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REVIEW

Recent Advances in Catalytic Conversion of Cellulose Into Variable Chemicals and Bio-Fuels

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Cellulose is expected to be a potential raw material for producing fuels and chemicals. In this review, we summarized the recent advances in catalytic conversion of cellulose into variable chemicals and bio-fuels by different types of catalysts, such as mineral acids, solid acids, transition metals, enzymes, functionalized ionic liquids (ILs), and metal halides. The catalysis reactions mainly involve with the hydrolysis, hydrogenation and hydrogenolysis of cellulose. Acids and enzymes can be used to promote the hydrolysis of cellulose into oligomers and glucose, while metal catalysts conduct hydrogenation and hydrogenolysis of initial products. In addition, pretreatment approaches and reaction media also play important roles for efficient conversion of cellulose.

Keywords: Catalytic Conversion, Cellulose, Hydrolysis, Hydrogenation, Hydrogenolysis, Pretreatments.

CONTENTS

1. INTRODUCTION

The consumption of large amounts of oil resources is not viable from the perspective of sustainable development and thus represents a challenge for developing new energy. Biomass formed by photosynthesis includes various plant components, such as lignin, starch, and cellulose. Starch, soluble in water, forms by polymerization of D-glucose with the generation of α-1,4-glycosidic bonds. Although much attention has been focused on the conversion of starch into fuels and chemicals to decrease the consumption of fossil energy, starch should preferentially meet the demand of human for food. On the contrary, cellulose, as a main component of lignocellulosic biomass (including cellulose, xylan, and lignin),[1, 2] is composed of β-1,4-glycosidic bonds of D-glucose, and not suitable for the food source of human due to its undigestible property for human body.[3] Cellulose takes up approximately 40% of annual net yield of photosynthesis, which totals up to 1.8 trillion tons.[4] This indicates that cellulose belongs to abundant renewable resource. The efficient utilization of biomass, such as its green conversion into fuels and chemicals, holds promising in reducing greenhouse gas emissions due to its gradual substitute for fossil energy and decreasing amount of CO_2 released from unreasonable treatment of many biomass feedstocks such as plants, crop straws, timber waste, and so forth.[5–8]

Cellulose is self-assembled through the linear β-(1,4) linked D-glucose polymers chains, and consisted of amorphous and crystalline region, respectively. Crystalline portion usually has a high weight percentage in biomass materials, such as forest biomass and agricultural biomass.[9] The repeating unit of cellulose molecule is uniform, and molecular surface is relatively flat, making it easy to stretch to the elongation direction. Besides,

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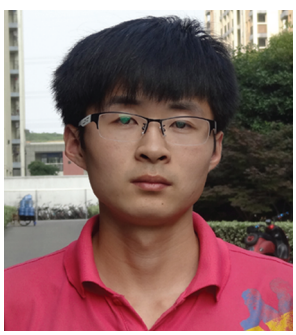
coupled with several hydroxyl groups from glucopyranose ring, it is very conducive to the formation of inter- and intra-molecular hydrogen bonds, so that the molecular chain can easily be gathered into a bundle to form a crystalline fibril structure, also known as the supra-molecular structure. Supra-molecular structure of cellulose consists of crystalline and amorphous region. The arrangement of the chain molecules in cellulose amorphous region is poor and relaxed, but not altogether in the disorderly state, tending to parallel to the cellulose spindle.

Crystalline cellulose has a different crystal structure, including I_α, I_β, II, III_α, III_β, IV_α, IV_β. Iα and I_β are the natural configuration of cellulose. Cellulose in the cell walls of algae and bacterium mainly contains I_α type, while cellulose in the wood, cotton and other plants is I_β type. Particularly, both native cellulose allomorphs can be converted back into cellulose II by mercerization or regeneration (e.g., from ionic liquids).[10,11] Cellulose II owes an antiparallel arrangement of the strands and some inter-sheet hydrogen bonding, and can be obtained through mercerization or solubilization-regeneration of native cellulose I. Thermodynamically, Cellulose II is more stable than cellulose I. However, cellulose II was reported to be more readily digested than cellulose I.[12,13] It is thought that the van der Waals interaction between hydrogen-bonded sheets in cellulose I is stronger compared to that in cellulose II, which plays a crucial role in resisting the hydrolysis of cellulose.[13] Cellulose III (III_α and III_β) can be obtained from the native cellulose by treatment with liquid ammonia and other amines.[14,15] While IIIα and III_β cellulose are heated to 206 °C in glycerine, the IVα and IV_β cellulose will be generated.

The complex structure of plant cellulose is basically an aggregation of micro-fiber bundles. Because there is no presence of free hydroxyl in the crystalline structures of cellulose molecules, many small molecules such as enzyme molecule and water molecules are hard to invade cellulose internal. Therefore, the degradation for cellulose crystalline part is difficult compared to that of the amorphous part.

In recent years, some approaches have been developed to change the structure of native cellulose for its pretreatment so as to make it more accessible for catalysts to enter the reactive sites. For example, Chundawat et al.[16] found that when cellulose I_β was treated by ammonia, the number of hydrogen bonds in the cellulose (namely cellulose III_1) intrasheet decreased with an increase of that in intersheet increased. This rearrangement of this hydrogen bond network increased the number of solvent-exposed glucan chain hydrogen bonds with water by ~50%, and achieved 60–70% lower maximum surface-bound cellulose capacity. A 5-fold enhancement of saccharification rates (closest to amorphous cellulose) was obtained, which attributed to the "amorphous-like" nature of the cellulose III_1 fibril surface that makes glucan chain extraction easier. Extended hydrogen bond network between the solvent-exposed surface chains and ammonia causes relative shifting of the cellulose layers, leading to the formation of channels orthogonal to the (100) and (−100) fibril surfaces (Fig. 1). These channels allow ammonia molecules to penetrate into the cellulose fibril. The cellulose fibril was solvated and each glucan chain was covalently connected to its periodic image along its main axis in order to mimic an infinitely long chain fibril.[17]



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Guohua Jiang was born in Zhejiang, China, in 1975. He received his Ph.D. degree in 2006 from the Zhejiang University in china. In the year 2006 to 2008, he worked as a post-doctoral researcher at the Nanyang Technological University, Singapore and the University of Michigan, USA. Since 2008 he joined in Zhejiang Sci-Tech University (ZSTU), China. Now, he is the Full Professor in the Department of Materials Engineering at ZSTU. His research focuses on: (1) design and preparation of composite photo-catalytic materials for degradation of cellulose or organic pollutants; (2) synthesis and application of environmental responsive polymers as the drug release or delivery carriers; (3) preparation and industrial application of organosilicon materials.

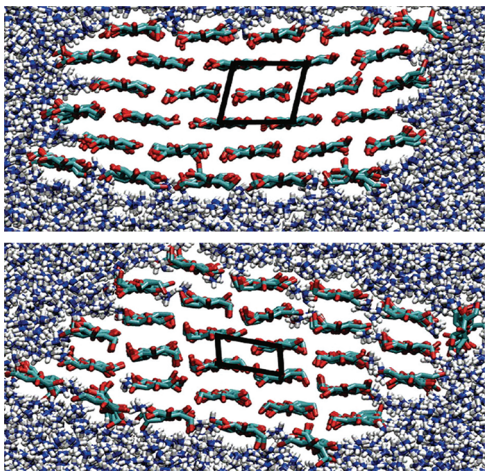

Fig. 1. Top: Starting configuration: Ammonia-solvated cellulose I_β fibril. Bottom: Cellulose fibril compatible with ammonia-cellulose I complex symmetry obtained after 76 ns at $T = 413$ K. Only partial ammonia penetration is observed. The black parallelograms indicate the respective crystal units in the a–b plane.

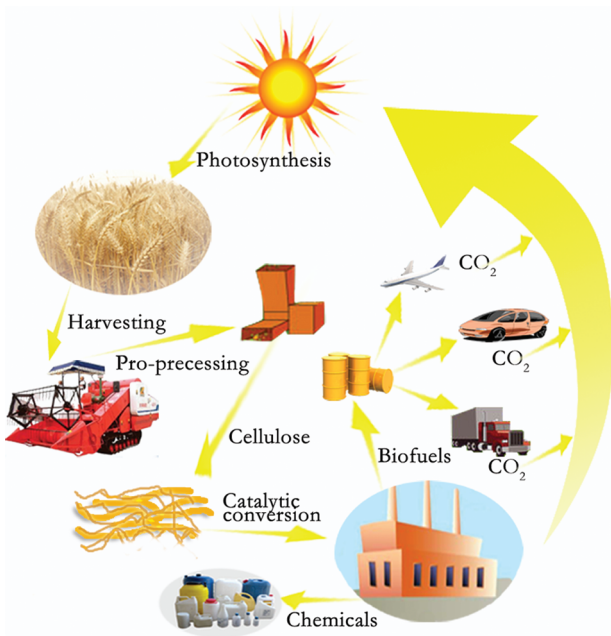

Fig. 2. Bio-refinery concept.

Catalytic hydrolysis of cellulose from vegetation, such as grasses, agricultural, and wood waste, is a significant process for the production of sugars because the total reducing sugars (TRS) can be converted into a series of valuable industrial chemicals, including ethanol, 5-hydroxymethylfurfural (HMF), furfural, levulinic acid (LA), and starting materials for producing polymers.[18] However, the hydrolysis of cellulose is usually required to be performed under drastic reaction conditions because of its high crystallinity and poor accessibility. As a consequence, an efficient and green method is urgently needed to be established for the de-polymerization of cellulose.[19] Presently, biorefinery is being developed based on two strategic goals: Replacing imported petroleum in order to make full use of renewable domestic raw materials (an energy goal) and establishing a powerful bio-based industry (an economic goal). Conversion of cellulose into chemicals is well studied by heterogeneous or homogeneous catalysis under the bio-refinery concept (Fig. 2).

2. PRETREATMENTS OF CELLULOSE

The recalcitrance of cellulose comes from the high crystallinity. Therefore, efficient conversion of cellulose requires an economic and environmentally friendly pretreatment method that uses less energy, operates and green solvents under mild conditions. Recently, Amiri and Karimi[20] expected that high glucose yields could be obtained by enzymatic hydrolysis from the solid residue pretreated with concentrated H_3PO_4 and then with dilute sulfuric acid. However, direct addition of the enzymes to the mixture of the hydrolysate and solid residue would give rise to an inefficient enzymatic hydrolysis, most probably because of the inhibitory effect of the produced glucose and other inhibitors generated during the hydrolytic enzymes actions. Thus, the supernatant is supposed to be separated by decantation, and the residual solid can be used for the hydrolysis. The introduction for some typical pretreatments, such as mechanic milling, microwave heating, and regeneration from ILs or organic solvents, are favorable to establish better pretreatment system in which robust cellulose macromolecule can be significantly improved.

2.1. Milling

Milling processes (i.e., ball milling, two-roll milling, hammer milling, and vibro energy milling) are usually utilized to increase cellulose hydrolysis. The microscopic dimensions and even the degree of polymerization of the cellulose treated by these processes can be decreased, thus making cellulose easier dissolve in the reaction media. Ball milling, one of the most effective milling treatments, has been recognized for its contribution to reducing particle size and crystallinity of cellulose. Although the ball-milling treatment of microcrystalline cellulose (MCC) cannot make it soluble in water, not only would the noncrystalline regions be greatly increased, but the degree of polymerization could be decreased. As presented in Figure 3, for this ball-milling treated MCC, no crystalline peak appears in its X-ray diffraction (XRD) pattern, indicating its complete transformation to amorphous cellulose. Amorphous cellulose is known to have a heterogeneous structure which consists of many chain segments with different lengths. Therefore, during early cellulose hydrolysis in hot compressed water (HCW), reactive components would be selectively consumed, leading to the decrease in specific reactivity (R) of cellulose.[21]

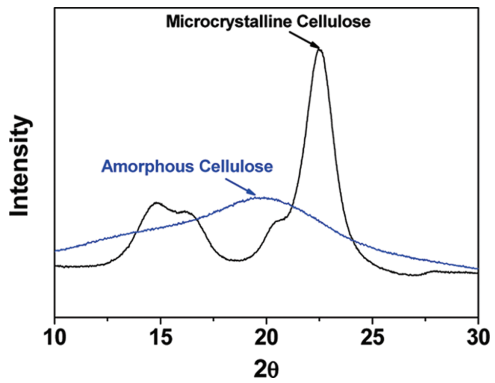

Fig. 3. X-ray diffraction patterns of raw and ball-milled 7-h cellulose samples.

Meine et al.[22] investigated the impregnation of α-cellulose with moderate amounts of strong acid catalyst. The milling of acid-impregnated cellulose showed a complete conversion of the substrate into water-soluble oligosaccharides within 2 h, followed easily hydrolysis in aqueous solution at 130 °C in 1 h. The order of water-soluble products yields by various acid catalysts is HCl > H_2SO_4 > p-toluenesulfonic acid (p-TSA) > CH_3SO_3H > CF_3COOH > oxalic acid > malic acid > terephtalic acid > benzoic acid, consistent with the order of their pK_a. The solid-state reaction requires strong acids because the protonation of cellulose is fundamentally important in solid-state reactions as demonstrated in the depolymerization of cellulose in ionic liquids. This acid-impregnation approach for the mechanically assisted solid-state reaction of cellulose is thought to minimize the contact problem between the substrate and the catalyst commonly encountered in conventional solid-state reactions.[23] Kobayashi et al.[24] achieved a high glucose yield by using simple activated carbons pretreated with oxygenation and subsequent mix-ball-mill with substrate to degrade microcrystalline cellulose at 0.012% HCl concentration in water (Fig. 4). This pretreatment approach created a good physical contact between the solid substrate and solid catalyst, making the catalysts more accessible to the reactive site of cellulose.

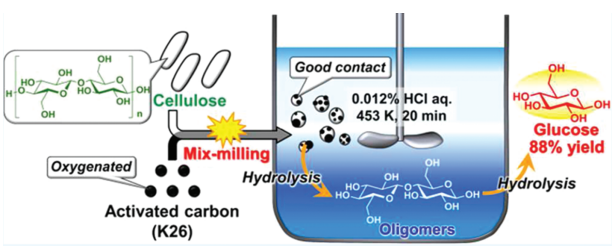

Fig. 4. Mix-ball-mill of oxygenated activated carbons and mcrocrystalline cellulose for subsequent hydrolysis into glucose.

2.2. Microwave

Ha and co-workers,[4] using cellulose from Trichoderma reeseienzymatic and ionic liquid 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]) as a catalyst and solvent, respectively, found that the initial hydrolytic rates of regenerated cotton cellulose IL from after [Bmim][Cl] pretreatment with microwave irradiation were at least 4-fold higher compared to those of regenerated cellulose after [Bmim][Cl] pretreatment with conventional heating only. Zhang et al.[25] investigated the effect of microwave on the hydrolysis of Avicel cellulose (prepared from wood by partial hydrolysis)[26] in ionic liquid 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl) by using H-form zeolites as a solid acid catalyst. The reaction was performed at 100 °C for 8 min with MI of 240 W. The results gave a 36.9% glucose yield, while the reaction system only produced the glucose with a 2.1% yield in the absence of microwave power, exhibiting the high catalytic performance for the hydrolysis of cellulose.

Orozco et al.[27] introduced a microwave heating reactor system for the dilute acid hydrolysis of cellulosic biomass. The result gave high yields of total sugars in short reaction times, suggesting an increase of the reaction rate with the assistance of microwave irradiation. For the hydrolysis of solid-state cellulose in the dilute acids, the Saeman model[28] has been widely used to study the kinetics of cellulose hydrolysis. Saeman used a simple two-step reaction model to adequately describe the hydrolysis of cellulosic wood to sugars.

2.3. Ionic Liquids

A typical pretreatment for cellulose feedstocks is its regeneration from ionic liquid solution by the addition of water, or other precipitating solutions, such as ethanol and acetone. Swatloski[29] thought that the macroscopic morphology of the regenerated cellulose is determined by the contacting of the ionic liquid solution and precipitating liquid. Some cellulosic biomass including monoliths, fibers, and films were applied by forming into an aqueous phase. Rapid mixing of the ionic liquid solution with an aqueous stream results in precipitation of cellulose as a powdery floc. By extrusion of the ionic liquid/cellulose solution into water, thin fibers and rods were prepared. Cheng and co-workers[30] reported that the regenerated cellulose pretreated with ionic liquid 1-Ethyl-3-methylimidazolium acetate ([C_2mim][OAc]) in 70 °C has a gradual transition from cellulose I to II, and this indicates the disruption of the intersheet structure of cellulose, which are more advantageous for cellulose dissolution and for the catalysts to attack.

Treatments with ionic liquids are recently regarded as an emerging pretreatment technology due to their unique properties in dissolving cellulose. Cheng and co-workers[31] investigated the effect of ionic liquid (using 1-ethyl-3-methyl imidazolium acetate ([C_2mim][OAc])) pretreatment

on the MCC (Avicel) crystalline structure. The feedstock treatment was carried out at 120 and 160 °C for 1, 3, 6, and 12 h. The fraction of cellulose chains transforming into cellulose II for 1 and 3 h was found to be greater at 160 °C than that of 120 °C, while the difference obviously become inappreciable after 6 h. This indicated that the initial conversion rate (before 3 h) of Avicel is faster at 160 °C in comparison to that of 120 °C, resulting from more complete conversion to cellulose II after pretreatment.

In 2010, Pereira et al. have demonstrated that biocompatible and biodegradable cholinium alkanoate ([Ch]AlkO) can be used for the dissolution of refined cork, which shows the potential of such media for biomass pretreatment.[32] Based on this, Zhang et al.[33] gave a clear diagram for the application of choline-derived ionic liquids in the decrystallization of microcrystalline cellulose, as presented in Figure 5. The cellulose completely dissolving in the [Ch]OAc/tributylmethylammonium chloride ([TBMA]Cl) (mass ratio 9:1) medium are treated at 110 °C for 5–10 min, and readily regenerated by the addition of ethanol. This caused the selective precipitation of cellulose, followed by the filtration process. Interestingly, the recovered cellulose, like a gel, was confirmed by XRD to have a transformation from a highly ordered crystalline to an amorphous form, indicating the significant decrystallization of MCC.

2.4. CO_2

Supercritical carbon dioxide ($ScCO_2$) has been broadly applied in polymer science such as chemical polymerization and gelation due to its low cost, environmentally benign, non-flammability, and low critical point (low energy demand).[34–36] Especially, for CO_2, its critical pressure and temperature (7.38 MPa and 31.1 °C) is relatively low. Furthermore, by changing the temperature and pressure, the properties of CO_2 at supercritical conditions can be readily adjusted, like the density, the viscosity, and dielectric constant.[37]

The experiments in Zheng et al.[38] suggested that supercritical carbon dioxide is effective for pretreatment of cellulose (Avicel). The increase of pressure makes CO_2 faster penetrate into the crystalline structures, thus more glucose is produced by pretreated cellulose hydrolysis catalyzed by cellulase. After CO_2 pretreatment, due to the destruction of the crystalline structures in cellulose, both the hydrolysis rate of cellulose and the glucose yield can be enhanced. Since this supercritical carbon dioxide treatment is carried out at low temperature, it will not give rise to the decomposition of the sugars obtained as compared to the steam processes involving the high-temperature. Besides, as an alternative approach, this pretreatment technique makes it possible in reducing expenses.

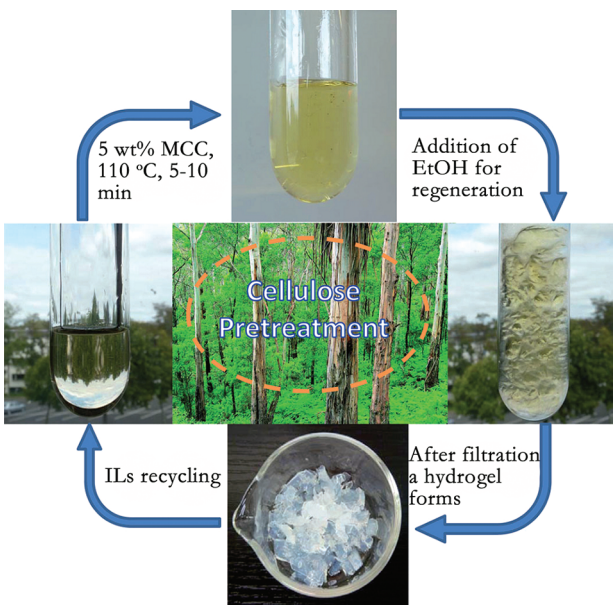

Fig. 5. Graphical representation of the decrystallization process of cellulose in choline-derived ILs.

2.5. Other Pretreatments for Cellulose

Ferreira et al.[39] found cellulose pretreated by high pressure showed smaller and more swollen morphology as compared to non-treated cellulose. Therefore, they give a conclusion that high pressure pre-treatments can enhanced the enzymatic hydrolysis rate due to the increased accessibility of cellulose to cellulose catalytic action (both amorphous and crystalline domains).

3. TYPICAL MEDIA FOR DEGRADATION OF CELLULOSE

3.1. Ionic Liquid

Ionic liquid is an ionic compound which consists entirely of ions. Compared to traditional molecular solvents, ionic liquids show many unique properties such as broad liquids temperature, high thermal stability, and negligible vapor pressure.[4,40] Considering low vapor pressure is advantageous for cellulose dissolution and activation, which is usually performed at high temperature, ILs provides many possibilities for this condition without the requirements of high temperature.[41] ILs have already been broadly applied in cellulose transformations, such as the derivatization of cellulose chains, the depolymerization of cellulose and the production of composite materials based on cellulose.

Since Swatloski et al.[29] reported that ionic liquid [C_4mim]Cl could be used to dissolve cellulose with up to 25 wt% solubility through microwave heating; more attentions have been concentrated on the hydrolysis of cellulose using ILs. For example, Kou et al.[42] reported to catalyze the conversion of cellulose into hexitols by Ru nanocluster dispersed in an ionic liquid [Bmim][Cl]. However, the reaction merely gave a 15% conversion of cellulose. In recent years, some ILs, especially those containing halide, acetate, formate, and phosphate anions, have shown good performance in dissolving cellulosic biomass.[4,43,44] They

can solubilize cellulose through hydrogen-bonding from hydroxyl functions to the solvent anions which are strong hydrogen bond acceptors.[29]

Cellulose can be easily regenerated from ILs solution by adding anti-solvent such as water, alcohol, or acetone.[29] Compared to traditional dissolution processes, the dissolution and regeneration of cellulose from ILs have great advantages because the use of ILs make cellulose pretreatment processes easier to operate, environmental friendly and less energy consuming. Besides, regenerated celluloses from ILs were reported to have amorphous and porous structures, which make it more easily hydrolyze.[45,46] Facing to the situation that ILs dissolving cellulose would inactivate cellulose, for one hand, regenerating of cellulose from ionic liquid is considered promising to alleviate this problem.[45] For another, a considerable challenge is to find the ionic liquids which do not denature cellulose without the remove of ILs in enzymatic hydrolysis procedure.[47] Recently, a 1:4 (v/v) mixture of 1-ethyl-3-methylimidazolium diethylphosphate with water has been reported to be effective in improving hydrolysis yields.[48]

To understand the inactivation mechanism of cellulose resulted by ILs, Engel et al.[49] investigated the cellulose storage stability in ionic liquids at 45 °C. For the cellulose incubated in 10% (v/v) ionic liquids including 1,3-Dimethylimidazolium dimethylphosphate ([Mmim][DMP]), 1-Allyl-3-methylimidazolium chloride ([Amim][Cl]), [Bmim][Cl] and 1-Ethyl-3-methylimidazolium acetate ([Emim][Ac]), after the first day, their activities decreased to 10–40% of the initial enzyme activity and could maintain at this level over 10 days. They attribute the decrease in enzyme activity within the first day to the possible adaptation of the enzymes to the new ionic liquid media. Compared to those ILs, there no significant inactivation over the entire time period when NaAc buffer solution was used to store cellulose.

Jadhav et al.[50] developed a series of 3,6-anhydrocelluloses, based on different degree of substitution (ds = 0.02, 0.07, 0.31 and 0.74), prepared by tosylation of cellulose material in dimethylacetamide and subsequent treatment with sodium hydroxide (Fig. 6), for the hydrolysis in 2 M HCl environment at 60 °C. They found that all 3,6-anhydrocelluloses hydrolyzed faster as compared to cellulose with the fastest hydrolysis rate (90 times of cellulose) of the anhydrocellulose with 0.07 ds, indicating the substantial property of far easier hydrolysis/degradation of anhydrocelluloses. Supposing that less expensive and economical ways for the preparation of the anhydrocelluloses could be found, this approach may provide huge potential for more efficient biomass conversion.

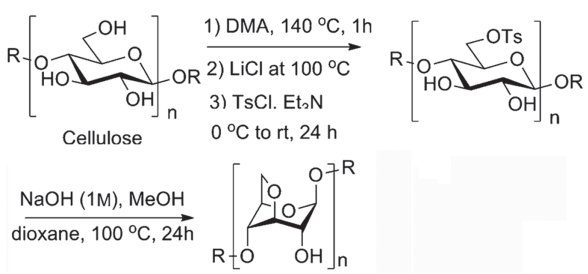

Fig. 6. Preparation of anhydrocelluloses.

[C4mim]Cl is the most common ionic liquid among the amounts of ionic liquids which are usually used as reaction media for cellulose processing and derivatization to produce valuable materials. However, the required times for complete dissolution of cellulose in [C4mim]Cl was reported to be 10 h[51] and is considered to be relatively long for practical large-scale industrial production. Notably, there is a need to investigate toxicity and biodegradation of ILs because environment accumulation of these stable ILs may occur.[52]

Recently, novel cellulose-dissolving ILs with interesting properties has been developed. Cholinium-based carboxylates[53] and pyridinium-based ILs[54] have been used as solvents for biomass pretreatment for saccharication. Ohira et al.[55] recently introduced a new class of biocompatible ILs with amino acid anions for cellulose dissolution. Ammonium-based ILs have been reported to be capable of dissolving biomass and, what is more, revealed good cellulose compatibility.[56] Aqueous tetrabutylphosphonium hydroxide (60% w/w) has been reported to effectively dissolve cellulose under ambient conditions.[57] In order to dissolve cellulose, King et al.[58] recently introduced a new class of ILs composed of acid–base conjugates of the organic superbase 1,1,3,3-tetramethylguanidine (TMG).

3.2. Sub- or Supercritical Water

Polar water molecules, forming an extensive H-bonding network among the molecules, are poor in solvating most organics. Physical properties of water (including viscosity, density, dielectric constant and ionic product) can be adjusted by changing its pressure and/or temperature. When water is heated to subcritical state, the weakening H-bonding allows dissociation of water to release large amounts of acidic hydronium ions (H_3O^+) and basic hydroxide ions (OH), and the ionization constant (Kw) for water would increases about three orders of magnitude higher than that of ambient water.[12] Meanwhile, the decrease of dielectric constant (ε) of water would also promote the solubilization of the organic compounds. As a consequence, subcritical water can be considered to potentially provide an acidic environment for cellulose hydrolysis.[59,60]

Recently, Deguchi and co-workers[61,62] reported that crystalline cellulose transformed to an amorphous state in subcritical water at 330–340 °C under 25 MPa pressure, followed by complete dissolution. Ehara et al.[63] investigated the difference between batch-type and flow-type

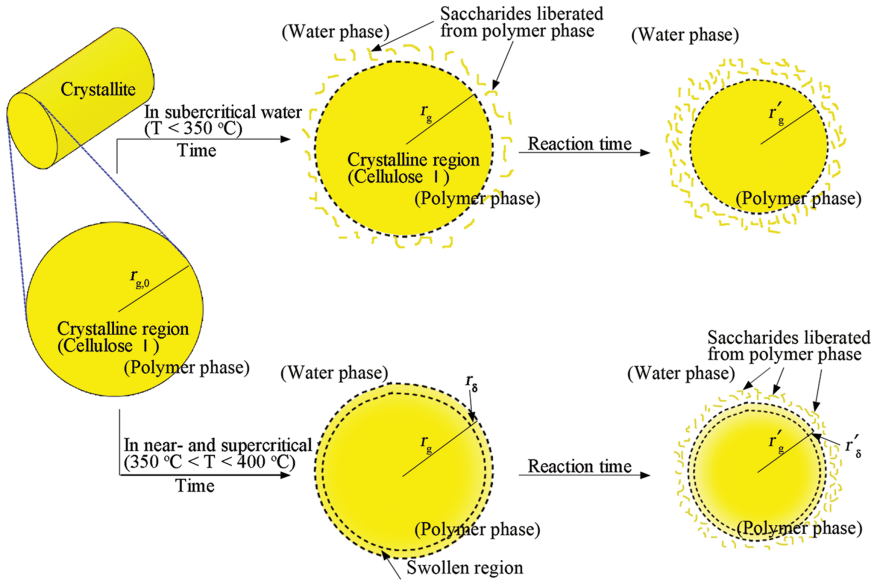

Fig. 7. Estimated reaction mechanism for the conversion of microcrystalline cellulose in subcritical and super-critical water.

systems in supercritical water (>374 °C, >22.1 MPa), and gave a conclusion that flow-type systems mainly hydrolyze cellulose with low occurrence opportunity of pyrolytic reaction, whereas batch-type systems gave higher pyrolyzed products because of the longer treatment time. Owing to the fast degradation of the resulting glucose in supercritical water, a combined approach holds promising in which cellulose in biomass is first dissolved and hydrolyzed in supercritical water to produce oligosaccharides, to which subcritical water is then applied for hydrolysis into fermentable hexoses.[64, 65]

The leading work by Sakaki et al.[66–68] described the hydrolysis of cellulose in a near-critical water system by a batch reactor, and found that the substrate rapidly decomposed to water-soluble compounds with a yield of close to 80%. In their work, the conversion of cellulose to water-soluble saccharides is more effective in supercritical water than in subcritical water. Kumar et al.[65] investigated the microcrystalline cellulose hydrolysis in subcritical and supercritical water in order to maximize the yields of hydrolysis products. Cellulose-water slurry is rapidly heated to the setting temperature, followed by a rapid cooling in a continuous reactor. They found that cellulose partially dissolves in subcritical water at 302 °C with complete dissolution at 330 °C. The reaction gave a cellulose conversion of about 65% into the oligomers and monomers at 335 °C in a residence time of 4.8 s under 27.6 MPa pressure. Ehara et al.[69] introduced a flow-type combined supercritical/subcritical system for cellulose under the conditions of 400 °C under 40 MPa for 0.1 s hydrolysis followed by 280 °C, 40 MPa and 15–45 s. The maximum yield of glucose reached 29.2%, while a single supercritical experiment (400 °C, 40 MPa, 0.1–0.3 s) gave the highest glucose yield of only 10.5%.

Sasaki et al.[70] propose a mechanism concerning MCC degradation in subcritical and super-critical water, as illustrated in Figure 7. In subcritical water, the MCC crystallite hydrolyzes at its surface without swelling or dissolving (Fig. 7 top), thus leading to a slow cellulose degradation rate. By contrast, in near- and supercritical water, the crystallite could swell or dissolve around the surface region to form amorphous-like cellulose (Fig. 7 lower), making it more easily degrade into oligosaccharides.

However, Jollet and co-workers[71] recently reported that the cellulose (Avicel) particles after hydrothermal reaction (cellulose conversion in subcritical and super-critical water) increased in morphology size, most probably due to the agglomerations of the primary cellulose crystals (Fig. 8).

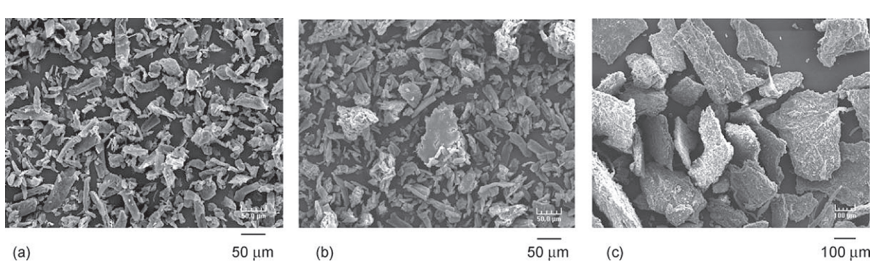

Fig. 8. SEM analysis of cellulose: (a) before reaction, (b) after 24 h of reaction, (c) after 100 h of reaction in water at 190 °C under 5 MPa H_2.

However, detailed mechanisms for the increase of cellulose particle size were not given. Though the crystallinity index of the increased cellulose did not change, the degradation of cellulose would become more difficult.

4. DEGRADATION OF CELLULOSE BY VARIOUS CATALYSTS

Natural cellulose is constituted though parallel arrangement of unbranched long-chain polysaccharide molecules. Large amounts of robust hydrogen bonds are distributed in cellulose, making it difficult to be degraded. As a result, hydrolyzing and destroying the glycosidic bonds plays a significant role in degrading natural cellulose, making it a prerequisite for the catalytic degradation of cellulose. To date, many methods have been developed in order to hydrolyze cellulose. For a long time, high temperature and thermochemical treatment have been used to convert cellulose, which is generally divided into two categories: gasification for producing syngas ($CO + H_2$) mixture in the presence of small amount of oxygen[72] and pyrolysis into oils, tar and char in the absence of oxygen.[73] With regard to these processes, not only is high energy input required, but also their selective formation is relatively low.[7] Meanwhile, mineral acid (i.e., sulfuric acid, hydrochloric acid) or base (i.e., sodium hydroxide) catalyzed hydrolysis for cellulose degradation is also not an ideal green conversion pathway because there exist many drawbacks including uncontrolled successive reactions of the resulting glucose, corrosion hazards, handling of dangerous acids or bases and generation of large amount of neutralization waste. In recent years, some new catalysts have been developed for relatively mild conversion of cellulose including solid acids, transition metal, functionalized ILs, and metal halide.

4.1. Acid Catalyzed Hydrolysis of Cellulose

Figure 9 displays the reaction pathways for the acid catalyzed hydrolysis of cellulose to glucose via the water-soluble intermediate oligosaccharides. It is generally accepted that hydrolysis of cellulose is a significant step in converting cellulose to fuels and chemicals. Furthermore, different types of acids could determine the reaction route to a large extent. In generally, Brønsted acids can facilitate dehydration of monosaccharide while Lewis acidic catalysts function to catalyze monosaccharides retro aldol reaction.[74] Based on the mature theory on carbohydrate, a cheap and efficient catalyst is required to be established so as to achieve a large scale industrial conversion for the degradation of cellulose.

According to the catalyst function and the reaction temperature, the major products vary from glucose to polyols. As shown in Figure 10, when the reaction is controlled

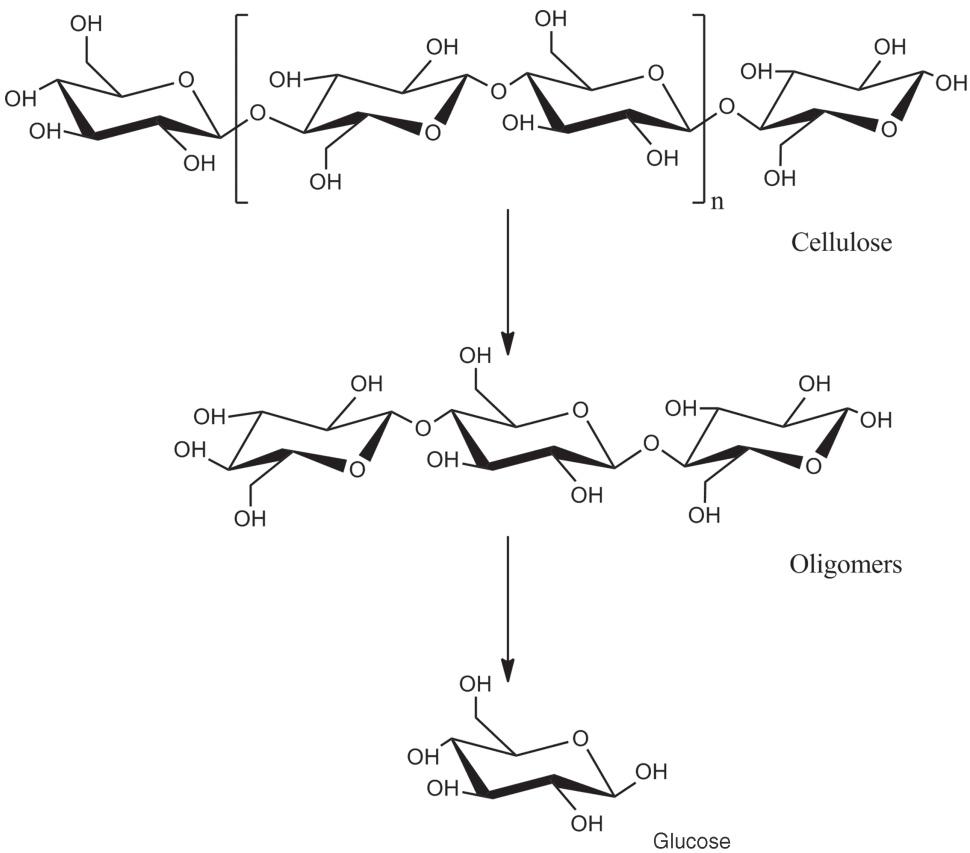

Fig. 9. Hydrolysis of cellulose into glucose.

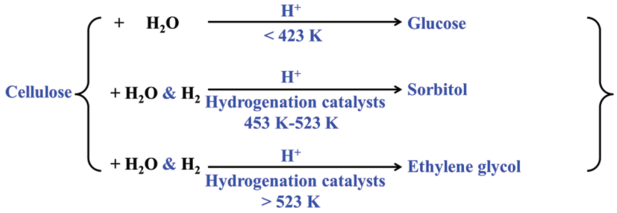

Fig. 10. Conversion of cellulose to different products depending on the catalyst and reaction temperature.

below 423 K, primary product is the glucose from hydrolysis of cellulose in the presence of acid catalyst. Nevertheless, under such conditions, microcrystalline cellulose is poorly accessible and less reactive, which therefore a long reaction time, a high catalyst/cellulose ratio, and effective cellulose pretreatment are inevitable for the reaction. On the other hand, hydrolytic hydrogenation of cellulose requires the involvement of pressurized H_2 and hydrogenation catalysts (e.g., supported Ru, Pt, Ir, etc.), and sorbitol is generally produced as the main product. This cascade reaction converted metastable glucose into stable sorbitol and is therefore allowed to proceed at a relatively high temperature (453–523 K), increasing the reaction rate of cellulose. The metal sites play an important role in the hydrogenation of glucose. The acid sites promoting the hydrolysis of cellulose originate from acidic groups on the support surface or simply from hot water. Beyond 473 K, the H^+ of the liquid water began to show the ability of acid-catalyzed reaction. Furthermore, it was reported that the heterolytic dissociation of H_2 on the metal surface can also produce H^+ with the ability to catalyze hydrolysis of cellulose.[75] When some transition metals, such as W and Ni, are adopted as hydrogenation catalyst, ethylene glycol usually generated as the main product with the assistance of high temperature (beyond 523 K) and H_2.

4.1.1. Mineral Acids

Over past decades, low cost conversion of cellulosic materials to sugars through the hydrolysis process catalyzed by mineral acids, such as diluted or concentrated HCl, H_2SO_4, and H_3PO_4, has been broadly investigated and also employed on an industrial scale. However, some main drawbacks for dilute-acid hydrolysis, including a low yield of cellulose hydrolysis and the difficulty of separation of products from the reaction mixure, have not been properly solved, which is considered as a big obstacle to its commercial use. It is thought that the inefficiency of dilute-acid hydrolysis is due to high crystallinity of cellulose, resulting in difficult diffusion of the acid into high crystalline parts.[76,77] Several processes, such as two-stage hydrolysis and utilization of special reactors (i.e., percolation, shrinking-bed reactors, etc.), have been established to achieve high cellulose hydrolysis.[78,79]

Amiri and co-workers[20] reported that a maximum glucose yield of 43% was obtained from H_3PO_4 pretreated cellulose by hydrolysis under 0.5% sulfuric acid concentration at 180 °C for 30 min (Table I), achieving the highest glucose production compared to other used pretreatments. These authors analyzed that increase of glucose yield from dilute-acid hydrolysis could be greatly affected by swelling capacity of pretreated cellulose. For dilute-acid hydrolysis (180 °C, 0.5% acid, and 30 min) of H_3PO_4 pretreated cellulose, the highest degree of swelling by calculation may lead to the highest glucose yield of 43.0% due to its high accessibility. Therefore, they concluded that the accessibility of pretreated cellulose by acid should be responsible for hydrolysis yield of cellulose. A possible mechanism is the formation of $H_4PO_4^+$ by auto-protolysis process, which interacts with OH-groups in cellulose to form new hydrogen bonds, thus destroying the inter- and intra-molecular hydrogen bonds of cellulose (Fig. 11).[80]

Mingot et al.[81] introduced a novel superacid HF–SbF_5 catalytic system for selective depolymerization of cellulose to water-soluble carbohydrates with glucose as a main product (Fig. 12). After polyprotonation, the mixed catalyst gave a 68 wt% yield of glucose at low temperature, thus avoiding the formation of side products. Moreover, HF–SbF_5 superacid revealed the ability to quasi instantaneously deconstruct cellulose because neither decreased hydrolysis time from 10 min to only 1 min nor greatly decreased treatment time (less than 1 min) of cellulose with SbF_5 gave similar yields of glucose. In regard to catalytic mechanism, they thought cellulose is first decrystallized by HF followed by a superacid polyprotonation due to exceedingly acidic nature of superacids (HF–SbF_5). The polyprotonated carbohydrate species further transformed into glucose with the addition of water. What is more, the charge repulsions in superacid would also restrict the production of side products, resulting in a high glucose yield.

4.1.2. Solid Acids

Acid catalyzed cellulose hydrolysis by inorganic mineral acid has been widely investigated in recent years, but some problems such as equipments corrosion, difficult purification of products, and environmental pollution are hard to solve. Recently, solid acid catalysts are expected to be able to deal with these problems. For instance, heteropolyacids, polyvalent transition metal salts, and supported sulfonic acid catalysts (i.e., sulfonated mesoporous

Table I. The yield of glucose production from untreated and pretreated high crystalline cellulose by dilute sulfuric acid hydrolysis.

Hydrolysis conditions			Glucose yield by dilute-acid hydrolysis (%)			
T (°C)	AC (%)	Time (min)	H_3PO_4	NMMO	NaOH	Untreated
180	0.5	30	43	15.2	26.1	13.2
180	0.5	60	31.9	28.2	28.5	23.9
180	1.0	30	18.7	38.7	30.4	28.6
180	1.0	60	15.0	20.3	19.8	21.3

Notes: AC: Acid concentration; NMMO: *N*-methylmorpholine-*N*-oxide.

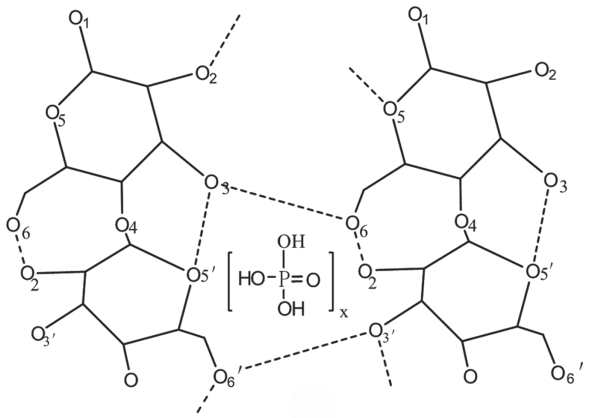

Fig. 11. Phosphoric acid molecule (H_3PO_4) embeds into cellulose inside for its destruction.

silicas, sulfonated activated-carbon (AC–SO_3H) catalyst[82] and amorphous carbon with a high density of sulfonic acid groups,[83] etc.) were reported to exhibit an efficient catalytic ability in catalyzing cellulose into glucose and other oligosaccharides with water or ionic liquids as solvent.[84–86] Glucose, as known to all, can be further used in candy manufacturing and pharmaceutical sectors. However, an urgent problem is the resulting glucose from initial hydrolysis of cellulose is not stable in the presence of acids under hydrothermal conditions, and would probably dehydrate, leading to the formation of various by-products.

H^+-exchanged layered transition-metal oxide is fascinating and of broad prospect for acid-catalyzed cellulose hydrolysis because of its strong acidity and good contact between interlayer acid sites and the reactant.[87,88] Shimizu and co-workers[89] found that heterogeneous heteropoly acids and polyvalent transition metal salts of $PW_{12}O_{40}^{3-}$ exhibited efficient catalytic performance for the selective hydrolysis of cellulose to saccharides. According to these pioneering works, the acid sites required for the hydrolysis of cellulose are most likely to form in the reaction medium or release from the solid material.[90]

Solid catalyst is a powerful tool and expected to achieve a green pathway for conversion of cellulose into polyols in an aqueous solution. Wang et al.[90] characterized the acidic properties of the as-prepared catalysts (SiO_2, ZrO_2, TiO_2, and SBA-15) and purchased HZSM-5s ($SiO_2/Al_2O_3 = 25$, 38, respectively) by temperature-programmed desorption of ammonia (NH_3-TPD). The results obviously indicate that the SiO_2 exhibited the highest desorption temperature, primarily signifying strong acid sites. Generally, hydrolysis activity of cellulose can be promoted by amounts of acid sites, strong acid strength, large specific surfaces, and suitable pore diameter.

With regard to the investigation on heterogeneous catalysts for the catalytic conversion of bulky cellulose, the challenge is to overcome the difficulty in the limited accessibility of the active catalytic sites. Their performance is probable to be influenced by the restricted space inside the pore systems which impedes cellulose biomacromolecules from penetrating to the reactive sites. Dhepe and Fukuoka[3] developed various porous materials, including HZSM-5, H-Beta, H form of Y zeolite (HY) (Si/Al = 2.6), H form of ultrastable Y zeolite (HUSY) (Si/Al = 15, 20, 30, 40), and folded sheets of mesoporous material (FSM-16), for cellulosic conversion, but the reaction only gave a low yield of glucose (<4%). Proper pore diameters of solid acids are crucial for cellulose utilization. Some solid supports, like zeolite, did not exhibit enough high performance for cellulose degradation because of their large number of pores in the microporous range. Functionalized mesoporous catalysts such as sulphonated silicas and carbon have been utilized. Nevertheless, these solid acids are usually not stable under compressed hydrothermal conditions. For example, high temperature above 403 K restricted the catalysis of supported sulfonic groups for the hydrolysis of cellulose because the sulfonic groups would possibly leach out into water solvent.[91]

The apparent distribution of the degree of polymerization (DP) of the cellulose isolated from [Bmim][Cl] solution was determined by gel-permeation chromatography. Microcrystalline cellulose is an insoluble residue isolated from the hydrolysis of the amorphous regions of α-cellulose.[92] As a consequence, the DP of

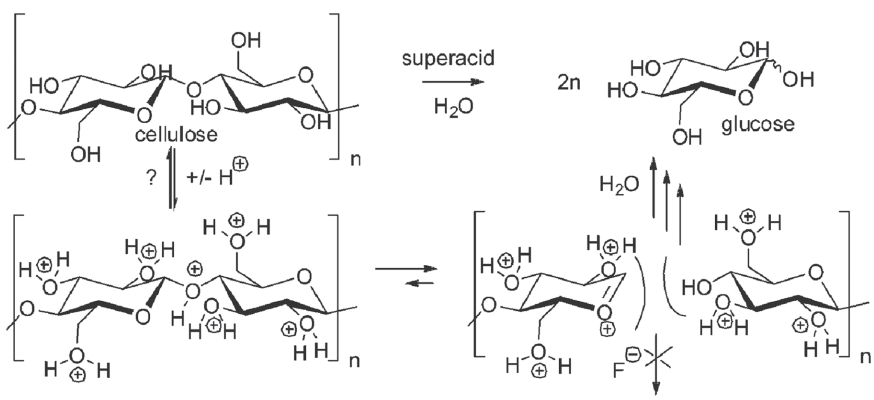

Fig. 12. Acid and superacid hydrolysis of cellulose. Proposed mechanism to account for the behaviour of cellulose in superacid HF–SbF_5.

microcrystalline cellulose lies in a more narrow range compared to that of α-cellulose. For the reaction catalyzed by Amberlyst 15DRY, the chains of cellulose initially was cleaved in a controlled way with a specific size. Thus the yields of reducing sugars would be notably restricted at the beginning of the reaction, resulting in long induction time (Fig. 13). In contrast, the reaction catalyzed by p-TSA proceeds much faster due to no restriction of size selectivity.[93]

An efficient solid acid catalyst should be water-tolerant, have a strong acidity and have many proper acid sites accessible for polysaccharides.[94] Fang et al.[95] synthesized an inorganic hydrotalcite nanoparticle $[Mg_4Al_2(OH)_{12}CO_3 \cdot 4H_2O]$ by co-precipitation with the efficient activation of $Ca(OH)_2$ saturated aqueous for the catalytic conversion of ball-milled microcrystalline cellulose. At 423 K for 24 h, this catalyst gave a glucose yield of 40.7% and achieved an 85.8% selectivity. The nanocatalysts exhibited a higher catalytic ability for cellulose hydrolysis compared to that of amorphous SO_3H supported activated carbon (AC-SO_3H).

Potvin et al.[96] investigated the effect of NaCl on the degradation of cellulose in water to glucose and levulinic acid over Nafion SAC-13 catalyst (Fig. 14). The reaction mixture was allowed to react between 190–200 °C for 5 days. When the aqueous solution of 25% NaCl was used, 72% levulinic acid yield was obtained, while the reaction only gave a levulinic acid yield of 14% in the absence of NaCl. This demonstrating NaCl remarkably took effect in cellulose degradation process. Furthermore, the author found that potassium chloride also enhanced levulinic acid yields. As a consequence, this finding is expected to be well developed in industrial production.

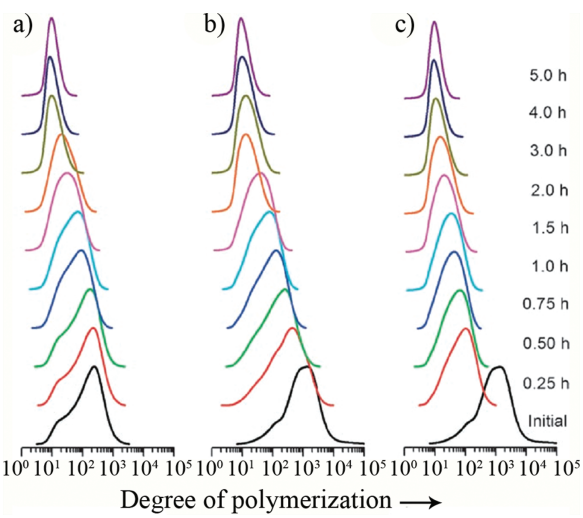

Fig. 13. Distribution of apparent degree of polymerization of the celluloses isolated from BMIMCl solution during the reaction: (a) Microcrystalline cellulose (Amberlyst 15DRY); (b) α-cellulose (Amberlyst 15 DRY); and (c) α-cellulose (p-TSA).

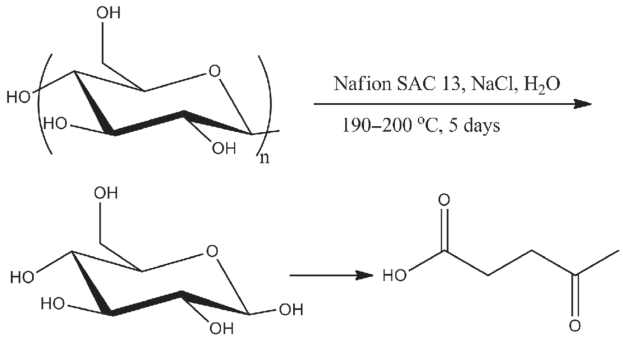

Fig. 14. The conversion of cellulose into LA.

4.2. Metal Catalyzed Hydrogenation/Hydrogenlysis

Over the past decades, heterogeneous catalytic degradation for cellulose has been widely employed to produce ethylene glycol,[97,98] glucose[82,83,93,99–101] and sugar alcohols.[71,102,103] The sugar alcohols can be used to produce foods and plastics. For example, sorbitol, as a platform chemical, is used not only in sweeteners but also in synthesizing isosorbide, 1,4-sorbitan, glycerol, glycols, and lactic acid. Currently, it is well accepted that cellulose can be decomposed into hexitols under pressured hydrothermal and hydrogen conditions over supported noble-metal catalysts.[104–106]

By using Pt/Al_2O_3 as a catalyst, Fukuoka et al.[3,8,107] investigated the degradation of cellulose into polyols at 463 K under 5 MPa H_2 pressure. The transformation process includes the hydrolysis of cellulose to glucose and the reduction of glucose to sugar alcohols.[3] The reaction gave sorbitol and mannitol yields of 25% and 6%, respectively. Nevertheless, the reaction has not given a high cellulose conversion. It was fund that H_2 dissociatively adsorbed on the Pt particles and then spilled over onto the surface of the support into the acid sites for the hydrolysis of cellulose except that intrinsic acid sites are responsible for the hydrolysis of cellulose. Based on Fukuoka's work, Luo et al.[106] studied this reaction further. By H^+ generated from high temperature water and Ru nanoclusters supported on active carbon, both the cellulose conversion rate and the sugar alcohols yields increased with a 39% hexitols yield including 30% sorbitol at 245 °C. This was attributed to the enhancement of the reaction temperatures and the strong catalytic performance of Ru/C in the hydrogenation reaction.

The acidity of a carrier for metal catalyst is a critical factor for cellulose degradation. A series of various supported Ru catalyst, including Ru/CNT, Ru/Al_2O_3, Ru/MgO, Ru/CeO_2, and Ru/SiO_2, were used to catalyze cellulose into polyols, especially into sorbitol (Fig. 15). Obviously, the catalyst Ru/CNT gave the highest sorbitol yield (~69%), which is in accord with its observable desorption temperature in NH_3-TPD profiles that indicates the strong acity of Ru/CNT.[108] However, for these mentioned

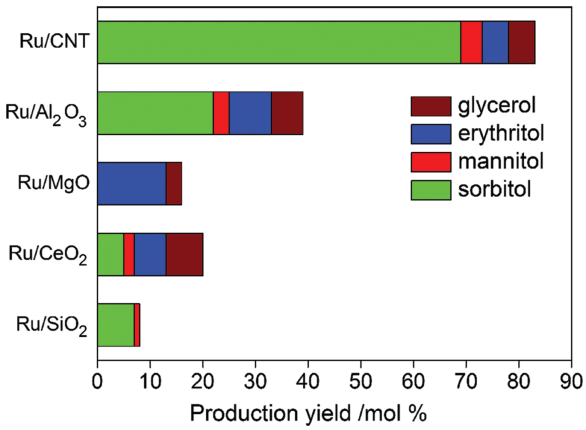

Fig. 15. Conversion of cellulose over various supported Ru catalysts. Reaction condition: Cellulose crystallinity, 33%; H_2, 5 MPa; temperature, 185 °C; time, 24 h.

metal catalysts, it is difficult to avoid the utilization of precious metal catalysts. Moreover, the relatively high ratio of noble-metal to cellulose is not suitable for large-scale industrial production from the point of efficient energy utilization and economic benefit.[109] As a result, with regard to efficient catalytic degradation of cellulose, it is highly desirable to develop a less-expensive and efficient supported metal catalyst as a substitution of conventional noble-metal catalyst.

Zhang and co-workers[97, 98, 103, 110] evaluated the performance of metal carbide catalysts prepared by carbothermal hydrogen reduction (CHR) method over the degradation of cellulose to polyols, especially to ethylene glycol. Tungsten carbide supported on activated carbon shows better catalytic performance for EG production compared to that of supported molybdenum carbides and platinum on different supports (i.e., activated carbon fiber (ACF), carbon black (CB), activated carbon (AC), Al_2O_3, etc.). In order to achieve higher EG yield, Ni was introduced to increase the selectivity to EG. The AC-supported WC_x catalyst gave the remarkably increased EG yield with 61.7%. The enhancement of EG yield is probably correlated with weak bonds between EG and Ni-promoted tungsten carbide surface. This is consistent with the reports that less-expensive Ni catalysts usually exhibit low catalytic ability in producing of sugar alcohol, which was attributed to their known unselective hydrogenolysis behavior.[102] In contrast, through the introduction of 2% Ni, either MC or CMK-3 supported WC_x catalysts only achieved a slightly increased EG yield (74.4 and 72.4%, respectively) due to the presence of large amounts of mesoporous on both MC and CMK-3. To the best of our knowledge, 74.4% is so far the highest yield ever reported for the direct conversion of cellulose into polyols.[97] What is more, the work by them suggested that the product selectivity can be readily controlled by changing W to M (8, 9, 10) ratio (m/m). The maximum EG yield of 75.4% was given by a SBA-15 supported Ni–W catalyst. With regard to M (8, 9, 10)–W bimetallic catalysts, W is found to play a critical role in cleaving C–C bonds during the catalytic conversion of cellulose, while the M (8, 9, 10) transition metals are mainly hydrogenate unsaturated intermediates.

4.3. Enzyme Catalysts

Several enzymes involved in cellulose enzymatic degradation generally include endoglucanases, β-glucosidases, cellobiohydrolases and hydrolases family GH61.[26, 111, 112] Different enzymes function at different sites of cellulose chains:

(i) exo-β-(1,4)-D-glucanases or cellobiohydrolases (CBHs) hydrolyze cellulose from the chain ends into soluble cellobiose;

(ii) endo-β-(1,4)-glucanases (EGs) hydrolyze the β-1,4-glycosidc bonds at the random sites of cellulose chains and proceed along the chain and thus introduce new chain ends for the action of CBHs, and

(iii) β-D-glucosidases cleave the cellobiose units produced by exoglucanases to generate monomer glucose.

The cellulose conversion catalyzed by enzymes results from the synergistic action of these enzymes.

Regarding the enzymatic hydrolysis of cellulose in aqueous ILs system, as far as we know, one of the earliest studies was reported by Turner et al.[113] They demonstrated that ILs can significantly inactivate cellulase. Recently, the leading work by Wahlstroöm et al.[115] described a study in which the activity and action of two Trichoderma reesei endoglucanases (Cel7B and Cel5A) for microcrystalline cellulose (Avicel) hydrolysis were evaluated in aqueous solutions containing 0–90% (v/v) of the ionic liquids 1,3-dimethylimidazolium dimethyl phosphate ([DMIM]DMP) or 1-ethyl-3-methylimidazolium acetate ([EMIM]AcO). Both [DMIM]DMP and [EMIM]AcO were strongly inactivating for the endoglucanases used. For these two kinds of ILs, their PH in the hydrolysis environment was found to be basic, indicating a possible reason inactivating the cellulases. The CBM in the native T. reesei Cel5A was found to be highly affected by based on the comparison of the effects of this IL on the cellulose hydrolysis yields by the native Cel5A and Cel5A Core without cellulose binding module (CBM). The effects of [DMIM]DMP on the CBM structure and the substrate recognition ability are both potential factors influencing the normal function of the CBM section in the endoglucanase on the cellulase.

Various factors inactivating cellulase in ionic liquids have recently been proposed. Basic anions such as Cl_2^-, Br_2^-, NO_3^- and $CF_3SO_3^-$ in ILs are found to cause strong inactivation for enzymes as they interact with the hydrogen bond network.[56] On the other hand, fluorinated anions, such as BF_4^- and PF_6^-, exhibit better compatible with enzymes. The "enzyme-friendliness" of ILs has been defined according to their chao- and chosmotropicity. The effect of anions on enzymatic stability was explained

by using Hofmeister series.[95] The high viscosity of IL solutions also plays the role of inhibitor to resist enzymatic reactions[49, 56] because of mass transfer constraints.

Many publications have demonstrated the potential of ILs in the pretreatment of cellulose for further hydrolysis of cellulose.[45, 116, 117] For example, Dadi et al. reported that regenerated cellulose from the precipitating of MCC dissolved in IL by the addition of an anti-solvent (e.g., water or alcohol) is more amorphous than the starting material, thus showing much better hydrolysis kinetics than untreated MCC.[45, 118] However, for this pathway, in order to recover the IL and avoid IL-induced cellulase inactivation, it must need a thorough washing for regenerated substrate, which results in the use of large amounts of water and intensive energy requirements for recycling of the much diluted IL from the washing liquid. Even so, it is inevitable that some IL is usually left in the regenerated substrate, giving rise to loss of IL and more importantly, enzyme inactivation in the hydrolysis step.[119] Therefore, it is highly desirable to find treatment approaches allowing efficient enzymatic hydrolysis without washing off the IL after precipitation.

Recently, Kamiya and co-workers have ever investigated the hydrolysis of cellulosic substrate with first dissolution in an IL, followed by a buffering, and direct addition of enzyme without removing the IL.[48] In this study, they found that the IL exceeding 40% (v/v) in the reaction would significantly limit the enzymatic hydrolysis of cellulose. Early, report has demonstrated the presence of ILs during cellulose hydrolysis would severely inactivate cellulases.[113] After dissolution pretreatment of the ILs containing imidazolium with subsequent buffer, the cellulase of hydrolysis matrix has been found to be quite basic,[49, 120] and accordingly, it is the basicity of the matrix that possibly makes the enzyme inactivated.[121] However, another study recently gave an opposite conclusion.[114] Thermo stability has also been reported to have contacts with cellulase activity.[122] Furthermore, increase of viscosity and ionic strengths both reduced enzymatic activity in ILs.[49] The inactivation of enzyme in both IL cations and anions were reported to correlate with Hofmeister series.[123] Kaar and co-workers found that hydrophilic anions such as AcO^-, NO_3^- and $CH_3SO_3^-$ in ILs is very inactivating, whereas fluorinated hydrophobic anions such as PF^-, on the other hand, exhibited higher compatibility with enzymes.[124] These authors proposed that enzymatic activity have a close contact IL anion. However, the paper did not provide whether ILs with PF_6^- anions can dissolve cellulose.[124]

Some publications have demonstrated that immobilization of enzymes could both enhance enzyme stability and decrease the use of eazymes hydrolyzing cellulase.[47] Cho et al.[125] design novel inorganic nanoparticles supported cellulase catalysts, containing three cellulases (Endoglucanase, Exoglucanase, and β-Glucosidase) co-immobilized on Au nanoparticle (AuNP) and Au-magnetic silica nanoparticle (MSNP), for the hydrolytic degradation of cellulose. The MSNP was modified by mercaptopropyltriethoxysilane (MPTES) to create attachment sites for AuNP on the surface of the MSNP, followed by the doping of the particles with spherical AuNP. The obtained Au-MSNP was eventually linked by three cellulases and expected to have high stability and catalytic performance for cellulose degradation.

Cellulosomes generally come into being by the assemblies of multiple celluloses with various catalytic functions on a giant scaffolding protein with a carbohydrate-binding module, and can depolymerize cellulosic materials through synergistically coupled hydrolysis reactions. In order to achieve excellent synergistic effect of catalysts, based on the concept of native cellulosomes, Nakazawa et al.[126] designed and constructed hybrid nanocellulosomes by clustering the biotinylated catalytic domains (CDs) of two catalytically divergent cellulases (equal amounts of endoglucanases and a possessive endoglucanases) and multiple biotinylated CBMs (CD/CBM = 7:23) on streptavidin-conjugated nanoparticles. The nanocellulosomes exhibited the efficient cellulase degradation activity for the production of reducing sugars from crystalline cellulose, 2.4 times as comparing to the amount given by the native free CDs and CBMs in the same proportions.

To date, though sub- and super-critical water and ILs can be utilized as the reaction media for cellulose conversion, some drawbacks such as high cost, low activity of enzymes, difficulty in product-enzyme separation and low selectivity for any product hamper have not been well settled.[7, 127] Therefore, in order to achieve high cellulose conversion rate by overcoming above-mentioned drawbacks, more efficient and stable enzymes urgently need to be developed based on the efficiently synergistically work of various enzymes. Cellulose thin films (e.g., regenerated cellulose, cellulose nanocrystals, and nanofibrillated cellulose) have been employed[128, 129] to monitor the binding and/or catalytic activity of cellulases by sensing techniques such as quartz crystal micro-balance (QCM),[112, 129, 130] ellipsometry,[131] neutron reflectometry[132] or surface plasmon resonance.[133]

4.4. Metal Ions and Functionalized ILs

Functionalized ionic liquids have been introduced for degrading cellulose including a series of alkylimidazolium salts containing chloride,[51, 134, 135] formate,[136] acetate,[137–139] and alkylphospahte.[48, 140, 141] Furthermore, various metal halides indicate the potential in catalyzing fructose and glucose to HMF. The efficient utilization of metal ions in ionic liquids was demonstrated for the transformation of cellulose into hydroxylmethylfurfural and furfural. For instance, Seri et al.[142] reported that $LaCl_3$ could catalyze cellulose into HMF in water at 250 °C with approximately 19% yield. Zhao and co-workers[25] investigated microwave-assisted hydrolysis of cellulose in ionic liquids by solid

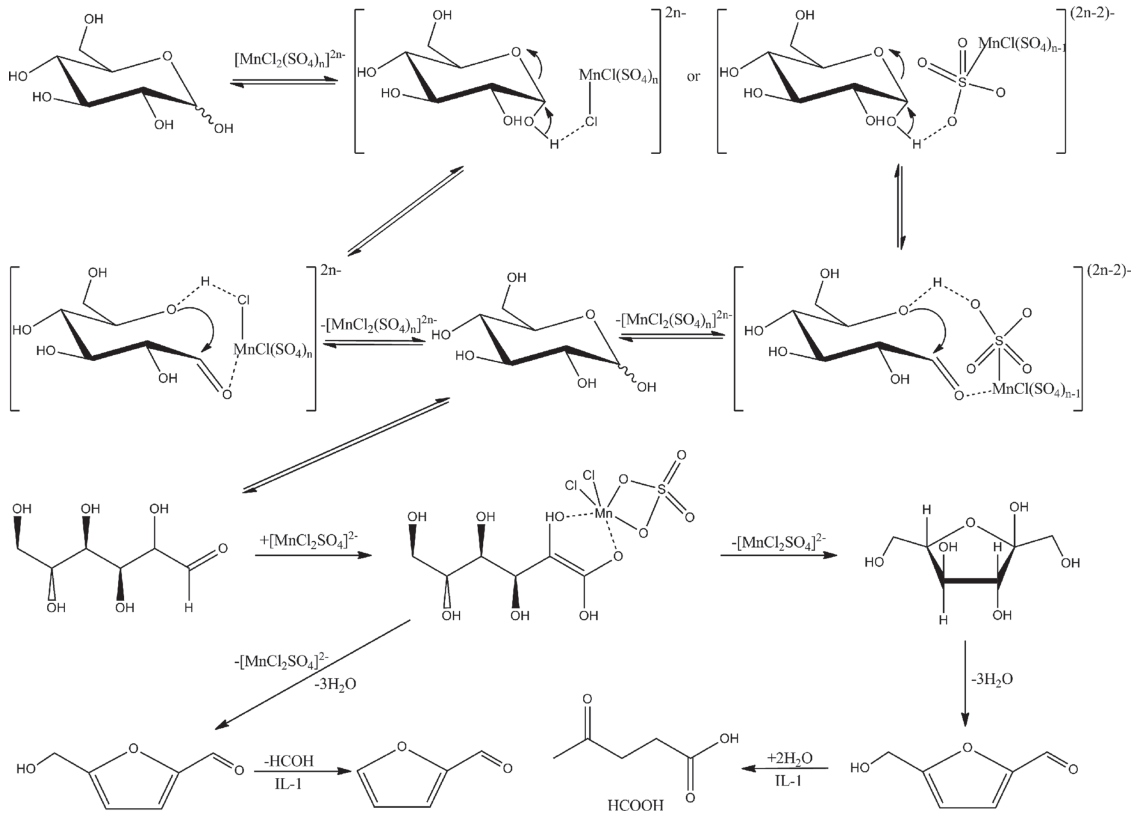

Fig. 16. Putative mechanism of $MnCl_2$ promoted conversion of glucose into the main products.

acid, and within 8 min, a 37% glucose yield was obtained. Binder and Raines[143] investigated the synthesis of HMF from lignocelluloses biomass in a single step by using DMA-LiCl as a solvent at 140 °C, a 48% HMF yield was obtained. The leading work by Su et al.[47] described the one-step conversion of cellulose dissolved in EmimCl into HMF by using bimetal chlorides ($CuCl_2$ and $CrCl_3$), and the reaction produced the HMF with an about 55% yield.

Tao and co-workers[144, 145] investigated several varieties of SO_3H-functionalized ILs for the catalytic hydrolysis of microcrystalline cellulose into 5-hydroxymethyl furfural, furfural and levulinic acid. In SO_3H-functionalized ionic liquid, the MCC conversion rate achieved a 91.2% maximum at 150 °C for 5 h with the addition of right amounts of $MnCl_2$, exhibiting a higher catalytic ability in hydrolyzing MCC than that of four different ILs (with SO_3H or not). For purpose of figuring out the role of $MnCl_2$, through the addition of $MnCl_2$ or not, the authors investigated the hydrolysis effect of microcrystalline cellulose using SO_3H-functionalized IL as solvent under the same condition above-mentioned. They reported that under these two conditions, the conversion rate of cellulose reached up to 86.2% and 71.4%, respectively. As a consequence, the author concluded that the addition of $MnCl_2$ promoted the hydrolysis of monosaccharide, giving rise to the increasing yields of HMF, Furfural, LA.

Based on the catalysis of metal chloride for cellulose conversion as reported by Rogers et al.[146] Tao et al. proposed a possible mechanism in which $MnCl_2$ in IL-1 formed $[MnCl_2(SO_4)_n]^{2n-}$ complexes in a similar manner to $LnCl_3$, as presented in Figure 16. These complexes could facilitate rapid transformation of the α-anomers of glucose residues to the β-anomers through hydrogen bonding between the hydroxyl groups at C1 bonds and the chloride anions or oxygen atom in SO_4^{2-}. Subsequently, the ring aldoses reversely convert to linear chain form, linking with $[MnCl_2(SO_4)]^{2-}$ complex to form an enolate structure. Enolate formation could promote the transformation of aldoses into ketoses, subsequently dehydrating to HMF. In the presence of acidic ionic liquid (1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulfate (IL-1)), the HMF interacts with water to form generate levulinic acid or lost aldehyde groups to furfural.

5. CONCLUSION

Cellulosic biomass, is an abundant and sustainable carbon source for producing fuels and chemicals. To develop efficient processes for the utilization of biomass resources, it is significant to understand carbohydrate chemistry and how catalysts interact with cellulose macromolecule. Varieties of value-added products can be formed from cellulose substrates such as glucose, sorbitol, ethylene glycol, HMF,

gluconic acid, alkyl glycosides, and LA, which are usually formed from primary reactions including hydrolysis, dehydration, isomerization, aldol condensation, reforming, hydrogenation, and oxidation. Considering that many of these catalytic reactions are still in an immature stage, future research emphasis should be focus on further optimization of reaction conditions to obtain higher product yield and greater tolerance of catalysts towards reaction medium. Fundamentally, promising and sustainable cellulose conversion system should have a synergetic and efficient work of all stages including cellulose pretreatment to make cellulose more accessible, degradation to variable chemicals and biofuels and post processing to eliminate environment pollution and improve energy utilization.

Conversion of cellulose with high selectivity for a valuable product is regarded as a considerable challenge. For acid catalyzed cellulose conversion, there exist some significant drawbacks such as corrosion of reactors, difficulty in separation of catalysts, high loading of catalysts and high cost of enzymes. Though some enzyme or precious metal, such as Pt and Ru, could catalyze this reaction, it is required to develop less expensive and stronger catalysts for this conversion. As a consequence, the study on carbohydrate processing contributes to provide a wide range of opportunities to develop innovative cellulose processing technologies.

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REVIEW