compared based on its estimate coefficient. The larger the absolute value of a coefficient, the higher the influence. For example, the coefficient of Ru loading is 16.12, and the coefficient of catalyst amount is -5.40, which indicates that a unit change of Ru loading has a more substantial effect on sorbitol yield than a unit change of catalyst amount. The SE is the standard deviation of the sampling distribution, which equals to the standard deviation divided by the square root of the sample size. The t Ratio reflects how an estimated value of a parameter departs from its hypothesized value to its standard error, which is often used in testing the hypothesis. Based on t Ratio, p value is generated and being used to determine the statistical significance of a factor. A p-value smaller than 0.05 indicates strong evidence against the null hypothesis and demonstrates that there is a relationship between the factors (temperature, pressure etc.) and response (sorbitol yield).

Table 5.4 Original second order regression model of cellulose hydrogenation over Ru catalyst.

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	75.62	1.65	45.76	<.0001
Ru loading*Ru loading	-54.28	2.75	-19.77	<.0001
Ru loading	16.12	0.91	17.64	<.0001
catalyst amount	-5.40	0.91	-5.91	0.0001
catalyst amount*Ru loading	-5.61	0.96	-5.82	0.0001
temperature*temperature	-8.07	2.42	-3.33	0.0067
temperature*catalyst amount	-1.63	0.97	-1.68	0.1209
H2 pressure*H2 pressure	3.52	2.42	1.45	0.1741
catalyst amount*catalyst amount	2.92	2.42	1.21	0.2532
temperature*H2 pressure	-1.05	0.97	-1.08	0.3027
temperature	-0.85	0.91	-0.93	0.3744
temperature*Ru loading	-0.68	0.96	-0.70	0.4972
H2 pressure	0.49	0.91	0.54	0.6015
H2 pressure*Ru loading	-0.30	0.96	-0.31	0.7637
H2 pressure*catalyst amount	0.09	0.97	0.10	0.9242

Table 5.5 Improved second order regression model of cellulose hydrogenation over Ru catalyst.

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	75.62	1.50	50.28	<.0001
Ru loading*Ru loading	-54.28	2.50	-21.72	<.0001
Ru loading	16.12	0.83	19.38	<.0001
catalyst amount	-5.40	0.83	-6.49	<.0001
catalyst amount*Ru loading	-5.61	0.88	-6.39	<.0001
temperature*temperature	-8.07	2.21	-3.66	0.0026
temperature*catalyst amount	-1.63	0.88	-1.85	0.086
H2 pressure*H2 pressure	3.52	2.21	1.60	0.1326
catalyst amount*catalyst amount	2.92	2.21	1.32	0.2065
temperature*H2 pressure	-1.05	0.88	-1.19	0.2546
temperature	-0.82	0.83	-0.99	0.34
H2 pressure	0.50	0.83	0.60	0.5552

Table 5.4 shows the origin second order regression model. The results reveal that Ru loading, catalyst amount and the interaction between Ru loading and catalyst amount significantly predict the sorbitol yield. For a better simulation, the insignificant terms ($p \text{ value} > 0.05$) should be removed by using a stepwise backward elimination method. The method is conducted as follow. First, all the

factors are listed in the model with an adjust R square value of 0.9776. Then a step backward is conducted by eliminating the least significant term H₂ pressure*catalyst amount and improves the adjust R square to 0.9795. Another backward step is taken by removing the second least significant term H₂ pressure*Ru loading and improves the adjust R square to 0.9809 and decreases the AIC and BIC values. One last step is taken backward which eliminates the term temperature* Ru loading and improves the adjust R square to 0.9815 and both AIC and BIC values further decrease accordingly. The edge of the significance is reached by the three-step backward elimination, as the further elimination of terms will lead to the decrease of the adjust R square and increase of both AIC and BIC values.

As shown in Table 5.5, after the three-step elimination, all the main variables and all the interaction terms which have significant p value stay in the improved model. It is worth mentioning that even the two main variables temperature and H₂ pressure are insignificant, their second-order variable and interaction terms are statistically significant, which signifies their roles in the improved model. Therefore, they will not be eliminated.

The relationship between the actual experimental results and the predicted results is demonstrated in Figure 5.3. Both models reveal strong statistical significance as the p values are smaller than 0.05. The R square of the two models are relatively high, which implies a proper fit of the experimental data. The RMSE (root-mean-square error) is used to measure distinctions between values predicted by a model and the values observed. The accuracy of the model is

improved after the three-step backward elimination as the RMSE decreases from 3.8771 to 3.5288.

Figure 5.3 Origin regression models of sorbitol yield.

Figure 5.4 Improved models of sorbitol yield after 3 steps backward elimination.

5.4 Canonical analysis of stationary points

The following section concentrates on the optimization of the reaction which aims to achieve the maximum yield of sorbitol in the experimental range of the four valuables. Mathematically, the maximum yield is examined through

the assessment of the stationary point, which represents a point when the partial derivatives of the response over the main variables equal to zero. The stationary point could be either a maximum value, a minimum value or a saddle point. Canonical analysis using the eigenvalue (λ) is commonly adopted to determine if a maximum value, a minimum value or a saddle point exists in a model. Specifically, if all the eigenvalues are positive, there will be a minimum value; if all the eigenvalue are negative, there will be a maximum value of the response; if both positive and negative values exist, then there will be neither a maximum value nor a minimum value, but a saddle point.

Table 5.6 Canonical curvature study: eigenvalue and eigenvectors of sorbitol yield.

	Eigenvalue and Eigenvector			
Eigenvalue	3.563	3.0963	-8.1457	-54.4216
temperature	-0.05748	-0.06049	0.99648	0.00818
H2 pressure	0.97888	-0.19956	0.04433	0.00259
catalyst amount	0.19585	0.97689	0.0702	0.04895
Ru loading	-0.01167	-0.04686	-0.01171	0.99876

As shown in Table 5.6, there are 2 positive eigenvalues and 2 negative eigenvalues, which indicates a saddle point in our study of sorbitol yield and no maximum or minimum value exists. Even though, the pursuit of the optimal yield of sorbitol is proved to be null in this case, it is still worthy to evaluate how the main factors and the interaction terms affect the sorbitol yield. This finding enables us to adjust those factors to meet the actual needs at the most suitable condition configuration.

5.5 Prediction profiler

Based on the reaction data from the DoE, which includes the reaction temperature, hydrogen pressure, catalyst amount and ruthenium loading as well as the sorbitol yield, we will be able to generate prediction profiler of each main variable by JMP.

The effect of each variable on sorbitol yield is described in Figure 5.5. The figure indicates that the relationship between temperature and sorbitol yield is quadratic, with a peak at around 200 °C. Elevating temperature from 190°C to 200°C helps to increase the sorbitol yield, while the sorbitol yield decreases if the temperature increases further. Similar to cellulose hydrogenation over platinum catalyst discussed in the last chapter, elevating temperature for cellulose conversion and sorbitol yield is necessary due to cellulose's structural stability. But as a sophisticated reaction system, cellulose hydrogenation involves many side reactions and produces various by-products such as xylitol, fructose, HMF, sorbitan and other small but innumerable fragment by-products. What ruthenium catalyst differs from platinum catalyst is that the main by-product under high temperature is gaseous alkane. Analysis of the gas content has confirmed that sorbitol will be consumed under high temperature and produce alkane by-product such as methane, ethane.

Hydrogen as the reactant pressure exerts a smaller influence on sorbitol yield, as negligible sorbitol change takes place across a wide range of hydrogen pressure changes. Unlike cellulose conversion over platinum catalyst which requires hydrogen pressure higher than 40bar, reactions over ruthenium catalyst produce similar sorbitol yield no matter the hydrogen pressure is 30bar or 50bar.

This result indicates that ruthenium catalyst has stronger hydrogen couple and decouple ability and relies less on hydrogen concentration.

Increasing catalyst amount places a negative effect on sorbitol yield since the trend of sorbitol decreases as catalyst amount increases. Ruthenium loading is the most influential factor in terms of sorbitol yield. Increasing ruthenium loading from 0.25% to 0.5% dramatically improves sorbitol yield from 5% to 63%. However, a further increase of ruthenium loading will decrease sorbitol yield. GC results suggest that more alkane gas product will be generated if ruthenium loading increases.

Figure 5.5 Prediction profile of each variable (temperature, Hydrogen pressure, catalyst amount and Ru loading).

5.6 Response surface plot analysis

Prediction profile of individual variables reveals the basic trend of their individual effect on sorbitol yield when other variables are fixed. However, a single variable prediction profile has limited predicting power on the sorbitol yield when other variables are changing. For example, the effect of temperature on sorbitol, as shown above, is only valid when hydrogen pressure is set at 40bar, catalyst amount at 40 mg and ruthenium loading at 0.55%. If one or more variables changes, the temperature effect on sorbitol yield might fluctuate accordingly. To obtain a more comprehensive understanding of the variables' effect on sorbitol yield and a better interpretation of the reaction, it is important to know how the interaction between factors such as catalyst-Ru loading, catalyst amount-temperature, temperature-hydrogen pressure, Ru loading-temperature exert an influence on sorbitol yield. Contour plot and response surface plot provided by JMP are useful in analyzing the combining effect of two variables with visualized 2D and 3D plots.

Figure 5.6 visualizes the effect of catalyst amount and ruthenium loading on sorbitol yield. This is an example of how we can analyze the synergistic effect between two factors, where the traditional trial and error method falls in short. The sorbitol yield surface is presented as a curved ceiling being roughly curled by the ruthenium loading. In this two-component system, the effect of ruthenium loading obviously outweighs that of catalyst amount. It shows that the catalyst amount hardly changes the trend of the effect of Ru loading. When ruthenium loading is smaller than 0.69%, increasing Ru loading will raise sorbitol yield. The effect of Ru loading is overturned at a point where ruthenium loading is 0.69%.

When ruthenium loading is larger than 0.69%, increasing Ru loading will lower the sorbitol yield. However, the effect of catalyst amount is not so rigid as Ru loading. Increasing catalyst amount at low Ru loading, negligible change of sorbitol yield is observed. In another word, catalyst amount has limited impact on sorbitol yield at low Ru loading. In contrast, when Ru loading increases, a significant effect of catalyst amount on sorbitol yield is observed. Increasing catalyst amount leads to a dramatic decline of sorbitol yield when Ru loading is near 0.69%.

Figure 5.6 Contour plot and surface plot of catalyst amount and ruthenium loading on sorbitol yield.

The coefficient of catalyst amount and temperature is demonstrated by the contour plot and response surface plot presented in Figure 5.7. The shape of the response surface resembles a saddle, which indicates that neither maximum nor minimum point exists in terms of tuning the effect of catalyst amount and temperature. From 190°C to 200°C, the yield of sorbitol is positively related to temperature, while in the range of 200°C to 210°C, sorbitol yield is negatively

related to temperature. For catalyst amount in the range of 30 mg to 45.6 mg, catalyst amount is negatively correlated with sorbitol yield, while the relationship is reversed when catalyst amount is larger than 45.6 mg. This explains the existence of saddle point: the two variables affect sorbitol yield in two opposite directions.

The density of the grid line in the contour plot also reflects the synergistic effect of temperature and catalyst amount. The axial width of the blue block indicates the additional amount of catalyst which may correspondingly decrease the sorbitol yield from 65.0% to 62.5%. It is found that the width increases as the temperature increases from 190°C to 200°C. The grids are more concentrated on the low temperature and the high temperature than the ones near 200°C, which indicates that the effect of catalyst amount is less effective around 200°C.

Figure 5.7 Contour plot and surface plot of catalyst amount and temperature on sorbitol yield.

Figure 5.8 demonstrates how temperature and hydrogen pressure mutually affect the sorbitol yield. As shown in the surface plot, another saddle

plot exists because it is a minimum point for the sorbitol yield in terms of hydrogen pressure, but a maximum point for temperature.

Figure 5.8 Contour plot and surface plot of temperature and hydrogen pressure on sorbitol yield.

Figure 5.9 Contour plot and surface plot of catalyst amount and H₂ pressure on sorbitol yield.

Figure 5.10 reveals that maximum yield of sorbitol can be obtained by optimizing the Ru loading and temperature. When the temperature is lower than 198°C and ruthenium loading smaller than 0.67%, increasing both will lead to a higher sorbitol yield, while further increasing beyond the optimized point, the

sorbitol yield will be reduced. The various density of the lines in different ruthenium loading range indicates that the effect of ruthenium loading may vary as the temperature changes. For example, at the optimized temperature (198°C), a small increment of ruthenium loading from 0.47% to 0.54% will bring a sorbitol yield increase about 10% (from 60% to 70%). However, when the temperature is set at 205°C, ruthenium loading should be increased from 0.51% to 0.68%, which is over twice increment compared to the case at 198°C, to achieve the same increasement. In a word, the contour plot and surface plot provided by the regression model helps us to understand the synergistic effect of reaction factors better and optimize the setup more practically.

Figure 5.10 Contour plot and surface plot of ruthenium loading and temperature on sorbitol yield.

5.7 Prediction formula

Last but not least, an experimental based prediction formula could be generated based on the reaction data. The empirical prediction formula is useful for the preliminary evaluation of other reaction settings. However, there are also many limits for the actual application of this data-driven formula. Reactions should take place in similar reactor and conditions should also fall in the range of this study. Otherwise, this prediction formula may not be accurate. Nevertheless, this method of producing prediction formula based on experimental data is quite handy to determine the sorbitol yield of certain reaction setups without the spent of actual reaction resource.

$$y = 75.62 - 0.82x_1 + 0.50x_2 - 5.40x_3 + 16.12x_4 - 1.05x_1x_2 - 1.63x_1x_3 - 5.61x_3x_4 - 8.07x_1^2 + 3.52x_2^2 + 2.92x_3^2 - 54.28x_4^2$$

In which x_i should be standardized according to the formula below:

$$\frac{x_i - (x_{max} + x_{min})/2}{(x_{max} - x_{min})/2}$$

Table 5.7 List of variables and abbreviation.

x_i	terms
x_1	temperature
x_2	H2 pressure
x_3	catalyst amount
x_4	Ru loading
x_1x_2	temperature*H2 pressure
x_1x_3	temperature*catalyst amount
x_3x_4	catalyst amount*Ru loading
x_1^2	temperature*temperature
x_2^2	H2 pressure*H2 pressure
x_3^2	catalyst amount*catalyst amount
x_4^2	Ru loading*Ru loading

5.8 Summary

In this chapter, we have studied the sorbitol yield of cellulose hydrogenation over ruthenium catalyst. The effect of temperature, hydrogen pressure, catalyst amount and ruthenium loading were comprehensively explored with a multivariate analysis method by the statistic software called JMP. Hydrogenation reactions were conducted based on a 2-level response surface design. Among all the 26 hydrogenation reactions, the highest sorbitol yield was observed as 71.9% with 98.3% cellulose conversion at 200°C, 40bar hydrogen, 30mg ruthenium catalyst and 0.5% ruthenium loading. After running the reaction data in JMP, a well fit regression model with R-square of 0.99 was generated and further improved after three steps backward elimination. The fitting model shows strong statistical significance (p value < 0.01), and high accuracy with a small RMSE (root mean square error) of 3.5288. The effectiveness of each reaction factor was examined and compared through the model. Through the canonical analysis of the stationary points, we found that no regional maximum value of sorbitol yield exists mathematically in the range of our study. A prediction formula was generated and allowed us to do a preliminary evaluation of other reactions. Even though this data-driven model has some limits in actual application, it has enabled us to study the synergistic effects of variables extensively with powerful visualize tools. Based on that, we believe optimization of the cellulose hydrogenation can be done in a more systematic way.

Chapter 6 Efficient dehydration of sorbitol to isosorbide over sulfonated carbon acid catalysts

6.1 Introduction

As shown in the previous chapters, sorbitol is the main product of cellulose conversion. Sorbitol yield of 50% can be obtained for Pt/AC (EG220) and 70% for 0.5% Ru/AC at optimized conditions. As a utility platform chemical, sorbitol is widely used as sweetener, fuel additive, cosmetic additive and precursor for the synthesis of other useful chemicals[359]. There are two major paths for further upgrading sorbitol. One is through the hydrogenolysis of sorbitol to produce smaller polyols, such as glycerol, ethylene glycol, propanediol[120]. The other is through the dehydration of sorbitol to produce isosorbide[358, 360], which finds its applications in medicine, surfactant synthesis, fuel additive and polymer synthesis.

Synthesis of isosorbide from sorbitol is completed with two steps of dehydration reactions (Figure 6.1). The first step starts with dehydration between the C1 and C4, which produces the reaction intermediate 1,4-sorbitan. The intermediate will then go through another dehydration step between C3 and C6 and form the final product isosorbide. If during the first dehydration step, the water is expelled from the C2 and C5, the by-product 2,5-sorbitan will be produced. As it is difficult to take another water out of 2,5-sorbitan, it will remain as one of the by-products. Since the reactions usually take place under high-temperature, by-products such as humin and coke will also be presented.

Figure 6.1a Sorbitol dehydration to produce isosorbide and side reactions.

Figure 6.1b Sorbitol dehydration mechanism for isosorbide synthesis.

Like many other dehydration reactions, mineral acids such as sulfuric acid, nitric acid show excellent performance in sorbitol dehydration[361]. Reactions conducted in such homogenous system are born with several drawbacks. Separation and recycle of mineral acid after the reactions are the main challenges. Corrosion of the equipment and environment issue will be costly to address. Whereas, heterogeneous solid catalyst with Brønsted acid sites, such as functionalized zeolite, niobium phosphate, sulfated zirconia, sulfated tin oxides and sulfated titania have recently been proved to be effective dehydration catalyst for isosorbide synthesis. In contrast, Lewis acids, such as aluminum chloride and tin chloride present much lower performance.

Aritomo Yamaguchi et al. reported dehydration of sorbitol under hot water without using catalyst[362]. Sung Hwa Jhung's group examined sulfated zirconia, sulfated tin oxides and sulfated titania and found a high yield of isosorbide under solvent-free reaction conditions[257, 363, 364]. Jin-Soo Hwang et al. found that organosulfonic acid functionalized ordered mesoporous silicas (SBA15) show higher catalyst performance than commercially available NR-50, Nafion® SAC-13 and sulfated ZrO_2 for solvent-free sorbitol dehydration conversion[365]. Zhenshan Hou et al. synthesized a new polymer-supported brønsted acid polymer catalyst (SO_3H -PS- SO_3H), which presents high selectivity towards 1,4-anhydro-D-sorbitol[366]. Feng-Shou et al. used a similar method to synthesize a superhydrophobic mesoporous polymer-based acid catalyst (P- SO_3H), which outperform than Amberlyst-15 and SBA-15- SO_3H [367]. Cai et al. synthesized an

environmentally friendly carbon solid catalyst (CCS) by using cellulose as the starting material, which exhibited good results of sorbitol dehydration[368].

In addition to those sulfuric acid modified catalysts, ionic liquid also shows its advantage in isosorbide production[369-371]. Jie Deng et al. reported a Brønsted acidic ionic liquids which shows an 82% yield of isosorbide. They proposed that the Gutmann acceptor number plays a more important role than the acidity[371]. Separation of isosorbide from the reaction product is the main challenge for ionic liquid. To overcome this challenge, Akio Kamimura et al. reported a simple method which uses an organic solvent to remove the ionic liquid[369]. In another study, they achieved a 60% yield of isosorbide by using [TMPA][NTf₂] combining with TsOH[370]. One innovation of their study is that the reaction was conducted in a microwave heating setup, which could be completed in 10 minutes.

Li et al. investigate the sorbitol dehydration using molten salt ZnCl₂ with temperature ranging from 150 to 220°C[372]. They further conducted a separate model study with the help of standard DFT B3LYP/6-31G[313]. The dehydration of sorbitol, as they proposed, started with the complexation of hydroxyl function group to Zn, followed by an internal S_N2 mechanism of a secondary hydroxyl function group attacking a primary hydroxyl function group as the Zn-complex acting as a leaving group.

Instead of using sorbitol as the starting material, several studies demonstrate the feasibility of producing isosorbide directly from cellulose. It was reported that bifunctional catalyst, which consists of heteropoly acid H₄SiW₁₂O₄₀ and Ru/C, could obtain a yield of isosorbide up to 50% from pure microcrystalline

cellulose[373]. In this study, polyacid shows better performance than homogenous acid like HCl. Peng Sun et al. investigated the conversion of cellulose to isosorbide using a bifunctional catalyst which combines Ru and mesoporous niobium phosphate[374]. They also examined the effect of ruthenium particle size on isosorbide yield. As revealed in the study, the mNbPO supports with strong acidity, thermal stability and high surface area plays an important role in the hydrolysis of cellulose. They also found that the size of ruthenium nanoparticle affected the isosorbide yield. In another study, Aritomo Yamaguchi compared supported platinum Amberlyst 70 with supported ruthenium Amberlyst 70 for one-pot conversion of cellulose to isosorbide with the help of ion-exchange resin[375]. Ruthenium catalyst shows a 55% isosorbide yield, which outperforms platinum catalyst by 20%. However, the ruthenium catalyst reveals poor reusability as the isosorbide yield decreased to 10% for the second run. It was suggested that the carbon precipitation on the metal surface during the reaction deactivates the glucose hydrogenation.

In this chapter, we will present our study on the synthesis of isosorbide over a set of sulfonated carbon catalysts. Carbon material such as active carbon, carbon nanotube shows advantages for their high stability, rich surface functional groups and high surface area. To better understand the relation between structure and performance, the catalysts mentioned above have been examined extensively by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), Transmission electron microscopy (TEM), scanning electron microscope (SEM), Brunauer–Emmett–Teller (BET), Elemental analysis (EA), Thermal gravimetric analysis (TGA) and Raman spectroscopy.

Figure 6.2 Proposed schematic structure of sulfonated active carbon catalyst (left) and sulfonated carbon nanotube catalysts (right).

6.2 Dehydration of sorbitol over mineral acid

The sorbitol dehydration reactions were conducted according to a depressurized solvent-free approach. As presented in Figure 6.3, the pressure inside the flask was controlled by a vacuum pump attached at the end of the condenser. The catalyst and stirring flea were added before sorbitol so that after the sorbitol melts the catalyst could be well dispersed within the sorbitol solvent. After the reactions, the flask was cooled down in an ice bath. DI water was added to dissolve the products with ultrasonication for 20 minutes. For reactions using mineral acid, required amount of acids were first mixed with sorbitol in 10 ml of water solution. Then the mixtures were dried in vacuum overnight before used in the reaction.

As described in Table 6.1, mineral acids, especially sulfuric acid, shows high performance for sorbitol dehydration. For example, sulfuric acid of 0.1 mmol presents up to 97.2% conversion of sorbitol dehydration with an isosorbide

yield up to 60.7%. On the contrary, the dehydration results are poorer if we reduce the sulfuric amount or use phosphate acid.

Table 6.1 Dehydration of sorbitol with mineral acids, 500mg sorbitol, 140°C, 2 hours, 0.8bar.

acid	amount(mmol)	conversion(%)	yield(%)		
			1,4-sorbitan	2,5-sorbitan	isorsorbide
H ₂ SO ₄	0.05	62.5	32.1	2.3	12.6
	0.10	97.2	2.3	5.6	60.7
H ₃ PO ₄	0.05	52.3	28.6	1.3	11.5
	0.10	89.2	41.6	5.2	19.3

Figure 6.3 Reaction set up for isosorbide synthesis from sorbitol

6.3 Characterization of sulfonated carbon catalyst

After comparing those mineral acids, sulfuric acid stands out for its high performance and stability. To overcome the drawback of mineral acids, it is crucial that the sulfonate group can be immobilized into solid support. Inspired by J.-S. Chang, the sulfonated carbon catalyst (AC-18, AC-622 and CNT) was prepared by sulfonation method using chlorosulfuric acid in chloroform[254]. In

detail, the 500 mg of fresh carbon material (AC-18, AC-622 and CNT) were sonicated in 25 ml of chloroform for 0.5 hours to ensure the even dispersion. Then 5 ml of chlorosulfuric acid was dropped into the chloroform mixture which was bathed in ice. Then the mixture was heated at 70°C for 4 hours with a cold-water condenser. After 4 hours, the suspension was cooled to room temperature and diluted with 75 ml chloroform in an ice bath, which was filtered and washed with excess ethanol and water until the pH of the filtrate becomes neutral. The sample was dried in an oven at 110°C overnight. Characterization methods such as SEM, BET, Raman, XRD, FTIR and acid site titration were conducted to examine the active carbon and carbon nanotube catalyst.

XRD patterns were employed to examine the AC, AC-SO₃, CNT and CNT-SO₃ as displayed in Figure 6.4. The broad XRD peak around 24° of AC and AC-SO₃ is attributed to the existence of amorphous carbon (0 0 2), while the weaker peak (1 0 1) around 43° is caused by the α axis of the graphite structure[74, 376-380]. As shown in the plot, no significant difference of the peak intensity is observed between fresh active carbon and sulfonated active carbon, indicating that chlorosulfuric acid treatment introduces negligible structure change. In contrary, significant XRD peak intensity decrease is observed for CNT and CNT-SO₃. The XRD peaks at 26.3° and 43.0° are attributed to the (0 0 2) and (1 0 0) crystalline facets of CNT[381]. The (0 0 2) peak which resembles the graphite-like peak, is usually used to determine the purity of CNT[382-386]. As the intensity of peak (0 0 2) of CNT dramatically decreases after the sulfonation treatment. It is considered that the chlorosulfuric acid treatment may destroy parts of crystalline CNT and turn those crystalline carbon to amorphous ones.

Figure 6.4 XRD patterns of carbon catalyst before and after sulfonation.

As shown in Figure 6.5, the overall morphology change of AC cannot be identified from the SEM images, since there is no specific morphology for the material before and after the chlorosulfuric acid treatment. It seems that the surface of active carbon after the acid treatment becomes smoother than the one without acid treatment. However, dramatic morphology change is observed for carbon nanotube after chlorosulfuric treatment. As can be seen in Figure 6.6 of carbon nanotube before and after the chlorosulfuric treatment, many the carbon tubes collapse and stack with each other compared with the fresh carbon nanotube. The change of carbon nanotube's morphology can be attributed to the acid treatment. As the carbon nanotube was heated with very strong acid, it was possible that the weak carbon tubes were destroyed and rearranged into amorphous carbon.

Figure 6.5 SEM images of AC-18 before (left) and after (right) chlorosulfuric acid treatment.

Figure 6.6 SEM image of CNT before (left) and after (right) chlorosulfuric acid treatment.

Figure 6.7 HRTEM of AC-18-SO₃ (top left), AC-622-SO₃ (top right) and CNT-SO₃ (Bottom).

Raman spectroscopy of the two fresh active carbons (AC-18 and AC-622) and sulfonated active carbon (AC-18-SO₃ and AC-622-SO₃) were conducted with an excitation λ of 633 nm. As shown in Figure 6.8, The D band situated at 1322 cm⁻¹ is attributed to amorphous carbon, while the G band centered at 1599 cm⁻¹ is considered as the graphite-oriented carbon[351]. The ratio of the intensity of the two peaks I(D)/I(G) roughly indicates the degree of structural disorder of the carbon material. The ratio of peak intensity of D band to G band of the fresh AC-18, sulfonated AC-18-SO₃, fresh AC-622 and the sulfonated AC-18-SO₃ are 2.06, 1.92, 1.96 and 1.99 respectively. The results of Raman spectrum of the active carbon catalysts indicate that there is no significant change in the catalysts' crystallinity and carbon composition before and after the acid treatment.

Table 6.2 Raman band position and peak ratio of carbon catalyst.

carbon catalyst	D band (cm^{-1})	G band (cm^{-1})	D' band (cm^{-1})	I(D)/I(G)
AC-18	1322	1599	N.A.	2.06
AC-18-SO ₃	1322	1599	N.A.	1.92
AC-622	1322	1599	N.A.	1.96
AC-622-SO ₃	1322	1599	N.A.	1.99
CNT	1331	1594	2658	1.4
CNT-SO ₃	1331	1594	2658	1.9

Raman spectrum of CNT and sulfonated CNT are shown in Figure 6.9. Amorphous carbon-oriented D-band is situated at 1331 cm^{-1} and the second-order harmonic D'-band is centered at 2658 cm^{-1} due to the impurity, lattice distortion and the structural defect[387]. The ratio of the peaks was found increased after the sulfonation treatment. The larger ratio of D to G band indicates the decline of purity of CNT, which is consistent with the observation in SEM image and XRD patterns.

Figure 6.8 Raman spectra of AC-18, AC-18-SO₃, AC-622 and AC-622-SO₃.

Figure 6.9 Raman spectra of CNT and CNT-SO₃.

FTIR was conducted to evaluate the surface functional group of CNT and CNT-SO₃. In Figure 6.10, OH stretching centered at 3427 cm⁻¹, CH₂ band at 2926 cm⁻¹ and 2855 cm⁻¹ are all observed in the two carbon catalyst[388]. The peak at 1638 cm⁻¹ is attributed to the aromatic C=C and the peak at 1112 cm⁻¹ is caused by the C-O stretching[389] of the carboxylic acid; and ketones and hydroxyl group are both presented for CNT and CNT-SO₃. On top of that, the peak caused by the sulfonic acid group of the CNT-SO₃ is also identified in the FTIR. The peaks at 592 cm⁻¹ and 1345 cm⁻¹, which correspond to the C-S and C-SO₃ bond, and the peak at 672 cm⁻¹ associated to S=O stretching[390] are identified in the

FTIR patterns of sulfonated CNT as shown in Figure 6.10.

Figure 6.10 FITR spectra of CNT and CNT-SO₃.

The SEM and Raman results are not sufficient to represent the effect of chlorosulfuric acid treatment, especially for active carbon catalysts. BET was conducted to characterize the textual properties of the three carbon catalysts before and after sulfonation. The results in Table 6.3 reveal that chlorosulfuric acid treatment greatly changes the textural properties of the catalysts. The BET surfaces of AC-18, AC-622 and CNT after sulfonation dramatically reduce to 497 m²/g, 583 m²/g and 49.5 m²/g respectively, when compared to the fresh ones. Pore volume and pore size of those sulfonated carbon catalyst are also observed decreasing to a certain degree.

The acid density and acid strength of carbon catalyst are the key factors in their dehydration reaction performance[391]. The SO₃H amount and acid density of the active carbon and carbon nanotube before and after sulfonation are

determined by an acid-base back titration method[391]. In specific, 30 mg of carbon catalyst was first added into 20 ml 0.1 M NaOH aqueous solution, which was then stirred for 4 hours and followed by ultrasonication for 1 hour at room temperature. The remaining OH⁻ ions in the solution after filtration was titrated by (COOH)₂ standard solution. Finally, the total acid density of the carbon catalyst was calculated by the formula below:

$$acid\ density = \frac{c_0 v_0 - 2c_1 v_1}{m}$$

where c_0 represents the original concentration of NaOH, v_0 represents the original volume of NaOH, c_1 and v_1 represents the concentration and volume used in titration.

To determine the amount of SO₃H, 30 mg of the carbon catalyst was added into 0.2M NaCl aqueous solution. The mixture was then stirred overnight and followed by ultrasonication for 1 hour at room temperature. The acid concentration of the supernatant after filtration was then titration using 0.1 M NaOH solution. Finally, SO₃H amount of the carbon catalyst was calculated by the formula below:

$$HSO_3\ amount = \frac{c_2 v_2}{m}$$

Where c_2 represents the concentration of NaOH, v_2 represents volume of NaOH used in titration.

As described in Table 6.3, the total acid density of the carbon catalyst hardly changes before and after the sulfonation treatment. However, the SO₃H amount increases significantly for those sulfonated carbon catalysts. For example, the SO₃H of AC-18-SO₃ increases to 0.47 mmol/g compared to fresh AC-18 of

0.00017 mmol/g. It is worthy to mention that the CNT-SO₃ contains a much higher amount of SO₃H (1.75 mmol/g) when compared to AC-18-SO₃ and AC-622-SO₃.

Table 6.3 Textural properties and acidity of carbon catalyst before and after sulfonation.

Catalyst	BET surface (m ² /g)	Pore Volumn (cm ³ /g)	Pore size (nm)	SO ₃ H amount (mmol/g)	Acid density (mmol/g)
AC-18	740	0.47	5.3	0.00017	9.64
AC-18-SO ₃	497	0.38	2.9	0.47	10.22
AC-622	814	0.49	6.2	0.00020	9.64
AC-622-SO ₃	583	0.36	5.1	0.48	8.45
CNT	173	0.42	16.2	0.00040	9.05
CNT-SO ₃	49.5	0.34	15.2	1.75	8.45

The results suggest that chlorosulfuric acid as one of the strongest acids have considerably changed the textural properties of carbon catalyst. Even though the percentage of disorder carbon to graphite carbon of active carbon hardly change, a lot of internal pore channels may have either collapsed or blocked by amorphous carbon, considering the decrease of their BET surface, pore volume and pore size. The morphology change of CNT is even more dramatically. The increase of impurity of CNT is observed by SEM and TEM image as few fine nanotubes are left and more amorphous carbon merged. It is believed that during the sulfonation process, the carbon tubes, which are not strongly bound, are arranged into amorphous carbon or burnt away. As a result, the ratio of disorder carbon increases, whereas BET surface decreases.

Figure 6.11 N₂ adsorption isotherms of the AC-18-SO₃, AC-622-SO₃, and CNT-SO₃.

Elemental Analysis was applied to examine the chemical composition of the carbon catalyst before and after the sulfonation. Table 6.4 describes the weight percentage of carbon decreases after the chlorosulfuric acid treatment. The carbon content of AC-18 decreases from 76.93% to 70.88%, and more significant descending of carbon weight percentage is observed for CNT from 93.78% down to 58.85%. On the contrary, the weight percentage of oxygen and sulfur increases after the chlorosulfuric acid treatment. The sulfur weight percentage of AC-18 increases from 0.352 to 1.892 after the catalyst sulfonation. It is worth noting that the sulfur weight percentage of CNT increases incredibly from 0.008% to 7.118%. The EA results confirm the successful crafting of sulfur content onto the carbon catalyst, which is further validated by EDAX results as shown in Figure 6.12, 6.13 and 6.14.

Table 6.4 Elemental analysis of carbon catalyst before and after sulfonation.

catalyst	weight percentage (%)				
	C	H	S	N	O ¹
AC-18	76.93	0.760	0.352	0.319	21.639
AC-18-SO ₃	70.88	0.634	1.892	0.350	26.244
AC-622	79.17	0.810	0.135	0.147	19.738
AC-622-SO ₃	74.89	0.847	1.456	0.151	22.656
CNT	93.78	0.060	0.008	0.015	6.137
CNT-SO ₃	58.85	2.070	7.118	0.048	31.914

1: the oxygen content was calculated by balancing other elements.

Figure 6.12 EDAX images of AC-18-SO₃ (red: C, green: O and blue: S).

Figure 6.13 EDAX images of AC-622-SO₃ (red: C, green: O and blue: S).

Figure 6.14 EDAX images of CNT-SO₃ (red: C, green: O and blue: S).

Lastly, thermogravimetric analysis (TGA) was applied to study the thermal stability of the carbon catalyst before and after sulfonation as captured in Figure 6.15 and Figure 6.16. The temperature was raised from 30 °C to 950 °C, at 10 °C/minute. The first step of the mass change around 100 °C is attributed to the loss of physically absorbed water. As shown in both plots, the first step mass change is higher for sulfonated catalysts than the fresh ones. The mass change of AC-18 at 100 °C is 4.6%, while it is 8.5% for AC-18-SO₃. It is believed that the sulfonation had introduced a lot ketone, carboxylic acid and hydroxyl group onto the catalyst surface. As a result, the surface polarity and wettability of the carbon materials increases, hence the increase of water they absorbed. It is also found that the sulfonated catalysts undergo a second step of mass change onset at 185°C compared to the fresh one. The second step mass change of AC-18-SO₃ is 6.4%, while it is 21.0% for CNT-SO₃. The mass changes at 185 °C is considered as the loss of sulfonation group in the form of SO₂ and parts of carbon in the form of CO₂ at elevated temperature. The mass changes are consistent with the sulfur weight percentage determined by EA (the weight loss due to SO₂ will be twice of the weight of the sulfur determined by EA, 1.89% for AC-18-SO₃ and 7.12% for CNT-SO₃). After the temperature was raised to 750 °C, all catalysts were observed with a final mass reduction to almost zero due to the burning of carbon at extremely high temperature. In a word, the TGA results suggest the successful craft of sulfur onto the carbon catalyst and prove its thermostability for temperature as high as 185 °C.

Figure 6.15 TGA analysis of AC-18 and AC-18-SO₃.

Figure 6.16 TGA analysis of CNT and CNT-SO₃.

6.4 Dehydration of sorbitol over sulfonated carbon catalyst

6.4.1 Effect of sulfonation treatment

All the carbon catalysts with and without sulfonation were tested in the sorbitol dehydration reaction at the same conditions. In specific, 500 mg of sorbitol was mixed with 40 mg of catalyst and heated under 140 °C for 2 hours under vacuum pump depressurized for 0.8 bar. After cooling down with an ice bath, 50 ml of DI water was added in to dissolve the products and filtered before tested using HPLC. The catalysts' dehydration performance is listed in Table 6.5. It is found that all sulfonation catalyst (AC-18-SO₃, AC-622-SO₃ and CNT-SO₃) show superior catalytic performance over its counterpart. Conversion of sorbitol increases from single digit to 82.1%, 79.2% and 95.2% for sulfonated AC-18, AC-622 and CNT, respectively. For sulfonated AC-18 and AC-622, the reaction intermediate 1,4-sorbitan are observed at relatively high amount (18.4% and 17.2%), which indicates the incompleteness of the two-step dehydration of sorbitol due to the low acidity. The results also indicate the conversion and yield of isosorbide are correlated with the HSO₃ amount of the carbon catalysts. CNT-SO₃ which presents the highest HSO₃ amount shows the best conversion and isosorbide yield.

Table 6.5 Sorbitol dehydration with different carbon catalyst (500 mg sorbitol, 40 mg CNT-SO₃, 140°C, 2 hours, 0.8 bar).

catalyst	HSO ₃ amount (mmol/g)	conversion (%)	yield(%)		
			1,4-sorbitan	2,5-sorbitan	isosorbide
AC-18	0.00017	2.1	0.5	0.4	0.1
AC-18-SO ₃	0.47	82.1	18.4	9.2	38.1
AC-622	0.0002	5.3	0.7	0.5	0.1
AC-622-SO ₃	0.48	79.2	17.2	7.8	36.5
CNT	0.0004	7.1	0.8	0.5	0.2
CNT-SO ₃	1.75	95.2	8.5	9.2	62.4

6.4.2 Effect of temperature

The effect of temperature on sorbitol dehydration is shown in Figure 6.17. It is found that conversion of sorbitol is highly dependent on temperature. Conversion of sorbitol is only 46% under 120°C, which gradually increases to 95% at 140°C. The yield of 1,4-sorbitan reaches its maximum of 38% at 130°C, which indicates insufficient dehydration of sorbitol dominated the reaction. Further increasing temperature, the decrease of 1,4-sorbitan yield to 8% and an increase of isosorbide yield to 62.4% are observed, which suggests that the 1,4-sorbitan as the dehydration reaction intermediate is replaced by isosorbide. Reaction conducted under higher temperature than 140°C shows less isosorbide yield, which indicates that isosorbide may be further consumed for side reactions.

Figure 6.17 Effect of temperature on sorbitol dehydration (500 mg sorbitol, 40 mg CNT-SO₃, 2h, 0.8 bar).

6.4.3 Effect of reaction time

The effect of reaction time on sorbitol dehydration is explored from 30 minutes to 150 minutes. As shown in Figure 6.18, conversion of sorbitol increases gradually from 50.1% to 96.2% as reaction time extends from 30 minutes to 150 minutes. Within the first 60 minutes, the main product is 1,4-sorbitan, whose yield reaches up to 38.1%. From 60 minutes on, the yield of 1,4-sorbitan starts to decrease and is overtaken by isosorbide, which reaches its maximum yield of 62.4% at 120 minutes. Further extending reaction time from 120 minutes to 150 minutes, the decline of isosorbide yield is observed as more unknown product appeared.

Figure 6.18 Effect of reaction time on sorbitol dehydration (140 °C, 500 mg sorbitol, 40 mg CNT-SO₃, 0.8 bar).

6.4.4 Effect of catalyst amount

The effect of catalyst amount on sorbitol dehydration is presented in Figure 6.19. Nearly no conversion of sorbitol is observed for blank reaction, which suggests sorbitol's stability under high temperature. As catalyst amount increases, conversion increases in the same way. Increasing the catalyst amount from 20 mg to 40 mg, the yield of the isosorbide increases to the maximum of 62.4% with a conversion rate of 95%. The results indicate the importance of the amount of the catalyst for sorbitol dehydration. When less catalyst is fed in the reaction, the two-step dehydration of sorbitol can only go as far as the first step since not enough sulfonation acid is provided. When the catalyst amount reaches 40 mg, the second step dehydration of the 1,4-sorbitan overtakes the first step dehydration and yield of isosorbide increases.

Figure 6.19 Effect of catalyst amount on sorbitol dehydration (500 mg sorbitol, CNT-SO₃, 140°C, 2h, 0.8 bar).

6.4.5 Recyclability of the catalyst

The catalyst after the first run was filtered and repeatedly washed with 95% ethanol and DI water. The recovered catalyst after dried in oven at 110°C overnight was then used in a second run to examine its recyclability. The same procedure was repeated until the fifth run of the same catalyst. As shown in Figure 6.20, the sulfonated carbon nanotube reveals excellent stability for the synthesis of isosorbide from sorbitol. Up to 90% conversion of sorbitol and 60% yield of isosorbide are maintained during all five runs. As indicated by the TGA graph, sulfonated carbon nanotube shows high thermal stability. Decomposition of HSO₃ group from CNT is only observed at a temperature higher than 185°C.

Figure 6.20 Recyclability of CNT-SO₃ in sorbitol dehydration reaction for 5 runs.

6.5 Summary

In this chapter, we have examined the synthesis of isosorbide from sorbitol dehydration over sulfonated carbon catalyst AC-18-SO₃, AC-622-SO₃ and CNT-SO₃. The acidity strength of the catalysts was crucial in the carbon catalysts' dehydration performance. As an effective surface modification method to increase catalysts' acidity, sulfonation of the carbon catalysts was realized by crafting of sulfonic acid groups onto the catalysts using one of the strongest acids chlorosulfuric acids. All the carbon catalysts were fully examined by various characterization methods. XRD and Raman results of the catalysts before and after sulfonation indicated the sulfonation treatment turned a part of the crystalline carbon into amorphous carbon, especially for carbon nanotubes, which was also confirmed by SEM and HRTEM images. The morphology and structure change of the carbon catalysts induced by sulfonation was also evaluated through BET, by which it was found that the surface area of the carbon catalyst had all decrease. The active sites of sulfuric groups were also confirmed by FTIR, as the peak of S=O, S-C bonds were identified. The successful addition of sulfur was proved directly by elemental analysis and EDAX images. The total acidity and amount of HSO₃ were quantified using titration methods. It was found that the total acidity of the carbon catalyst hardly changes before and after the sulfonation treatment, while the amount of HSO₃, as a strong acid indicator, increased significantly. CNT-SO₃, AC-18-SO₃ and AC-622-SO₃, which possess a larger amount of HSO₃ than their counterparts, all show superior sorbitol dehydration performance. Therefore, it is the strong acid of the HSO₃ that catalyzes the dehydration of sorbitol to isosorbide. TGA results confirmed the

thermal stability of the sulfonated carbon catalyst. The effect of reaction temperature, reaction time and catalyst amount were evaluated for CNT-SO₃. Under the optimized reaction condition (140°C, 40 mg CNT, 2 hours), isosorbide yield up to 60% could be achieved with nearly 100% conversion of sorbitol with satisfying recyclability up to 5 runs.

Chapter 7 Conclusions and Future Perspectives

7.1 Conclusions

In this Ph.D. work, we have examined biomass conversion and upgrading over carbon catalyst as an effort to promote green energy and green chemistry production. Cellulose, which represents the most abundant biomass resource, has been examined over noble metal supported carbon catalyst as an example of biomass conversion. Sorbitol, which is the main product of cellulose hydrogenation, has been analyzed over sulfonated carbon catalyst as an example of biomass upgrading. Physical and chemical properties of the catalysts have been evaluated by advanced and extensive characterization technique. Optimization of the catalysts and effect of different factors have been studied by trial and error method as well as multivariate analysis method.

The highlight of novelty in this work can be summarize by three points: we firstly propose an effective method for performance enhancing of the JM catalyst and explain the enhancement mechanism by comparing the oxidative and reductive ability of catalyst after such optimization by the help of CV scan; we are also one of the very few who have studied and compared the effect of reaction parameters using multivariate analysis method; we also introduce the sulfonated catalyst preparation method using chlorosulfuric acid for the sorbitol dehydration and identify the important role of strong acid in such reaction.

Platinum supported on active carbon catalyst supplied by our sponsor Johnson Matthey has been thoroughly investigated for hydrogenation of crystalline and milled cellulose. Milled cellulose performs better than crystalline cellulose as more amorphous cellulose was observed by XRD in milled cellulose

than those in crystalline cellulose. Effect of reaction parameters such as reaction temperature, hydrogen pressure, catalyst amount and Pt loading have been examined by the trial-and-error method. Even though cellulose hydrogenation is considered as a two-step reaction, the actual mechanism is much more complicated as many side reactions such as oxidation, isomerization, dehydration and hydrogenolysis are competing with the hydrogenation reaction. As a result, tuning reaction conditions to minimize the side reactions is crucial for achieving high sorbitol yield. The maximum yield achieved for Pt/AC from JM is limited to 25%. To overcome the low yield of JM catalyst, we discovered a simple catalyst optimization method, which helps to increase the sorbitol yield from about 25% to almost 50%. The optimization of platinum catalyst was realized by further reducing the catalyst in ethylene glycol under pressurized hydrogen at elevated temperature. Characterization results from XRD and TEM revealed that the particle size of platinum particle increased. CV scan of the Pt/AC before and after EG reduction indicated that the decline of platinum's oxidation and reduction activity, which suppresses the side reactions during cellulose hydrogenation might be the reason for the improvement of the sorbitol yield.

Finishing the study of Pt/AC from JM, we find the trial and error method shows disadvantage in explaining how reaction factors affect the hydrogenation reaction collectively. A thorough examination of different parameters are time consuming and resource intensive. To better understand the relationship between reaction performance and reaction factors, we have adopted a multivariate analysis method to evaluate cellulose hydrogenation over ruthenium catalyst. Ru/AC with different loading were prepared and used in a DOE (design of

experiment) according to the central composite design (CCD). The experiment number required is greatly reduced from 81 for a full factorial design to 26 for the CCD design. Those 26 reactions are good enough to capture how temperature, catalyst amount, hydrogen pressure and Ru loading play independently and collectively on the cellulose hydrogenation. We also evaluated the effectiveness of each factor quantitatively, among which the loading of ruthenium has the greatest influence. The highest sorbitol yield now can be achieved at 71% when optimized reaction conditions are selected. A handy prediction formula was also generated to determine the sorbitol yield of certain reaction setups without the spent of actual reaction resource.

Conversion of cellulose to sorbitol is only the halfway towards fully utilization of cellulose, the most abundant biomass. Integration of sorbitol into various industries is believed as the key to realize the goal of green energy and green chemistry. Sorbitol, as the main product of cellulose hydrogenation and a versatile platform chemical, has been studied to produce value-added chemicals. In this PhD work, we have synthesized isosorbide via sorbitol dehydration over sulfonated carbon catalyst as an example of biomass upgrading. The sulfonated carbon catalysts were prepared through acid treatment by chlorosulfonic acid. The as-synthesized carbon catalysts show advantages of superior reaction performance, easy separation, and good recyclability. The physical and chemical properties of the carbon catalysts were fully examined by XRD, TEM, SEM, BET, FTIR, EA, EDAX, TGA and Raman spectroscopy. The successful introduction of sulfonated group in carbon catalyst is identified as the main driving force for sorbitol dehydration. Catalytic performance of sulfonated catalysts has been

optimized through the studies of the effect of reaction temperature, reaction time and catalyst amount. The yield of isosorbide reached up to 60% with full conversion of sorbitol, with small activity loss after five runs.

7.2 Future Perspectives

Based on the discoveries of this PhD study, several topics are worthy of further investigation. In Chapter 4, we have found that the size of platinum particle showed a great effect on sorbitol selectivity, and we proposed the selectivity be attributed to the oxidation and reduction activity change caused by size effect. However, the mechanism behind is still open to discuss. For example, DFT (density function theory) calculation can be applied to study the oxidation and reduction ability of platinum particles and the apparent activation energy of side reactions and hydrogenation reaction. With those theoretical calculation results, the effect of particle size on cellulose hydrogenation will be elucidated more clearly. Inspired by the size effect, we think it is also worth studying the shape effect or facet effect of platinum nanoparticle to have a better understanding of the reaction and improve the reaction performance. In Chapter 5, we have examined the hydrogenation of cellulose over ruthenium catalyst using multivariate method. Our preliminary attempts showed that Ru/AC with 5% or higher loading could effectively produce methane from cellulose, or real biomass feedstock like tree leaves, grass and corncob with yield up to 80%. In light of the promising results, further work on this topic may help to realize the goal of producing energy from real biomass. In Chapter 6, we have presented the synthesis of isosorbide from sorbitol over sulfonated carbon catalyst. As a versatile platform chemical, sorbitol can also go through hydrogenolysis reaction

to produce smaller polyols such glycerol, ethylene glycol or propanediol. However, currently sorbitol hydrogenolysis was hindered due to the structural stability of sorbitol and design of proper catalyst. We suggest that further work on this area should integrate sorbitol into the mainstream chemical industry for the production of smaller polyols in a green way.

Besides, we expect more discussion over the net value of cellulose conversion and upgrading according to current results. In another word, to examine the profit of produced sorbitol and isosorbide compared to the cost of the resource spent during these processes under a bigger framework which takes into the consideration of the cost of equipment, pressurized hydrogen, and electric power spent for heating and separation. Most importantly, we are looking forward to the study that identifies and compares cost of different sections, which helps to decide where to spend our precious research resources.

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Appendix

Journal Publications

[1] Chen Xiaoping, Yang Yanhui, Lee Jong-Min, Multivariate analysis of the hydrogenolysis of cellulose over noble metal catalyst (in preparation).

[2] Chen Xiaoping, Yang Yanhui, Lee Jong-Min, Efficient dehydration of sorbitol to isosorbide over sulfonated carbon acid catalysts (in preparation).

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