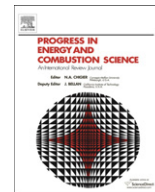


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Review

Solid acid mediated hydrolysis of biomass for producing biofuels

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ABSTRACT

Solid acid catalysts, which have favorable characteristics such as efficient activity, high selectivity, long catalyst life and ease in recovery and reuse, have great potential for efficiently transforming lignocellulosic biomass into biofuels and can replace many conventional liquid acids for hydrolysis and pretreatment. This work briefly introduces conventional biomass pretreatment and hydrolysis techniques, and reviews in detail the characteristics of biomass hydrolysis for five types of solid acid catalysts grouped as H-form zeolites, transition-metal oxides, cation-exchange resins, supported solid acids and heteropoly compounds. Carbonaceous solid acid (CSA) catalysts are considered as the most promising catalyst for cellulose hydrolysis, since they provide good access of reactants to the acidic sites of SO₃H groups. High glucose yields of up to 75% with 80% selectivity have been achieved at 150 °C for 24 h with CSA. However, separation of CSA from un-hydrolyzed cellulose residues after hydrolysis needs further research since these catalysts have similar physical and chemical properties to the residues. Use of functionalized CSA catalysts that contain paramagnetic groups is one method to improve CSA separation and reuse. Suggestions are given for promoting catalytic efficiency for each kind of solid acid catalysts. Methods to promote reactions or increase selectivities such as microwave, ultrasonication and nanotechnology are introduced. Finally, we highlight a recent strategy that exploits acid-functionalized paramagnetic nanoparticles suitable for cellulose hydrolysis, and address new opportunities for the use of solid acid catalysts.

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Contents

1. Introduction	00
2. Lignocellulosic biomass pretreatment methods	00
2.1. Lignocellulosic biomass	00
2.2. Pretreatment methods	00
2.2.1. Acid and alkali pretreatment	00
2.2.2. Chemical agent pretreatment	00
2.2.3. Ionic liquid (IL) pretreatment	00
3. Conventional hydrolysis methods and auxiliary techniques	00
3.1. Direct hydrolysis	00
3.2. Enzymatic hydrolysis	00
3.3. Auxiliary techniques	00
3.3.1. Microwave irradiation	00
3.3.2. Ultrasonic treatment	00
4. Solid acid catalysts mediated hydrolysis	00
4.1. H-form zeolites	00

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4.2.	Transition-metal oxides	00
4.3.	Cation-exchange resins	00
4.4.	Supported solid acid catalysts	00
4.4.1.	Supported metal oxide solid acid catalysts	00
4.4.2.	Supported carbonaceous solid acid catalysts	00
4.5.	Heteropoly compounds	00
4.6.	Comparison of solid acid catalyst activities	00
5.	Catalytic biomass hydrolysis with nanoparticle solid acid catalysts	00
5.1.	Nano solid acid catalysts	00
5.2.	Paramagnetic nanoparticle solid acid catalysts	00
6.	Concluding remarks and future outlook	00
	Acknowledgements	00
	References	00

1. Introduction

Owing to the depletion of fossil resources and the increasing demand on fuels, it is important to develop renewable resources to produce fuels and chemicals for energy security. Much success has been achieved in the conversion of grain-based glucose into bio-fuels and chemicals, but such processes have been criticized as they have led to increases in food prices, which is unacceptable in the world [1]. Clearly, strict management of agricultural practices is needed to avoid competition between biomass-derived chemicals, fuels and food.

Biomass can provide a rich source of sustainable commodity products, such as biofuels (biodiesel, bio-ethanol, and marsh gas) and chemicals (acetic acid, malic acid, acetone, lactic acid) that are now primarily derived from petroleum. Annual biomass growth on the continents amounts to 118×10^9 tons in dry matter [2]. The IEA (International Energy Agency) reported that the world oil consumption in 2007 was 3.53×10^9 tons, equivalent to 148.26×10^{18} J of energy, which is less than 10% of the annual global biomass growth in terms of energy content [3]. The US Department of Energy and the US Department of Agriculture have demonstrated that 1.3 billion tons of biomass can be produced exclusively for biofuel production in the US each year with only moderate changes in terrestrial crop practices and the best available conversion technologies [4].

Abundant supply of low-cost lignocellulosic materials can guarantee stable production of bulk liquid fuels and bio-chemicals via sugar or syngas platforms if methods and infrastructure can be sufficiently advanced. Carbohydrate content of lignocellulosic biomass (e.g., wood) is typically 75% [2], and this can be converted into soluble sugars *directly* by acid hydrolysis or *indirectly* by a two-stage process involving pretreatment and enzymatic hydrolysis. Cellulose-derived sugars can then be converted into ethanol, other biofuels, various chemicals, foods, and medicines by chemical and biochemical technologies [5]. The US Energy Independence and Security Act (EISA, 2007) has targeted the production of 15 billion gallons (56.9×10^6 m³) of biofuels by 2020, which is approximately 15 times US current production (~ 1 billion gallons in 2010).

Cellulosic ethanol has been regarded as a promising alternative to petroleum-based transportation fuels because it is derived from abundant renewable cellulosic bioresources and does not consume any food. Similarly, other potential biofuels like butanol and dimethyl ether can also be produced from lignocellulose by hydrolysis and subsequent microbial fermentation or chemical conversion. A schematic biorefinery for biofuels is shown in Fig. 1. Sugars hydrolyzed from biomass are conveniently used for the production of liquid fuels (e.g., ethanol and butanol) and gaseous fuels (e.g., hydrogen and methane) through biological or chemical conversion routes. Fermentation of hexose sugars generally does

not pose special difficulties as ethanol is commonly produced from glucose and sucrose by fermentation [6,7]. Pentose sugars are fermentable in practical operations [8]. Sugars can be anaerobically digested to H₂ and CH₄ with yields of 13% and 75%, respectively, being reported [9]. In chemical routes, sugars are used for H₂ production by catalytic hydrothermal process in batch and flow reactors. At moderately high temperatures (550–600 °C) and short reaction times in flow reactors, glucose can be 100% gasified with activated-carbon or KOH catalyst with gas containing up to 60 mol% H₂ [10–12]. With Pt catalyst, it is found that 67 wt% gasification rates (with up to 44 mol% H₂) can be obtained at 360 °C and 30 MPa [13,14]. Hexose and pentose sugars can be catalytically converted to liquid alkanes or 5-hydroxymethylfurfural (5-HMF) and then into 2,5-dimethylfuran (DMF) [15–17]. However, by-product lignin from hydrolysis can be used to produce bio-gasoline and biodiesel via more sophisticated pathways [18].

Over the past century, much effort has been made to develop processes for the efficient conversion of carbohydrates to sugars and biofuels [19–23]. World biofuel production from cellulose is predicted to increase by 6.7% per year to reach 2.7×10^6 barrels of oil equivalents per day in 2030 [24]. Conversion of world crop residues into bio-ethanol has the potential to replace 32% of the global gasoline consumption [25]. However, the current world bio-ethanol production only accounts for 6.25% of the total potential bio-ethanol production [26]. As cellulose and hemicellulose are the major components of grasses and agricultural biomass, the generation of water-soluble sugars from them has received great interest for the production of bio-ethanol and other biofuels.

Numerous reviews have been published on the hydrolysis of lignocellulosic materials and the subject has been studied extensively [4–8,25–28]. In these reviews, technologies for pretreatment, such as pyrolysis, steam explosion, ammonia fiber explosion, CO₂ explosion, ozonolysis and biological pretreatment are described in detail.

It is clear that many methods are available for converting biomass into biofuels and that biomass conversion processes will continue to have industrial interest. However, some of the key challenges are in the design of the biomass feedstock processes that are environmentally friendly, economic, versatile and efficient in view of the variable composition and diffuse distribution of biomass. The use of solid acid catalysts can address some of these challenges due to their use of mild operating conditions coupled with selective and efficient reactions. Solid acid catalysts allow simple separation of products from the catalysts thus ease of recycle. In this review, biomass pretreatment methods are introduced. Then, hydrolysis characteristics of biomass are given. Finally, solid acid catalysts used in solid acid mediated hydrolysis of biomass are introduced according to various types to guide the readers in their selection and potential for an application. Concepts

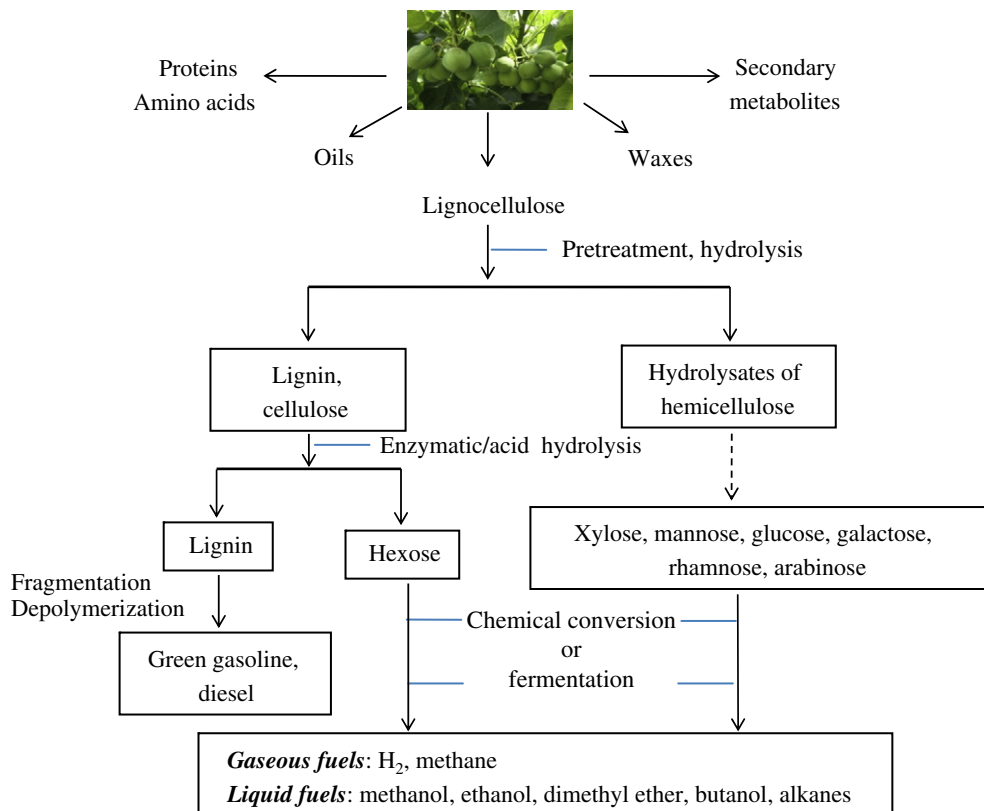


Fig. 1. Schematic of a biorefinery for lignocellulosic biomass.

for using nanoparticle solid acid catalysts are introduced through a proposed application.

2. Lignocellulosic biomass pretreatment methods

2.1. Lignocellulosic biomass

The total content of hydrolyzable biopolymers (cellulose: 50%; hemicellulose: 25% and lignin: 20%) in a typical lignocellulosic biomass (e.g., wood) is approximately 95% by mass [2]. Enzymatic hydrolysis of lignocellulosic materials is a slow process (ca. days). For the purpose of achieving satisfactory hydrolysis rates, the materials require specific pretreatment to overcome structural barriers. The chemical structures of these compounds are briefly introduced.

Cellulose, which is a straight chain polymer that is insoluble in water, is composed of cellobiose unit formed from D-glucose via β -1,4 glycosidic bonds. It can be hydrolyzed catalytically by cellulases into fermentable products. However, there are many factors affecting cellulase accessibility to cellulose, such as high microcrystallinity of cellulose, extensive intermolecular hydrogen bonding, van der Waals forces (Fig. 2) and the obstruction caused by hemicellulose and lignin.

Hemicellulose is a heteropolysaccharide composed mainly of C-5 carbohydrate monomers [6,29]. It is a branched polymer containing several monosaccharide units including xylose, mannose, glucose, galactose, rhamnose, and arabinose.

Lignin is a non-carbohydrate biopolymer. Owing to its complex and cross-linked aromatic structure, i.e., β -O-4, α -O-4 and C–C linked phenylpropanes (e.g., guaiacyl propane, syringyl propane and hydroxy-propane), lignin reduces cellulose accessibility to enzymes and chemical agents in the degradation of cellulose.

Therefore, cellulose bound by lignin is difficult to hydrolyze, and lignin is removed in many industrial processes such as paper production. Lignin has many industrial applications, e.g., as a potential feedstock for the production of phenolic resins, polyester, stabilizer, activated-carbon and catalyst support [30–34].

2.2. Pretreatment methods

For enzymatic hydrolysis, physical or chemical pretreatment is required to reduce cellulose crystallinity, increase material porosity and remove lignin [23]. Pretreatment is the first step in the conversion of lignocellulosic biomass to chemicals, because it significantly improves processing and reduces operating costs of down-stream units [24].

The purpose of pretreatment is to breakdown the lignin that binds the cellulose and to destroy the crystalline structure of cellulose and increase its surface area so that fragments become accessible to enzyme active sites [25]. The main methods of pretreatment are physical, chemical, physical-chemical and biological pretreatments. Physical-chemical (e.g., steam or ammonia explosion) and biological pretreatment have been reviewed in depth [25–28].

Typical physical pretreatment includes chipping, grinding, milling and thermal methods [35–39]. Millett et al. [39] found that woody biomass could be almost completely hydrolyzed by enzymatic hydrolysis after 60 min of milling or by dilute acid hydrolysis with vibratory milling. Physical treatment is effective for reducing particle size and crystallinity of biomass, but it is less efficient and consumes much more energy than chemical pretreatment methods.

To increase cellulose susceptibility to enzymes or chemical catalysts, chemical pretreatment is usually needed. Chemical

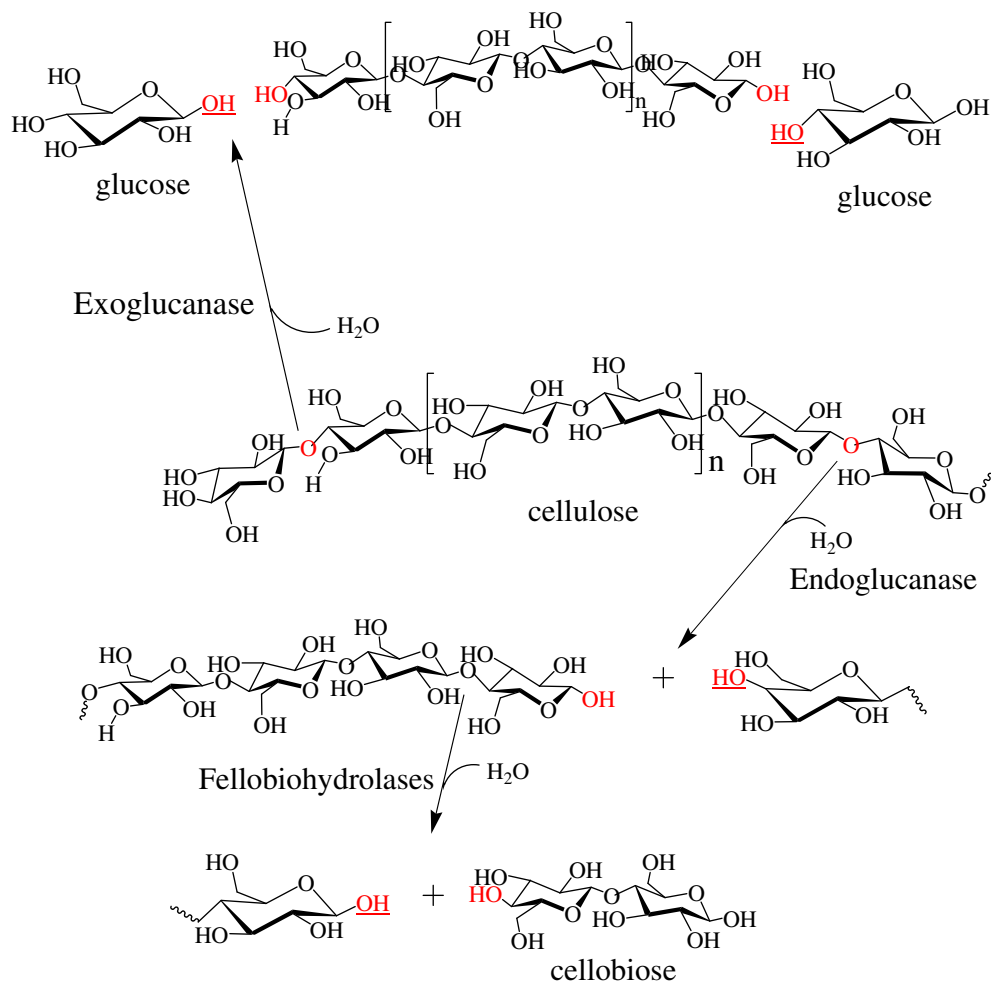


Fig. 2. Structure of cellulose and its enzymatic hydrolysis pathway.

pretreatment effectively removes and recovers most of the hemicellulose portion as soluble sugars, and disrupts the lignin making it partially soluble in aqueous solutions of H_2O_2 or ammonia [26]. After pretreatment, glucose yield from subsequent cellulose hydrolysis can be greatly increased with yields of 50–85% being reported. Chemical pretreatment with acids has proven to be effective for breaking down hydrogen bonds leading to the intracrystalline cellulose swelling [40]. Although these pretreatment methods have been comprehensively reviewed, we introduce their principles (Table 1) [38,41–55] since they have relevance to comparisons with solid acid mediated hydrolysis methods.

2.2.1. Acid and alkali pretreatment

Acid pretreatment is a process in which hydronium ions breakdown or attack intermolecular and intramolecular bonds among cellulose, hemicellulose and lignin. Acid pretreatment increases the porosity of the substrate and accessibility of cellulose to enzymes for subsequent hydrolysis. During an acid pretreatment process, very little cellulose is hydrolyzed. Acid pretreatment includes methods that use either concentrated or dilute acid solutions. Dilute sulfuric acid is the most popular catalyst for the commercial production of glucose from cellulosic materials [55]. However, the process is usually accompanied by further degradation of monomers, and it has drawbacks such as equipment corrosion and issues in the recovery and recycle of the acids. Organic acids such as maleic acid and fumaric acid have been

suggested as alternatives for sulfuric acid because these acids inhibit the formation of side-products [42].

Alkali (e.g., NaOH, KOH) is a swelling agent for both crystalline and amorphous celluloses that can destroy the linkages between lignin and carbohydrates by saponification of intermolecular ester bonds [26]. All lignin and parts of hemicellulose can be removed by alkali treatment, so this pretreatment is widely used to enhance the digestibility of cellulose in enzymatic hydrolysis.

2.2.2. Chemical agent pretreatment

Some chemical agents, such as peroxides and acidic alcohol solutions, have advantages for dissolving lignin and loosening the remaining hemicellulose from insoluble crystalline cellulose. Some solvents such as LiCl/N,N-dimethylacetamide (LiCl/DMAc), NaOH/urea, cadoxen (a cadmium ethylenediamine solvent) and carboxymethylcelluloses (CMCs) are able to dissolve crystalline cellulose and restructure it so that precipitation creates a suitable form for the subsequent hydrolysis [46–49]. Ishii et al. [46] studied the effect of solvent exchange as an activator for cellulose solutions. When solid cellulose was in the state of dynamic heterogeneity, solvent exchange affected molecular mobility. The dissolution of cellulose was attributed to changes in the cellulose hydrogen bonding state caused by the solvent. Besides the effect of hydrogen bonding, surface fractal dimension also promotes the dissolution of cellulose. Surface fractal dimension is a statistical quantity that gives an indication of how completely a fractal appears to fill

Table 1
Chemical and solvent pretreatment methods for lignocellulosic biomass.

Chemical pretreatment	Functional mechanisms	References
Acid pretreatment	Acid solution breaks down the covalent bonds, hydrogen bonds, and van der Waals forces in the cellulose/hemicelluloses/lignin, and increases porosity and accessibility of the cellulose to enzymes.	[38,41–43]
Alkali pretreatment	Alkali solution destroys the linkages between lignin and carbohydrates by saponification of intermolecular ester bonds that cross-linked hemicellulose and lignin. Alkali solution dissolves lignin by the same mechanism as pulping, particularly under high pretreatment severity.	[44,45]
Organic solvent	Organic solvent dissolves lignin which loosens structures of remaining hemicellulose and crystalline cellulose. It changes the crystalline structure of cellulose for subsequent hydrolysis by breaking down intermolecular hydrogen bonds between OH-2 and O-6.	[46–49]
Ionic liquids (ILs)	IL interacts closely with cellulose due to its high dipolarity and large dispersion forces and strong hydrogen bonds. Hydroxyl groups are separated from lignocellulosic structures through the π - π -interactions and hydrogen bonds between IL and cellulose-OH. This effect results in opening of the intermolecular hydrogen bonds and disrupting of the three dimensional network of cellulose. Lewis acidity of IL favors total reducing sugar selectivity.	[50–55]

a space as one zooms down to finer and finer scales. Surface fractal dimension can be calculated from small-angle X-ray scattering profiles of cellulose particles. Cellulose particles that have a large fractal dimension are able to dissolve faster than those with a small fractal dimension [46].

2.2.3. Ionic liquid (IL) pretreatment

Ionic liquids (ILs) are organic salts with melting temperatures below 100 °C that are being applied as reaction solvents and as catalytic reagents [56]. ILs are non-volatile and generally thermally stable, hence, they have many favorable attributes compared with traditional organic solvents or other pretreatments. ILs are efficient for the pretreatment and hydrolysis of lignocellulosic materials, and can dissolve biomass and overcome many of the physical and biochemical barriers for hydrolysis at ambient conditions [57,58]. Many ILs have been shown to be effective solvents for cellulose. The ILs, 1-butyl-3-methylimidazolium chloride {[BMIM][Cl]} and 3-allyl-1-methylimidazolium chloride {[AMIM][Cl]} can dissolve 10 wt% cellulose at 50–100 °C [54]. Under microwave irradiation, the dissolution rate of cellulose in ILs increases to 25 wt% [54]. Zavrela et al. [59] screened 21 ILs to examine their ability to dissolve cellulose and lignocellulose, and 1-ethyl-3-methyl imidazolium acetate ([EMIM][Ac]) was found to be the most efficient one. Swatloski et al. [53] showed that high chloride concentration and activity in ILs promoted the breakdown of the hydrogen bonding network in cellulose, and that water was an inhibitor for the dissolution of cellulose. Hence, water can be used to regenerate the cellulose dissolved in ILs. The crystallinity of regenerated cellulose decreases by dissolution and precipitation of the cellulose so that the amorphous product becomes much easier to hydrolyze compared with the native cellulose. Zakrzewska et al. [54] assessed the current status of studies regarding the solubility of lignocellulosic components in ILs, such as cellulose, lignin, chitin, and monosaccharides. Wang et al. [60] conducted a study on the

extraction of cellulose from wood chips with [AMIM][Cl] and found that 62% cellulose could be dissolved in [AMIM][Cl] under mild conditions. They were able to recover cellulose by adding dimethyl sulfoxide/water as a precipitation solvent. Separation of cellulose from ILs seems to have several methods and so the isolation of cellulose from lignocellulosic biomass seems to be feasible [60–62]. High recoveries of cellulose with controlled selectivity especially under reaction conditions through solvent selection or addition, however, still has many opportunities for development.

Acidic ILs with functional groups are new-types of catalysts with high-density active sites as liquid acids but are non-volatile like solid acids [63,64]. They can increase pretreatment efficiency by partially degrading biomass components chemically. Cations and anions of ILs can be designed to bind a series of groups with specific properties to regulate acidity. SO₃H-functionalized ILs show high activities in cellulose hydrolysis and in the transformation of cellulose I into cellulose II [57]. In our work, we used ILs to produce *Jatropha* biodiesel [65] and 5-HMF [66,67]. Presently, however, the high cost of ILs limits their large-scale application for pretreatment. It can be expected that with the advancement of production and chemical techniques, that ILs can be used advantageously with solid acid catalysts in commercial hydrolysis and pretreatment processes for cellulose.

3. Conventional hydrolysis methods and auxiliary techniques

Hydrolysis is a process related to the breakage of β -1,4 glycosidic bonds in cellulose. For the case in which there are no by-products or side reactions, glucose is the major product of cellulose hydrolysis. Two conventional methods to hydrolyze lignocellulosic biomass are (1) direct hydrolysis and (2) enzymatic hydrolysis after pretreatment. Direct hydrolysis is performed mostly in the presence of mineral acids, and 72% sulfuric acid is generally used [68–70]. For enzymatic hydrolysis, physical or chemical pretreatment is required to reduce cellulose crystalline, increase material porosity and remove lignin [71].

3.1. Direct hydrolysis

Direct hydrolysis of lignocellulosic biomass with inorganic acid dates back to the early 19th century and its commercialization in the early 20th century [68]. Concentrated acids can enter into the structure of cellulose, which leads to cellulose swelling and glycosidic bond breakage. At atmospheric pressure and low temperature (e.g., 50 °C), cellulose swells when sulfuric acid concentration is higher than 50%. As the concentration is increased further to above 62% (or 39% hydrochloric acid), cellulose changes from a limited swollen state into a soluble state [69]. Camacho et al. [70] studied the effect of H₂SO₄ concentration [31–70%, (w/v)] on the solubilization rate of microcrystalline cellulose. Acid promoted the total solubilization of cellulose when its concentration was above 62% (w/v). Subsequently, the glycosidic bonds were attacked by water molecules catalyzed by the acid, and then hydrolyzed to give many intermediates, such as hydrolyzed celluloses, resembling starches, cellulose dextrans, oligosaccharides and D-glucose. The intermediates were further converted into sugar esters or degraded products such as aldehydes and furfurals. Concentrated acid hydrolysis has low energy consumption during operation since it operates at low temperatures (e.g., 20–50 °C) and at atmospheric pressure [68]. However, the process has strict requirements on water content of raw materials. Further, concentrated acid pretreatment has corrosion and recovery issues as mentioned previously.

Dilute acids can change the spatial orientation and the construction of cellulose. The hydrated protons in dilute acid solution lead to the protonation of oxygen atoms in glycosidic bonds, and

eventually activate the glycosidic bonds. Dissociation of the β -O-4 is rate-limited with the hydrolysis rate of hemicellulose being much faster than that of cellulose. Therefore, hydrolysis is carried out in two stages for hemicellulose and cellulose, respectively [72]. Kim et al. [73] developed a two-stage hydrolysis process where hemicellulose was mainly hydrolyzed at mild conditions in the first stage. More than 50% of the cellulose that survived at the first stage was further hydrolyzed. In the second stage, hydrolysis of the remaining insoluble cellulose with dilute sulfuric acid required a higher temperature (e.g., 200 °C) than the first stage because cellulose was more difficult to be hydrolyzed than hemicellulose.

Compared with concentrated acid hydrolysis, dilute acid hydrolysis usually operates at temperatures above 180 °C and at pressures from 1.2 to 1.3 MPa [68] with a reaction time from minutes to hours. The conditions lead to a high cellulose conversion rate (e.g. 50%) but give low glucose selectivity (e.g. 46% of the theoretical maximum).

Biomass can be hydrolyzed hydrothermally, without catalysts, in high temperature liquid water (>300 °C). The elevated temperatures require high pressures (e.g., 10–15 MPa). Hydrothermal hydrolysis is promoted at high temperatures due to the enhanced ion product of water, in which both hydrogen ion and hydroxyl ion concentrations increase. Water at high temperature becomes similar to a weakly-polar solvent that can dissolve biomass and provides a homogeneous phase for hydrolysis without catalysts [74–77]. In our previous work, we found that microcrystalline cellulose could be completely dissolved in water at temperature above 320 °C and became a ‘cellulose solution’, which allowed study of the hydrolysis with a continuous flow reactor. Continuous reaction of microcrystalline cellulose 20 wt% in water at supercritical conditions (>374 °C and 22.1 MPa) gave water-soluble products (with 100% conversion) containing 80% hydrolyzates (glucose and oligomers) for short reaction time (ca. 0.05 s) [92]. By adding 0.8 wt% Na₂CO₃, actual wood can be completely dissolved to form a ‘wood solution’ at 329–367 °C at short reaction times [77]. The ‘wood solution’ can be rapidly (ca. 15 s) hydrolyzed to sugars/sugar oligomers under homogeneous conditions. Without catalysts, the results show that fast refining of ‘biomass solution’ is possible on a continuous basis [78–80].

3.2. Enzymatic hydrolysis

Enzymatic hydrolysis of biomass with cellulases after pretreatment has received much attention in academia and industry. Cellulases are a mixture of endoglucanases, exoglucanases and cellobiohydrolases, and catalyze the degradation of cellulose to oligomers according to the following proposed mechanism: (1) endoglucanase cleaves β -1,4 glycosidic bonds in the long-chain polymer, and free ends are created; (2) exoglucanases, such as β -glucosidases, act on the reducing and non-reducing ends to liberate oligosaccharides; and (3) cellobiohydrolases cleave the polymer from the reducing ends to liberate cellobiose. Catalyzed by the above three cellulases, cellulose hydrolyzes to glucose [81–83]. The factors that affect cellulase activity are substrate concentration, end-product inhibition, reaction temperature and pH [27]. Cellobiose inhibits cellulase activity [84], so it is important to remove it as the reaction process.

Weak acids, furan derivatives and phenolic compounds in the solution of lignocellulosic hydrolyzates are inhibitory to microorganisms. Palmqvist and Hahn-Hägerdal [85] reviewed inhibitors and their mechanisms during fermentation of lignocellulosic hydrolyzates. Marques et al. [86] reported simultaneous fermentation and enzymatic hydrolysis process of recycled paper sludge for ethanol, without pretreatment or substrate supplementation. Simultaneous saccharification and fermentation process can obtain

conversion yield of 51% of available carbohydrates. However, temperature difference between enzymatic hydrolysis and fermentation is the primary problem that limits product yield in simultaneous saccharification and fermentation processes.

Liquid acid pretreatment followed by enzymatic hydrolysis is one of the most common processes for cellulosic ethanol production. The major issues in processes with liquid acids are: (1) the pretreatment leading to secondary degradation products that inhibit subsequent hydrolysis and fermentation; and (2) the recovery and recycle of the spent acid solutions.

3.3. Auxiliary techniques

To increase the contact area between catalysts and substrates and to increase conversion yield and efficiency, some auxiliary techniques for hydrolysis of substrates have been proposed (Table 2). Commonly used auxiliary techniques are microwave, ultrasound and nanotechnology [87–92] as discussed in more detail in the following sections.

3.3.1. Microwave irradiation

Microwave irradiation is a physicochemical process since both thermal and non-thermal effects are often involved when used for biomass. Microwave energy of 300–700 W power has been used to promote the liquefaction of biomass [93,94]. Microwave heating has found many applications in affecting chemical reaction pathways and in accelerating reaction rates. Water is an effective absorber of microwave energy. Microwave energy absorption capacity for different components, structural densities and inorganics contained in biomass is different. The length of induction period of lignin, wheat straw and cotton wood is much shorter than that for cellulose [95]. The functional mechanism of cellulose dissolution under microwave irradiation is shown in Table 2. There are many reports on cellulose dissolution under microwave irradiation.

Table 2
Auxiliary technologies for cellulose hydrolysis.

Auxiliary technologies	Functional mechanisms	References
Microwave	Microwave heating, causes rapid rise in temperature that results in vaporization of intra-water in biomass and increases intra-particle pressure to loosen the biomass structure due to expansion. Cellulose crystallinity is reduced, and hydrolysis efficiency is improved.	[87,88]
Ultrasound	Ultrasound causes water bubbles within the lignocellulosic material to rapidly expand and contract, causing compression and extension of the particle, resulting in a destructive effect. Ultrasound produces high frequency oscillations and causes mutual friction inside the medium, thus generating heat, resulting in a large local temperature differences.	[89,90]
Nanotechnology	Nanoparticles have large superficial areas that enhance the surface chemistry of the catalyst materials. Monodispersed nanoparticles are more accessible to the oxygen atom in the ether linkage of cellulose. High acid strength of magnetic nanoparticles is effectively to catalyze the hydrolysis of β -glycosidic bonds in cellulose.	[91,92]

Wang et al. [60] reported that cellulose extraction rates as high as 62% could be achieved, and the reaction time could be significantly reduced from 15 to 2 h by microwave irradiation compared with oil bath heating. ILs were introduced to enhance the dissolution of wood because they could efficiently absorb microwave radiation. The increment in collision frequency between the ILs (anions and cations) and the wood macromolecules was the main reason of effective dissolution [96,97]. Microwave assisted cellulose dissolution in ILs, however, can lead to incomplete degradation of cellulose. Possidonio et al. [97] demonstrated that this problem can be avoided by using low energy microwave heating coupled with efficient stirring. Pretreatment of biomass with microwave irradiation remarkably enhances the accessibility of the materials for enzymatic hydrolysis, as well as for acid hydrolysis and alkali hydrolysis [88,98]. The use of microwave irradiation as a heating source for lignocellulose pretreatment is a rapidly growing research area for improving cellulose hydrolysis.

3.3.2. Ultrasonic treatment

Ultrasonic treatment is the common term for sonication (Table 2). Sonication is the act of applying ultrasonic energy to agitate particles in a sample, for various purposes. In the laboratory, it is usually applied using an ultrasonic bath or an ultrasonic probe. Sonochemistry uses sound waves with frequencies between 20 and 40 kHz to promote cavitations and micro heating in a solution [99,100]. It has been shown that ultrasonic treatment has little effect on the surface conformation of the granulated lignocellulosic materials due to the low energy (<100 W) of the ultrasonic vibration [101,102]. However, ultrasonic treatment assisted pretreatment effectively promotes lignocellulose dissolution and destroys the intermolecular hydrogen bonding in lignocellulose. When applying ultrasonic treatment to cellulose hydrolysis, the energy changes cellulose morphology and enhances its accessibility to catalysts [103,104]. Ultrasonic treatment promotes solvent penetration into cellulosic materials and improves mass transfer during reactions. Ultrasonic treatment changes the structure of cellulose and enhances the accessibility of cellulose to catalysts. Thus, ultrasonic treatment intensifies cellulose dissolution, and can be used effectively for extracting hemicellulose, cellulose and lignin from lignocellulosic biomass [103]. Ultrasonic treatment can facilitate the mass transfer of the dissolved components from lignocellulosic biomass and enhance the release of polysaccharides. The polysaccharide fraction prepared with ultrasonic treatment had a slightly lower thermal stability than that without treatment. Therefore, the reaction processing intensity, time and amounts of catalyst required can be reduced with ultrasonic treatment and the technique can probably be used to further enhance solid acid catalyst mediated hydrolysis. Over the years, most research on ultrasonic treatment has been limited to phenomenological description of solutions under laboratory conditions. However, industrial applications of ultrasound in plastic welding, cleaning, materials chemistry, food products modification etc. represent a useful effort for application of ultrasonic treatment to enhance cellulose hydrolysis [105–107].

4. Solid acid catalysts mediated hydrolysis

Chemical pretreatment and hydrolysis techniques that use homogeneous catalysis are attractive from the point of view of mass transfer and reaction efficiency, however, these methods have major drawbacks in product separation, reactor and equipment corrosion, catalyst recycle and treatment of waste effluents. Many catalytic systems have not been commercialized due to the difficulty in separating the homogeneous catalysts from product solutions [20]. Solid acids on the other hand can overcome many of the disadvantages of homogenous catalysts, and also have many unique properties and advantages.

A solid acid catalyst is defined as solid which can donate protons or accept electrons during reactions. The catalytic function for a solid acid catalyst is derived from its acidic centers, existing mainly on its surface. Accordingly, solid acids with Brønsted acid sites can catalyze biomass hydrolysis.

Solid acid catalysts have numerous advantages over liquid catalysts regarding activity, selectivity, catalyst life and ease in recovery and reuse. They are widely studied as direct replacements for liquid acids to reduce pollutants and to lower operating costs. However, it is a challenge to develop hydrothermal catalytic hydrolysis processes with solid acid catalysts. First, their acid strengths and catalytic activities decrease when water is present [108]. Second, most solid acids do not function effectively for cellulose hydrolysis because the surfaces of these solids do not have strong acid sites or cannot allow close contact of β -1,4-glucans. As a result, a good solid acid catalyst need to be water-tolerant, have a strong acidity and have many acid sites for polysaccharides to access [108,109].

Up to now, some reviews concerning the hydrolysis of cellulose using solid acid catalysts have been reported [110,111]. This review summarizes and analyzes current achievements in the hydrolysis of cellulose using solid acid catalysts. The present review, in addition to providing research progress in ILs, hydrothermal, microwave, and ultrasonic methods, gives characteristics and theories of five kinds of solid acid catalysts, with the purpose to develop efficient methods for promoting biomass conversion. Moreover, the article discusses obstacles in the applications of solid acid catalysts for cellulose hydrolysis that can be considered research areas. Several types of solid acids for biomass hydrolysis are introduced in the following sections and are summarized in Table 3 [59,108,109,112–123].

4.1. H-form zeolites

Zeolites are widely used as catalysts in organic synthesis, as they are non-toxic and non-corrosive, and easy to recover for reuse. They have shape-selective properties, and can provide stereo- and regio-control in chemical reactions. The number of Brønsted acid sites in H-form zeolites is related to the atomic ratio of Al/Si, so that high ratios have high acidity [124]. Modified H-zeolites (HY) as industrial catalysts maintain a stable framework at temperatures up to 127 °C [125]. The hydrophilic or hydrophobic properties of a zeolite can also be modulated in terms of reactant characteristics without compromising its functionalized acidic sites. Moreover, zeolites can be synthesized with extensive variation of acidic and textural properties. Acidic zeolites have been successfully used for conversion of sucrose into mono-sugars at mild operating conditions [108]. In the process, sucrose diffuses into the internal pores of zeolite and the glycosidic bonds of sucrose then extend into the vicinity of Brønsted acid sites where catalytic hydrolysis occurs.

The hydrolysis mechanism of a water-soluble polysaccharide for an H-form zeolite has been proposed (Fig. 3). As shown in Fig. 3, the mechanistic route consists of the following steps: (1) a water molecule adsorbs onto the acid site of an H-form zeolite via an intermolecular hydrogen bond; (2) the soluble polysaccharide diffuses into the internal pores of the zeolite; (3) the polysaccharide undergoes hydrolysis over the acid site with the adsorbed water; and (4) the hydrolysis products diffuse out of the pores. Thus, for cellulose hydrolysis over an H-zeolite catalyst, cellulosic materials need to be dissolved in a solvent and be converted into short sugar chains to make full use of Brønsted acid sites in internal channels of the zeolite. ILs are able to dissolve cellulosic biomass at low temperatures, so it is possible to use these solvents for biomass hydrolysis. Zhang and Zhao [126] performed cellulose hydrolysis by H-zeolite in IL solvents in a microwave reactor at 400 W, and a 37% glucose yield was obtained in 8 min. Under similar conditions,

Table 3
Comparison of catalytic properties and activities of solid acid catalysts for cellulose hydrolysis to glucose.

Catalyst	Amount	Amount of acid sites (mmol/g)	Substrate	Amount	Pretreatment method	Water amount	Reaction temperature (°C)	Reaction time (h)	Glucose yield (%)	Selectivity	Ref.
HSM-5B	0.2 wt%	0.3	Cellobiose	1 wt %	—	—	175	0.5	33.7	74.4	[108]
H-ZSM5	50 mg	—	Cellulose	45 mg	Milling	5 mL	150	24	12	—	[112]
HY	10 mg	—	Cellulose	100 mg	[BMIm][Cl]	10 mg	(240 W)	0.12	35	76	[59]
γ -Al ₂ O ₃	1.5 g	0.05	Cellulose	1.5 g	—	15 mL	150	3	—	—	[113]
Layered HNbMoO ₆	0.2 g	1.9	Cellobiose	1.0 g	—	10 mL	100	18	41	—	[110]
HT-OH _{Ca}	0.5 g	1.17	Cellulose	0.45	Milling	150 mL	150	24	40	85	[92]
Nafion-50	0.1 g	—	Cellulose	0.2 g	[BMIm][Cl]	20 mL	160	4	35	—	[109]
Sulfated ZrNDSBA-15	50 mg	—	Cellobiose	250 mg	—	50 mL	160	1.5	55	65	[114]
FeCl ₃ /Silica	0.47 g	—	Cellulose	2.0 g	[BMIm][Cl]	30 mL	130	24	3	—	[109]
FeCl ₃ /Silica	0.47 g	—	Cellulose	2.0 g	[BMIm][Cl]	30 mL	190	24	9	—	[109]
Amberlyst-15	50 mg	1.8	Cellulose	45 mg	Miling	5 mL	150	24	25	—	[115]
Amberlyst-15	1.5 g	4.4	Cellulose	1.5 g	—	15 mL	150	3	15	—	[113]
Dowex 50wx8-100 ion-exchange resin	26 mg	—	Cellulose	50 mg	[EMIm][Cl]	270 mg	110	4	83	—	[116]
AC-SO ₃ H	50 mg	1.25	Cellulose	45 mg	Milling	5 mL	150	24	40	95	[115]
AC-SO ₃ H-250	0.3 g	2.23	Cellulose	0.27	—	27 mL	150	24	62	74	[117]
Fe ₃ O ₄ -SBA-SO ₃ H	1.5 g	1.09	Cellobiose	1.0 g	—	15 mL	120	1	98	—	[118]
Fe ₃ O ₄ -SBA-SO ₃ H	1.5 g	1.09	Cellulose	1.0 g	[BMIm][Cl]	15 mL	150	3	50	—	[118]
Fe ₃ O ₄ -SBA-SO ₃ H	1.5 g	1.09	Starch	1.0 g	—	15 mL	150	3	95	—	[118]
Fe ₃ O ₄ -SBA-SO ₃ H	1.5 g	1.09	Corn cob	1.0 g	—	15 mL	150	3	45 ^a	—	[118]
PCPs-SO ₃ H	0.2 g	1.8	Cellulose	25 mg	—	2.0 g	120	3	1.4	27	[119]
Ru-CMKs	50 mg	—	Cellulose	324 mg	—	40 mL	230	24	34	51	[120]
Cellulase-MSNs	4.5 mg	—	Cellulose	15 mg	—	—	50	24	90	—	[121]
HPA	0.08 mmol	—	Cellulose	0.1 g	—	5 mL	180	2	51	90	[122]
Cs-HPA	0.07 mmol	—	Cellulose	0.1 g	—	7 mL	170	8	39	89	[123]
Micellar HPA	0.07 mmol	—	Cellulose	0.1 g	—	7 mL	170	8	60	85	[123]

Activated hydrotralcite (HT-OH_{Ca}); Sulfonated activated-carbon (AC-SO₃H); Sulfonic group functionalized magnetic SBA-15 catalyst (Fe₃O₄-SBA-SO₃H); Ru-mesoporous carbon materials (Ru-CMKs); Cellulase immobilized mesoporous silica nanocatalysts (Cellulase-MSNs); Porous coordination polymers decorated with sulfonic acid functional groups (PCPs-SO₃H); Heteropoly acid H₃PW₁₂O₄₀ (HPA).

^a Total yield of reduce sugars.

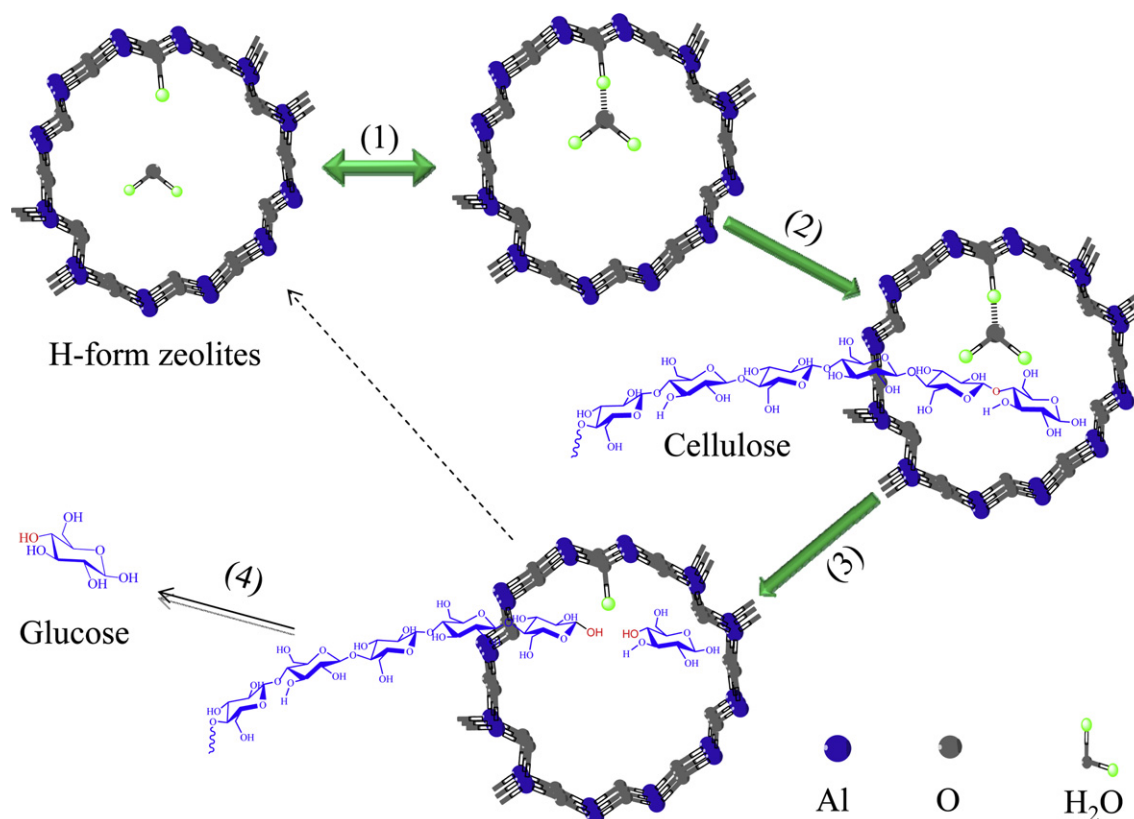


Fig. 3. Mechanism of H-form zeolite catalyzed hydrolysis of cellulose into glucose.

except for heating at 100 °C by oil bath, a yield of 2.1% was achieved after 10 h. Microwave-assisted hydrolysis seems to provide higher selectivity in the reaction pathways than convective heating and also seems to give fewer by-products [127]. These findings strengthen the evidence that solid acid catalysts can provide sufficient activity for biomass hydrolysis with the aid of proper solvents and heating.

Natural cellulosic materials have high crystallinity and unless powdered, they have large particle sizes, and thus they are difficult to disperse into the inner pore of a zeolite. For example, after premilling cellulose, a glucose yield of 12% is obtained using H-ZSM-5 catalyst, but the catalytic efficiency is still lower than that of other solid acid catalysts (Table 3). Onda et al. [115] used mild hydrothermal treatment with solid acid catalysts to hydrolyze cellulose and obtained glucose selectivities higher than 90%. Among the solid acid catalysts they tested, H-form zeolite catalysts gave lower glucose yields than sulfonated activated-carbon catalysts. The apparent reason for the poor performance of the zeolite catalysts was their small pore diameters that limited accessibility and their weak acid sites.

To use H-zeolite catalysts effectively for cellulose hydrolysis, cellulosic materials must be either dissolved in a solvent or catalysts be processed to have pore sizes that allow substrates access to their catalytic sites. Although H-form zeolites have a large surface area and strong acidity, they have been difficult to use in practice due to mass transfer limitations. The active species of protons (H^+) in such catalysts are not freely accessible to the β -1,4-glucans in cellulose. So, from the point of view of industrial practitioners, H-form zeolites are perceived as not being useful for cellulose hydrolysis due to their low activity.

To improve the catalytic efficiency of zeolites, some proposed modifications are discussed below:

- (1) *Loading of cations.* Several alternative cations, such as lanthanum [128] and cerium [129], help to increase the weak acidic sites of zeolites. Loading of cobalt increases total surface acid sites with decline of acid strength [130]. Brønsted acid sites mainly exist in the zeolite crystals, so weak acid surface sites play an important role in hydrolysis of cellulose. An increase in the number of weak acid sites is workable as a method to enhance catalytic activity as these modifications have been used successfully in promoting catalytic efficiency of zeolites in organic reactions [131,132]. Presently, there are no reports on the application of cation modified zeolites for cellulose hydrolysis and so research on the use of these types of catalysts for hydrolysis reactions is needed.
- (2) *Synthesis of zeolites with super-large pores.* Increasing the aperture in zeolite structures would facilitate mass transfer of oligosaccharides to catalytic sites. Techniques of increasing aperture include change of synthesis conditions, addition of pore-formers and change of templates. However, aperture diameters of most current zeolites are on the scale of nanometers [133–135]. Nanometer-scale apertures are not large enough to allow transport of sub-micron scale cellulose through the aperture. It can be concluded that current methods to increase aperture are limited and present zeolite catalysts cannot accommodate many sizes of oligosaccharide particles so that their application is limited. However, these methods may be useful for targeted conversions for which aperture does not limit the substrate, such as dehydration of glycerol, isomerization/cracking of hexane, produce of lighter olefins [136–138]. Cellulose can be processed into nanoparticles, however, it has high-energy requirements and is prohibitive, and the material handling becomes complex including safety due to dust explosions. Increasing acid sites located on the external surface

of zeolites to enhance the external hydrolysis reactions is possible but limited. The external surface hydrolysis reactions result in a non-shape-selective reaction as well as deposition of un-hydrolyzed cellulose, leading to short lifetimes for the catalysts. These issues can be avoided by adopting other treatment methods such as ultrasound. To use the internal acid sites of zeolites effectively, cellulose or its constituents can be dissolved in organic solvents or ILs and processed.

- (3) *Loading of super acids.* Heteropoly acids (HPAs) and super acids are usually supported on zeolites to enhance acidity. HPAs are readily soluble in water and polar organic liquids, and have been applied successfully in homogeneous catalysis. Gagea et al. [139] supported HPAs on ordered mesoporous silica SBA-15, which showed the highest yield (45%) of n-decane for a hydroisomerization reaction. The common method used to obtain zeolites supported HPA catalysts is the direct impregnation of the support with an HPA solution. However, this method is not feasible to obtain high efficiency catalysts for cellulose hydrolysis, because most internal HPAs do not function properly. Incorporation of HPA into zeolites carrier by mixing HPA and zeolites synthesis seems to be able to achieve a strong solid acid [139]. For example, it has been reported [139,140] that the intrinsic acidity of the heteropoly compounds is maintained in zeolites supported HPA catalysts. Since HPA can be incorporated into zeolites, it can be stabilized and is not easily leached during hydrolysis reactions compared with HPA supported on metal oxides by direct impregnation [139].
- (4) *Synthesis of composite zeolites.* Composite zeolites, including micro/micro, micro/mesoporous, micro/macroporous and mesoporous/macroporous composite, have created much interest due to their synergistic performance in catalytic reactions [141–143]. There are many technical factors during synthesis processes, such as amorphism of pore walls formed during synthesis. Such factors lead to low acid strength and poor thermal stability. Composite zeolites that are suitable for shape-selective catalysis in fine chemical industries do not fully display the activity of their internal acid sites for hydrolysis of cellulose that may be attributed to the particle size of cellulose. Yarlagaadda et al. [144] demonstrated that composite zeolite catalysts (HA/ZSM-5/SiO₂–Al₂O₃) are effective for the oligomerization of ethene and propene, while the selectivity remained close to that of pure ZSM-5. Zeolite-based composite catalysts have been employed very successfully in the area of pollution control and synergistic reactions [145,146]. Nevertheless, these composite materials with many attractive features as effective catalysts can be expected to be developed for cellulose hydrolysis in the near future.

Among these four modification techniques, super acid incorporated zeolites are probably the most likely to be applied in cellulose hydrolysis. During the process of cellulose hydrolysis, surface super acid catalysts cleave the β -1,4 glycosidic bonds and the formed oligosaccharides undergo further hydrolysis over the internal acid sites. Therefore, both surface and internal acid sites can participate in hydrolysis reactions, and use of super acid incorporated zeolites has the potential to increase the efficiency of the catalytic system.

4.2. Transition-metal oxides

Metal oxides are composed of cations possessing Lewis acid sites and anions with Brønsted base sites. They are classified into single metal oxides and mixed metal oxides. Transition-metal oxides have catalytic activity for cellulose hydrolysis, and when used as solid acid catalysts, they are reusable and easily separated from reaction

products. Mesoporous transition-metal oxides, such as Nb₂O₅ [147], WO₃ [147], Zr–TMS (transition-metal oxide mesoporous molecular sieves) [148], TiO₂ [149] and Ta₂O₅–WO₃ [150], are widely studied as heterogeneous acid catalysts. The mesopores in a transition-metal oxide allowed the access of reactants to active acid sites inside the pores.

Mesoporous metal oxides have many favorable properties and of these properties, most notably is their high catalytic efficiency. Roggenbuck et al. [151] studied the decomposition of methanol using mesoporous CeO₂ and found that the transformation efficiency increased from 13 to 96% as compared with non-mesoporous CeO₂.

Mesoporous metal oxides have the following special structure properties: (1) high specific surface area, (2) adjustable pore size, and (3) enhanced thermal stability. However, it has been shown that highly crystalline pore walls and high mesoporous order cannot always be achieved for the same material. High temperature heat treatment helps to increase the crystallinity of pore walls, but leads to the collapse of mesoporous structure. Nevertheless, mesoporous metal oxides will become an important research area due to their high catalytic efficiencies.

Tagusagawa et al. [147] used mesoporous Nb–W oxide to catalyze the Friedel–Crafts alkylation of anisole and the hydrolysis of sucrose and cellulose. The mesoporous structure and different acid properties were formed by specific Nb and W concentrations. The turnover frequency of mesoporous Nb–W oxide was more than two times that of non-porous Nb–W oxide. However, total yield of glucose and cellobiose was only 8.5%, indicating that the mesoporous Nb–W oxide had a lower activity for cellulose hydrolysis than conventional acids. Takagaki et al. [109] tested layered transition-metal oxide HNbMoO₆ in the hydrolysis of sucrose, cellobiose, starch and cellulose as shown in Fig. 4. Compared with Amberlyst-15, which is a strongly acidic macro-reticular polymeric resin based on cross-linked styrene divinylbenzene copolymers, layered HNbMoO₆ had a higher turnover frequency due to its strong acidity, water-tolerance, and facile intercalation of saccharides in the strongly acidic interlayer gallery of the catalyst. However, glucose yield was still only about 41% for the hydrolysis of cellobiose. The moderate activity for the layered transition-metal catalyst is interpreted as the protons of the solid acid sites not being freely accessible to the glycosidic linkage of starch and cellulose. Generation of a large amount of protons is needed to compensate for the limited accessibility of the substrate to the solid acid sites [147]. In general, high temperature leads to a high glucose yield, although more side-products (e.g., 5-HMF) are produced.

Hydrolysis efficiency is strongly promoted by the co-catalysis of Lewis acid and Brønsted base sites. Reaction rate and acid strength can be increased by adjustment of proportional transition-metal oxides. In our research, the mixed metal oxide, nano Zn–Ca–Fe oxide, exhibited moderately good catalytic activity for hydrolyzing crystalline cellulose [152]. Cellulose conversion rate and glucose selectivity was 42.6 and 69.2%, respectively. Nanoscale diameter Zn–Ca–Fe oxide suspension can provide more active sites

per gram and has many characteristics of a fluid solution. Nano Zn–Ca–Fe oxides achieve higher cellulose hydrolysis rates and glucose yields compared with fine particle Zn–Ca–Fe oxides. Furthermore, nano Zn–Ca–Fe oxide is paramagnetic due to the presence of iron, and so it has the potential to be separated from products by magnetic filtration techniques. Transition-metal oxides have many favorable characteristics such as simple preparation methods, easy operation and favorable conversion rates, making them good candidates for practical applications.

Mesopores in the oxides enable reactants to access additional active acid sites, so, design of the mesoporous structure is required to improve the surface area and reactant accessibility. Some new techniques can be imagined to allow modification of the metal oxides for catalytic purposes. One-dimensional (1D) nanomaterials have attracted much interest due to their distinct anisotropic shape, unique properties, and great potential in catalytic applications [153]. Some 1D paramagnetic inorganic–organic hybrid nanomaterials have been investigated by Yuan and coworkers [154], who studied various synthetic strategies such as template-directed synthesis, electrospinning and 1D conjugation of building blocks. However, present techniques are lacking for working with these materials due to their anisotropy and super small size. The control of 1D growth is an active research topic as structure control of such 1D paramagnetic nanomaterials might allow the β-1,4 glycosidic bonds in cellulose to become more accessible to catalytic sites and thus could result in many favorable reaction characteristics. Furthermore, 1D paramagnetic nanomaterials may have great utility since they can be physically separated from product mixtures through the introduction of an external magnetic field. Synthesis temperatures are important in forming these 1D paramagnetic materials.

Thus far, ILs have been shown to allow syntheses to occur at room temperature [155,156]. It is speculated that ILs can be used to form 1D paramagnetic nanomaterials for future solid acid catalytic systems.

4.3. Cation-exchange resins

Cation-exchange resins are used commercially as solid acid catalysts in many organic reactions, such as esterification [157], alkylation [158], hydration/dehydration [159,160], and condensation reaction [161]. They are also used to hydrolyze many kinds of compounds such as cellulose [126] and aliphatic esters [157]. As early as the 1960s, Hartler et al. [162] studied cellulose hydrolysis with acidic resins, and found that little hydrolysis occurred for glycosidic bonds but the resins themselves underwent degradation. Later, ion-exchange resins were improved and a maximum glucose yield of 38.9% was obtained using acidic resin NKC-9 for catalytic hydrolysis of cellulose [126]. Amberlyst-15 is an effective catalyst for the selective conversion of cellulose to glucose. More than 25% glucose yield could be obtained at reaction conditions of 150 °C for 24 h with Amberlyst-15 (50 mg) from milled cellulose (45 mg) and distilled water (5.0 mL). Nafion[®] NR50 has a very similar acidic

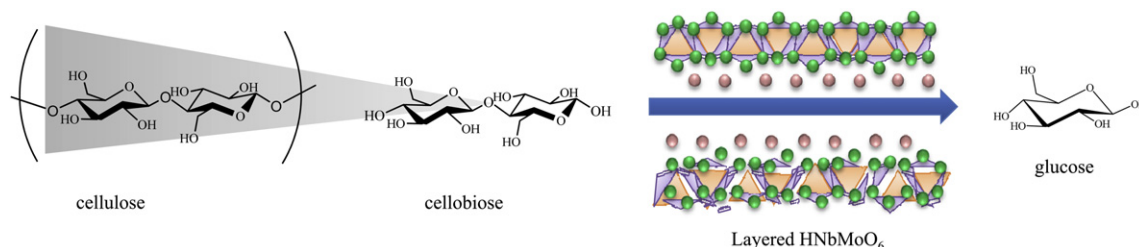


Fig. 4. Glucose production from cellulose using layered transition-metal oxide HNbMoO₆. Reprinted with permission from [109]. Copyright © 2008, The Royal Society of Chemistry.

character to Amberlyst-15 but has better thermal stability. Kim et al. [163] proposed a strategy to enhance the overall process efficiency by combining of ILs and Nafion® NR50, which resulted in the glucose yield of 35%.

A unique merit of cation-exchange resins is that inhibitors in the hydrolyzates can be removed by the resins themselves [164]. Besides acting as catalyst, a cation-exchange resin functions as a membrane that can allow permeation of products during hydrolysis (Fig. 5). Other kinds of solid acids, however, do not have this bifunctional role. Removal of inhibiting compounds would play a positive role in subsequent fermentation processes. However, one problem with cation-exchange resins is that they typically lack stability in hot-water reaction conditions ($>100^{\circ}\text{C}$), and this creates the issue of catalyst recycle due to large amounts of SO_4^{2-} ions that are leached under hydrothermal conditions [115]. Furthermore, pretreatment (e.g., with ILs or dilute acids, Fig. 5) of biomass are needed to improve substrate accessibility to the catalyst.

The catalytic activity of an ion-exchange resin can be improved by loading active sites onto the resin material. Abreu et al. [165] demonstrated that tin oxide modified ion-exchange resin was highly active for the transesterification reaction of vegetable oil and methanol. Upon adding 1-butyl-3-methylimidazolium chloride hexafluorophosphate {[BMIM][PF₆]}, Sn(3-hydroxy-2-methyl-4-pyrone)₂ could be supported by the ion-exchange resin [165]. It was shown that tin oxide modified ion-exchange resin was active for soybean oil methanolysis with biodiesel yields up to 93% being obtained in 3 h. However, from the view point of synthetic chemistry, the above heterogeneous catalysts are not generally useful because tin oxide is easily leached from the modified ion-exchange resin. Especially for cellulose hydrolysis in water medium, catalytic sites will become less stable. Nevertheless, there appears to be opportunities for this method if suitable immobilization or adsorption methods are developed.

The combination of ILs and solid acids can potentially be applied to lignocellulose hydrolysis, because ILs in the hydrolysis reaction

mixture can help to initiate the intrinsic activity of the resins. It has been shown that the dehydration of glucose into 5-HMF can be efficiently performed in ILs. Qi et al. [166] studied the production of 5-HMF from fructose in [BMIM][Cl] using a sulfonic ion-exchange resin as catalyst, and a 5-HMF yield of 82% could be achieved at 120°C in 1 min reaction time. The resin catalytic activity in [BMIM][Cl] was superior to that in the mixed aqueous system. When the dehydration was carried out in acetone-water medium (70:30 w/w), a 5-HMF yield of 73% was achieved at 150°C in 15 min with microwave irradiation [160]. Microwave irradiation appears to affect dehydration reaction rates and as an example, when the dehydration of fructose was conducted in hot compressed water by microwave heating, both fructose conversions and HMF yields (71 and 35%, respectively) were much higher than those obtained by sand bath heating (27 and 12%, respectively). On the basis of the above observations, Qi et al. [116] proposed an effective conversion technique for transforming cellulose into 5-HMF via a two-step process. In the first step, high glucose yield of 83% could be obtained from the cellulose hydrolysis by a strong acidic cation-exchange resin in 1-ethyl-3-methyl imidazolium chloride [EMIM][Cl] with gradual addition of water (Table 3). Previous research by Qi et al. [116] showed that the addition of water inhibited glucose polymerization and thus stabilized glucose in [EMIM][Cl] even in the presence of the strong acidic resin catalyst. It is presumed that hydrolysis of cellulose into glucose by ion-exchange resin can be efficiently promoted in the presence of ILs with microwave heating.

4.4. Supported solid acid catalysts

Supported solid acid catalysts are promising for the depolymerization of cellulose in water, since they have substantial surface acidic species (e.g., 1.5 mmol/g; sulfonated activated-carbon) compared with zeolites (e.g., 0.3 mmol/g; HSM-5B) and transition-metal oxides (e.g., 0.3 mmol/g; Nb₃W₇ oxide) [108,109,112], and specific functional groups. Reported modified

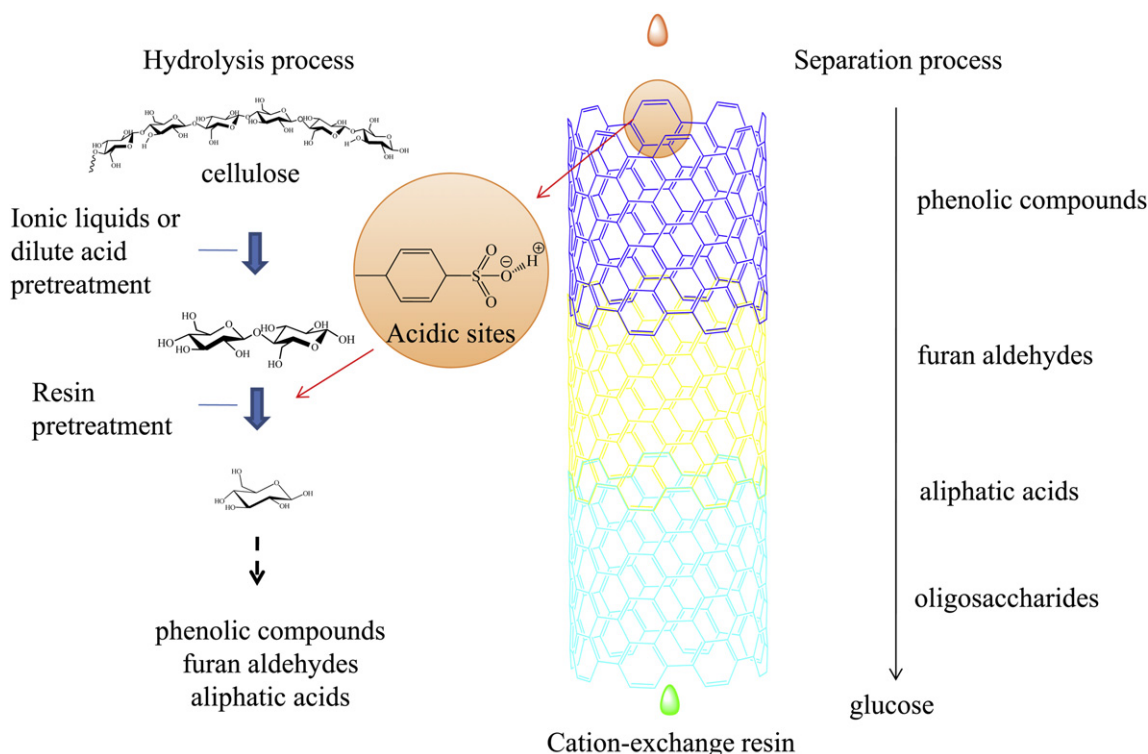


Fig. 5. Combination of cellulose conversion and product separation by cation-exchange resin.

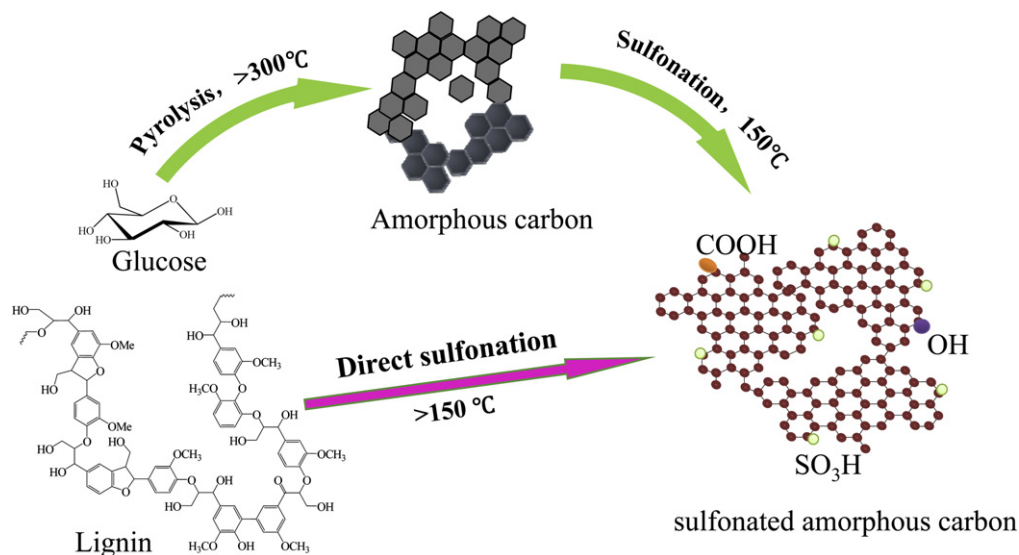


Fig. 6. Preparation of sulfonated amorphous carbon from glucose and lignin by different synthesis pathways.

supports include silica [108,114], polymer resins [167], porous coordination polymers decorated with sulfonic acid functional groups (PCPs-SO₃H) [119] and amorphous carbons [168–170]. Supports should be modified during preparation of catalysts so that catalytic species become anchored and thus can be reused [171,172]. Some amorphous carriers as zeolites and metal oxides mentioned earlier also show good activity (e.g., 37% and 42.6% glucose yields for H-zeolite and metal oxides, respectively) in cellulose hydrolysis [126,152].

4.4.1. Supported metal oxide solid acid catalysts

Metal oxides are widely used as catalyst supports because of their thermal and mechanical stability, high specific surface area, and large pore size (>15 nm) and pore volume (>0.2 mL/g) [173,174]. Because solid acids function the same as H⁺ for cellulose hydrolysis, sulfonated metal oxides, such as SO₄²⁻/Al₂O₃, SO₄²⁻/TiO₂, SO₄²⁻/ZrO₂, SO₄²⁻/SnO₂ and SO₄²⁻/V₂O₅, can supply many acidic species. Such solid acids are usually prepared by impregnating the hydroxides from ammonia precipitation of corresponding metal salt solutions with aqueous sulfuric acids followed by calcination. Metal oxide supported Pt or Ru show high activity for converting cellulose to sugar alcohols with 31% yield being reported [175]. They showed high activity for catalyzing cellulose hydrolysis and glucose isomerization, simultaneously with 88% selectivity of glucose being obtained [175]. The catalysts are active in heterogeneous liquid–solid systems and are recoverable and reusable. However, one limitation of these types of solid catalysts is that the acidic sites become leached from silica surfaces under hydrolytic conditions. Thus, the thermal stability under hydrolytic conditions of the supported solid acid catalysts is an important factor in considering their application since this affects both product separation and catalyst recycle.

4.4.2. Supported carbonaceous solid acid catalysts

Of all of the various types of solid acid catalysts that have been investigated, carbonaceous solid acids (CSAs) seem to be the most effective. The activity and recyclability of CSAs have been demonstrated to be good for biofuel precursors [115], suggesting that they are promising as catalysts for the conversion of cellulose into biofuels. CSAs are derived from sulfonation of carbonized D-glucose or sucrose that was firstly reported by Toda et al. [176] and used in

further studies in the transesterification of vegetable oils with alcohol for biofuels [176–180]. The CSA catalysts were prepared by carbonizing carbohydrates at 400 °C under N₂ atmosphere and then sulfonating the formed materials at 150 °C. CSA catalysts can also be prepared by direct sulfonation of lignin consisting of polyethers and C–C linked phenylpropanes as shown in Fig. 6. The carbon carriers are amorphous, polycyclic aromatic carbon sheets containing SO₃H groups as active sites. The polycyclic carbon sheets can absorb β-1,4-glucans for reactants in solution to access SO₃H groups. Hydrolysis of cellulose to saccharides using such amorphous carbon bearing SO₃H (1.5 mmol/g), COOH (0.4 mmol/g), and OH (5.6 mmol/g) species add functionality [168,181]. Carboxylic acid species, COOH, generally provide more active sites than Nafion NR50 and Amberlyset-15 which could not help to hydrolyze cellulose into glucose. Phenolic OH groups bonded to the graphene sheets can absorb β-1,4 glycosidic bonds and provide good access of solubilized reactants to the SO₃H groups in the carbon material. High glucose yields of up to 75% with 80% selectivity have been reported for reaction conditions at 150 °C and 24 h reaction time by Fukuhara et al. [181].

The mechanism of cellulose hydrolysis with CSA catalysts is similar to that for sulfuric acid. Namely, protons in SO₃H attack the β-1,4 glycosidic bonds in the solid crystalline cellulose. The apparent activation energy (110 kJ/mol) for cellulose conversion into glucose with CSA catalysts is lower than that for sulfuric acid (170 kJ/mol) under optimal conditions. This is attributed to an increase in acidity of the SO₃H groups on the carbon material with a decrease in the amount of water, as was previously demonstrated by Sukanuma and coworkers [168]. CSA catalysts have been shown to convert cellulose into saccharides with high efficiency at temperature of 100 °C and moderate reaction times of 6 h, and they can be recycled [170]. CSA catalysts effectively catalyze hydrolysis of crystalline cellulose that is difficult to realize with conventional strong Brønsted acid catalysts.

CSA catalysts ground to nanosize (10–100 nm) have high catalytic activity for cellulose that has been similarly ground with product selectivities being reported that are higher than 90% [169]. It is interesting to note that in some cases, recycled CSA catalysts exhibit no deactivation in the course of catalytic runs with fresh non-treated cellulose [115]. Furthermore, CSA catalysts are highly efficient for the oxidation of sulfides, tertiary amines, aldehydes

and esterifications, and show many prospects in their applications [182,183].

Although CSAs are highly efficient for cellulose hydrolysis, there are needs for their improvement in the areas of separation and recovery from un-hydrolyzed cellulose residues. Some studies exist on this topic. A report by Lai et al. [118] demonstrated that a paramagnetic solid acid, $\text{Fe}_3\text{O}_4\text{-SBA-SO}_3\text{H}$, could be separated from reaction residues with an external magnetic field. When [BMIM] [Cl] was used as solvent for the pretreatment of microcrystalline cellulose, glucose yields could be increased from 24 to 52% in 3 h (Table 3). Though the used $\text{Fe}_3\text{O}_4\text{-SBA-SO}_3\text{H}$ could be separated from the resulting mixture with a magnetic field, the regeneration for recycle on a large-scale is a research topic. As one possible method, Fe_3O_4 could be introduced as a separation agent into CSA ($\text{Fe}_3\text{O}_4\text{-CSA}$) to provide an efficient mechanism for catalyst recovery. The fundamental prerequisite for using paramagnetic solid nanocatalysts is the incorporation of paramagnetic nanoparticles into the carbonaceous carriers. Compared with immobilizing the nanocatalysts on a solid substrate, the proposed method can regenerate the acidic sites by directly sulfonating the carbonaceous carriers. Thus $\text{Fe}_3\text{O}_4\text{-CSA}$ not only provides good access of reactants to the SO_3H groups, but also has functional characteristics that allow it to be separated and regenerated.

4.5. Heteropoly compounds

HPAs are favored as environmentally benign and economical solid catalysts due to their inherent characteristics of having strong Brønsted acidity, stability and high proton mobility [92]. Owing to their unique physicochemical properties, HPAs are being profitably used in homogeneous, biphasic and heterogeneous systems [184–186]. HPAs (e.g., $\text{H}_3\text{PW}_{12}\text{O}_{40}$) are soluble in water and possess acidic strengths as strong as sulfuric acid. Homogeneous catalysis by HPAs is in principle similar to sulfuric acid in that $[\text{H}^+]$ leaches into solution and interacts with the oxygen atoms in the glycosidic bonds of cellulose. Even under heterogeneous conditions, HPAs are more effective than conventional acid catalysts. For example, glucose selectivities and yields of up to 92% and 51%, respectively, have been reported for conditions of 180 °C and 2 h reaction time [121]. Recovery of the homogeneous catalyst is problematic, however, since extraction with diethyl ether was unsuccessful and thus the catalyst could not be sufficiently extracted and after 6 runs, 8.8% of the $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was lost [121].

Cellulose hydrolysis using solid HPAs was reported by Tian et al. [187]. Several types of acidic cesium salts, $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ ($X = 1-3$), were prepared. The salt $\text{Cs}_1\text{H}_2\text{PW}_{12}\text{O}_{40}$ was found to give the highest glucose yield (30%) at 160 °C for 6 h reaction time.

Solid heteropoly compounds, derived from homogeneous HPAs, are being used as green catalysts in many fields [188–192]. These solid HPA catalysts are obtained by loading HPA species onto

functional carriers like amorphous silica [179], molecular sieve MCM-41 [193] and activated-carbon [194]. Misono [195] proposed three catalytic modes for solid HPAs-surface type, pseudo-liquid (bulk-type I) and bulk-type II (Fig. 7). In some cases, polar molecules are absorbed into the solid bulk, forming a pseudo-liquid phase, and bulk-type I catalysis occurs. The bulk-type II applies to certain catalytic oxidations that largely occur on the catalyst surface, with the bulk diffusion of electrons and protons assisting the redox surface. Cellulose, which has a large molecular size, hydrolyzes on the surface of solid HPA catalysts. Small molecular size intermediate hydrolyzates diffuses into the solid catalyst and then undergoes reaction with pseudo-liquid and then bulk-type II diffusion takes place.

Moderate Lewis acidity favors total reducing sugar (TRS) selectivity so that it can be logically inferred that glucose yield in cellulose hydrolysis can be improved by using solid HPA catalysts in ILs that have a Lewis acid property (Table 1). To allow cellulose molecules access to catalytic sites, micellar HPA catalyst $\text{C}_{16}\text{H}_2\text{PW}$ has been proposed by Cheng et al. [123]. As expected, the micellar HPA catalyst exhibited high activity (Table 3) that can be attributed to cellulose accumulation around the micellar cores. Previous research showed that IR spectrum of the micellar HPA adsorbed cellulose gives four characteristic peaks which indicated that some interaction occurs between the O atom from cellulose and the terminal O atom from the HPA molecules [123]. Cellulose was hydrolyzed for three continuous repeated runs under the same reaction conditions, and complete hydrolysis was achieved. The highest glucose yield reached with the micellar HPA was 60% with 85% selectivity (Table 3) for the three continuous runs. The catalyst was separated from reaction mixtures by simple centrifugation, and recycle has been demonstrated based on three cycles [123]. Solid HPA catalyst process is clean, non-corrosive, energy- and resource-efficient, and probably will find application in industry.

4.6. Comparison of solid acid catalyst activities

Catalyst properties and catalytic activities for the above five types of solid acid catalysts are summarized in Table 3. The most active solid acid is sulfonated amorphous carbon bearing SO_3H , COOH , and OH functional groups. The low yield of hydrolysis products with Nb_3W_7 oxide is due to low mass ratio of catalyst to cellulose and low reaction temperature as compared with the other catalysts.

The highest yields that have been achieved with CSA catalysts are with those that have had a modest surface area and acid amount along with a high catalytic site concentration [170,181]. These conclusions are related to the previously mentioned characteristics of CSA catalysts that make them highly-accessible to reactants. On the other hand, there are still practical issues associated with CSA catalysts. Separation of CSAs from solid biomass residues after hydrolysis for reuse tends to be difficult, since they

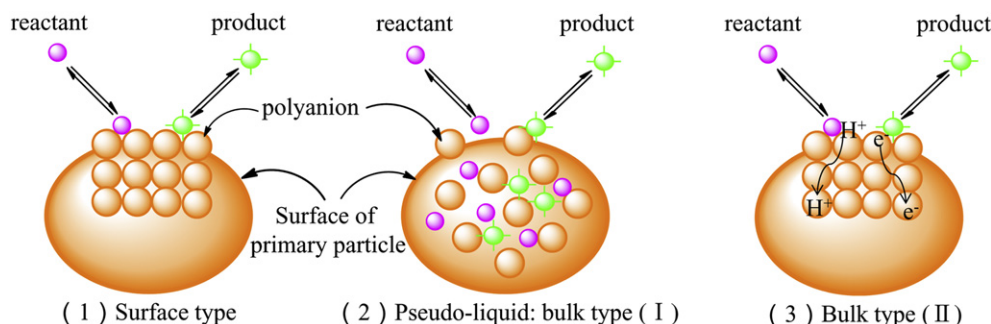


Fig. 7. Catalytic modes for solid heteropoly acids (HPAs). Reprinted with permission from [195]. Copyright © 2008, The Royal Society of Chemistry.

have similar physical and chemical properties as those of the unhydrolyzed cellulose residues. Nevertheless, in terms of their overall performance, solid HPA catalysts have great potential for industrial applications due to their high hydrolysis rates and selectivities. More research is needed both to understand their catalytic properties and to develop effective separation methods.

In concluding this section, it can be seen that solid acid catalysts are relatively easy to apply to chemical processes compared with concentrated or dilute liquid acids for biomass pretreatment or hydrolysis. Solid acid catalysts used as Brønsted acids have many advantages over liquid acids in that they are efficient, non-corrosive, environmentally benign and readily recyclable. The replacement of liquid acids with solid acid catalysts is an exciting trend in the chemical and biotechnology fields, and there are needs for many types of solid acid catalysts.

5. Catalytic biomass hydrolysis with nanoparticle solid acid catalysts

Solid acid catalysts are promising for conversion of cellulosic materials into soluble sugars and have the characteristics that they are environmentally friendly and recoverable. However, there are a number of catalytic systems that have low efficiency, which leads to high-energy consumption and generation of by-products. To improve conversion rates, high temperatures ($>160\text{ }^{\circ}\text{C}$) and high catalyst/substrate ratios ($>1:1$) are used [112,115–120]. However, this cannot only increase the cost of production, but also lead to low product selectivities. Solubilized biomass and nanocatalysts can be used to solve or improve many aspects of solid acid catalysts.

5.1. Nano solid acid catalysts

Nanocatalysis uses nanoparticles that are mixed with solvents and lignocellulosic materials (Table 2). Monodispersed nanoparticles in a solution have the advantage of having the characteristics of a fluid solution, which means that they are more accessible to the oxygen atom in the ether linkage of cellulose. Catalytic species, such as heavy metal complexes, enzymes and organic catalysts, are able to form bonds to the nanoparticles via a monolayer of long-chain

alkanethioles with an SH- or -S-S- terminus [196]. With the domain sites bonded onto the nanoparticle surface, the reaction media become accessible to active sites. The reaction efficiency may also be related to the position and degree of substitution of catalytically active sites in the framework structure, where the active site can be an acidic group that might function by hydrolysis [196].

Although some desired properties can be obtained by means of adjusting the particle size, recycle of nanoparticle materials can be seen as a research barrier due to adsorption, agglomeration, and viscous effects of the reaction mixture. However, by introducing paramagnetic components into the nanoparticle catalysts, it may be possible to separate and recycle solid acid catalysts, since separation factors can be influenced with an external magnetic field [197].

In the work of Gill et al. [196] (Fig. 8), two kinds of acid-functionalized magnetic nanoparticles were prepared: alkyl-sulfonic acid function upon silica-coated magnetic nanoparticles (AS-SiMNPs) and perfluoroalkyl-sulfonic acid function upon silica-coated magnetic nanoparticles (PS-SiMNPs). The hydronium ions (H_3O^+) formed on surface of magnetic nanoparticles lead to promotion of glucose yield in cellulose hydrolysis reaction. Nevertheless, more work is needed to improve the thermal stability, dispersion and affinity of biomass to the catalysts for practical applications.

In our work, hydrotalcite nanoparticles were synthesized and used for catalytic cellulose hydrolysis with good conversion yields [92]. With activated hydrotalcite nanocatalyst, cellulose conversion rates and glucose selectivities of 46.6% and 85.3%, respectively, could be obtained. After 4 cycles of catalyst use, catalytic activity remained stable and thus the nanocatalysts could be reused. Compared with amorphous carbon bearing sulfonic acid groups ($\text{AC-SO}_3\text{H}$), which have high catalytic activity for hydrolysis of cellulose, the activated hydrotalcite nanocatalyst was more stable and easier to separate than the sulfonic acid type catalysts.

5.2. Paramagnetic nanoparticle solid acid catalysts

As discussed previously, dissolution of cellulose and hemicellulose completely or partially in some organic solvents or ILs facilitate solid acid catalysts to approach the β -1,4 glycosidic bonds in cellulose. Furthermore, the large surface area to volume ratio of the solid acid

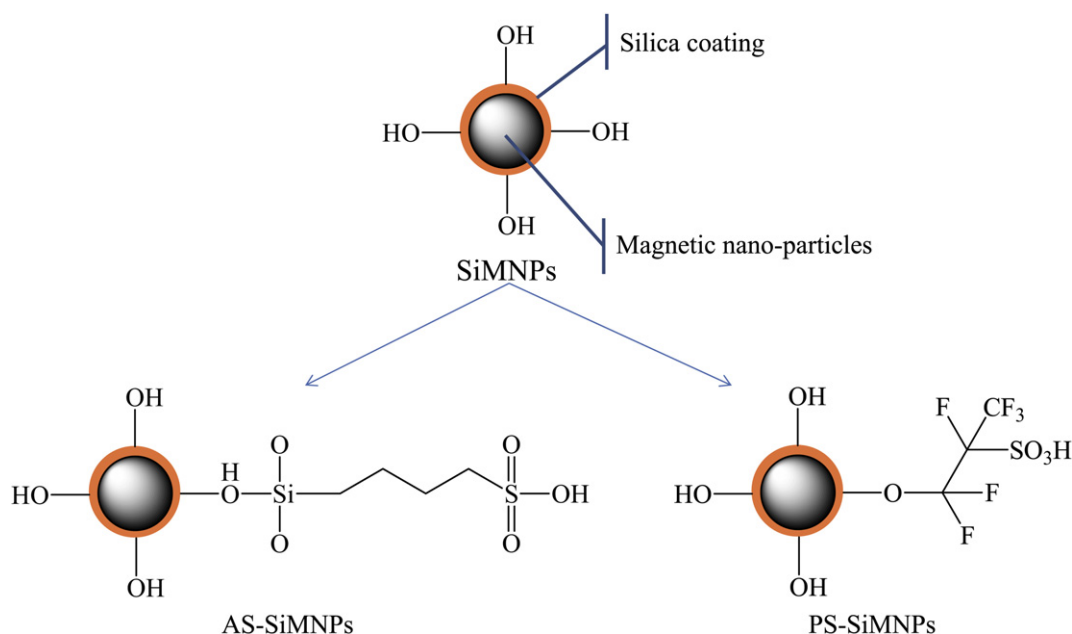


Fig. 8. Acid-functionalized magnetic nanoparticles. Reprinted from [196] with permission. Copyright © 2007, Elsevier. SiMNPs: silica-coated magnetic nanoparticles; AS-SiMNPs: alkyl-Sulfonic acid function upon silica-coated magnetic nanoparticles; HPS-SiMNPs: perfluoroalkyl-sulfonic acid function upon silica-coated magnetic nanoparticles.

nanocatalyst ($>5 \times 10^8$ m), and a large number of surface acid sites per mass (>1 mmol/g) lead to high catalytic activity for hydrolysis [90,198]. Thus, aspects of their recovery need to be addressed.

Monodispersed paramagnetic nanoparticles that are mixed with biomass solutions and can possibly be recovered with external magnetic fields. To take full advantage of solid catalysts in applications, a process is proposed as shown in Fig. 9. In the hydrolysis process, first, raw cellulosic materials are milled to fine powders (micro/nano-meter size). After that, they are dissolved into organic solvents, ILs, alkaline solutions, supercritical fluids and hydrothermal water or mixture of them. Then, hydrolysis of the biomass solution is catalyzed with acid-functionalized paramagnetic nanoparticles that are used with controllable conditions. To overcome mass transfer resistances and to allow acidic sites full access to the β -1,4 glycosidic bonds, the nanoparticles are mixed with the biomass solution by mechanical stirring. After the reaction, the paramagnetic nanoparticles can be recovered for reuse by magnetic filtration. It can be expected that there are many ways to modify the procedure such as heating by microwave radiation, sonication, immobilization, sequential or staged solid catalyst addition, and cascade reactions.

6. Concluding remarks and future outlook

Compared with liquid acid catalysts, solid acid catalysts have distinct advantages in recycling, separation, and environmental friendliness. Solid acid catalysts are easily separated from the

products mixture for reuse after reaction. Besides specific surface area, pore size and pore volume, the active site concentration and acidic type are important factors for solid acid performance. Solid acid catalysts being considered for cellulose hydrolysis should have a large number of Brønsted acid sites, good affinity for the reactant substrates and good thermal stability. Catalyst composition, porosity, and stability in the presence of water are other important properties for solid acids in biomass hydrolysis processing. A good solid catalyst with sufficient catalytic activity combined with appropriate reactor design should make it possible to realize biomass hydrolysis on a practical scale. Among the solid catalysts introduced in this review, acid-functionalized paramagnetic nanoparticles are promising materials for study, since they have the potential to facilitate separation and recycle aspects. Innovation and breakthroughs in hydrolysis efficiency is a key for commercialization of solid acid catalysis.

Recent advances in nanotechnology, such as synthesis of nanoparticles with supercritical water [112] and ILs [199], and in complete solubilization of biomass in ILs, organic electrolyte solutions [200], alkaline solutions, hydrothermal water as well as other green solvents, to biomass solutions may allow biomass to become fully accessible to water molecules and to the acidic sites of nanoparticles [201]. The development of highly acidic solid catalysts with nanometer size that have special characteristics (e.g., paramagnetic properties) is an interesting avenue of research for developing practical systems for biomass hydrolysis. In view of the

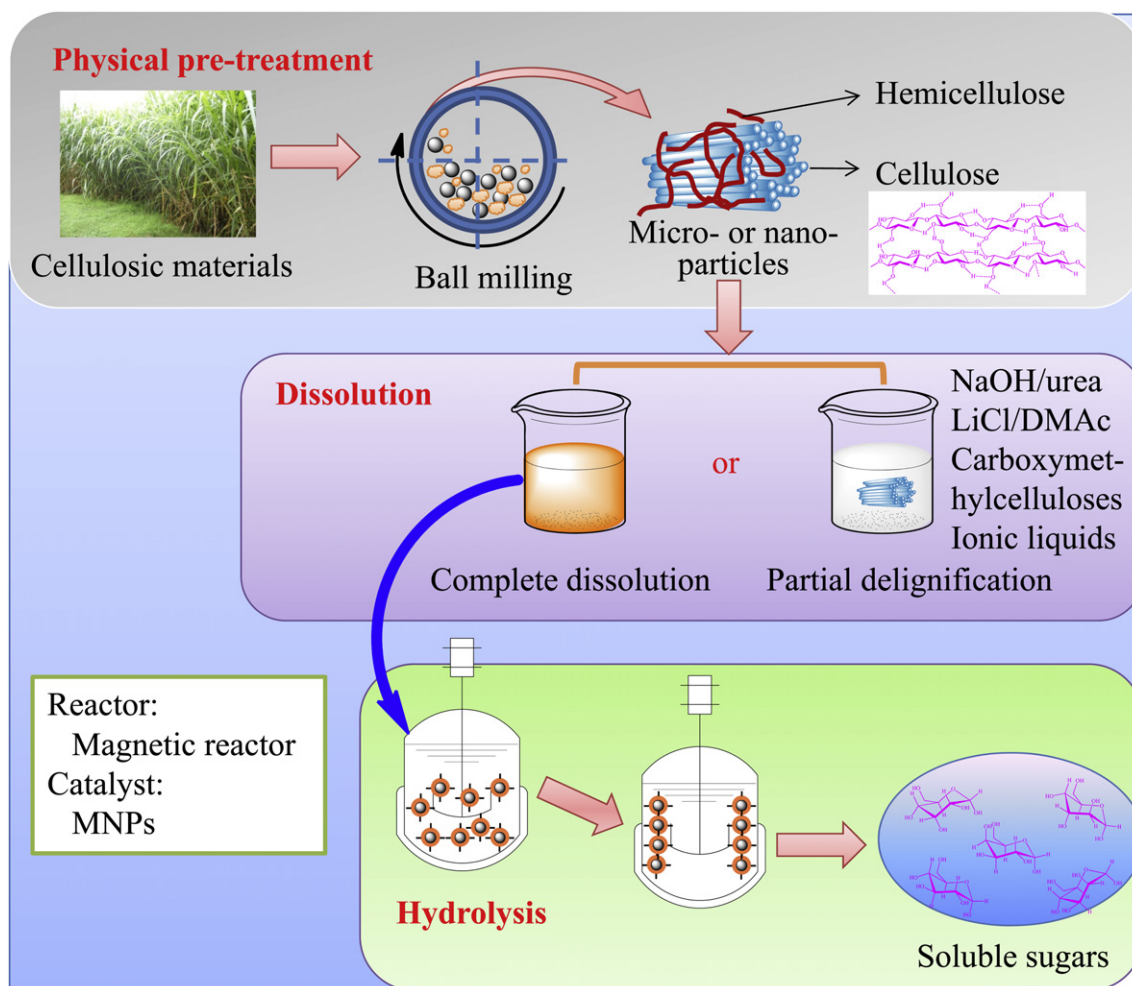


Fig. 9. Hydrolysis of cellulosic material into soluble sugars by metal nanoparticles (MNP).

structural features of cellulosic materials and catalytic characteristics of solid acid catalysts, a process for hydrolyzing cellulosic materials was introduced that uses paramagnetic nanocatalysts. In the near future, through the combination of green solvents, nanoparticle techniques, and functional solid acid catalysts, it can be expected that chemical processes based on the catalysis of biomass will begin to replace petroleum-based processes so that new bio-economic industries will emerge.

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References

- [1] Solomon BD, Barnes JR, Halvorsen KE. Grain and cellulosic ethanol: history, economics, and energy policy. *Biomass Bioenerg* 2007;31(6):416–25.
- [2] Bobleter O. Hydrothermal degradation of polymers derived from plants. *Prog Polym Sci* 1994;19:797–841.
- [3] International energy agency. Key world energy statistics 2009 (http://www.iea.org/textbase/nppdf/free/2009/key_stats_2009.pdf).
- [4] Perlack RD, Wright LL, Turhollow AF, Graham RL, Stokes BJ, Erblich DC. Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply. NREL Report 2005. (http://www1.eere.energy.gov/biomass/pdfs/final_billionton_vision_report2.pdf).
- [5] Binder JB, Raines RT. Fermentable sugars by chemical hydrolysis of biomass. *PNAS* 2010;107(10):4516–21.
- [6] Gírio FM, Fonseca C, Carvalheiro F, Duarte LC, Marques S, Bogel-Lukaski R. Hemicelluloses for fuel ethanol: a review. *Bioresour Technol* 2010;101:4775–800.
- [7] Brethauer S, Wyman CE. Review: continuous hydrolysis and fermentation for cellulosic ethanol production. *Bioresour Technol* 2010;101:4862–74.
- [8] Zhu JY, Pan XJ. Woody biomass pretreatment for cellulosic ethanol production: technology and energy consumption evaluation. *Bioresour Technol* 2011;101:4992–5002.
- [9] Giordano A, Cantù C, Spagni A. Monitoring the biochemical hydrogen and methane potential of the two-stage dark-fermentative process. *Bioresour Technol* 2011;102(6):4474–9.
- [10] Yu D, Aihara M, Antal Jr MJ. Hydrogen production by steam reforming glucose in supercritical water. *Energ Fuel* 1993;7:574–7.
- [11] Xu X, Matsumura Y, Stenberg J, Antal Jr MJ. Carbon-catalyzed gasification of organic feedstocks in supercritical water. *Ind Eng Chem Res* 1996;35:2522–30.
- [12] Schmieder H, Abeln J, Boukis N, Dinjus E, Kruse A, Kluth M, et al. Hydrothermal gasification of biomass and organic wastes. *J Supercritical Fluids* 2000;17:145–53.
- [13] Fang Z, Minowa T, Fang C, Smith Jr RL, Inomata H, Kozinski JA. Catalytic hydrothermal gasification of cellulose and glucose. *Int J Hydrogen Energ* 2008;33(3):981–90.
- [14] Fang Z, Minowa T, Smith Jr RL, Ogi T, Kozinski JA. Liquefaction and gasification of cellulose with Na₂CO₃ and Ni in subcritical water at 350 °C. *Ind Eng Chem Res* 2004;43:2454–63.
- [15] Huber GW, Chheda JN, Barrett CJ, Dumesic JA. Production of liquid alkanes by aqueous-phase processing of biomass-derived carbohydrates. *Science* 2005;308:1446–50.
- [16] Roman-Leshkov Y, Barrett CJ, Liu ZY, Dumesic JA. Production of dimethylfuran for liquid fuels from biomass-derived carbohydrates. *Nature* 2007;447:982–6.
- [17] Thananattachon T, Rauchfuss TB. Efficient production of the liquid 2,5-dimethylfuran from fructose using formic acid as a reagent. *Angew Chem Int Ed* 2010;49:6616–8.
- [18] Sannigrahi P, Pu YQ, Ragauskas A. Cellulosic biorefineries - unleashing lignin opportunities. *Curr Opin Env Sust* 2010;2:383–93.
- [19] Klass DL. Biomass for renewable energy, fuels, and chemicals. An imprint of Elsevier. London: Academic process; 1998.
- [20] Rinaldi R, Schüth F. Design of solid catalysts for the conversion of biomass. *Energy Environ Sci* 2009;2:610–26.
- [21] Torget R, Walter P, Himmel M, Grohmann K. Dilute-acid pretreatment of corn residues and short-rotation woody crops. *Appl Biochem Biotech* 1991;28-29:75–86.
- [22] Qi BK, Chen XG, Wan YH. Pretreatment of wheat straw by nonionic surfactant-assisted dilute acid for enhancing enzymatic hydrolysis and ethanol production. *Bioresour Technol* 2010;101:4875–83.
- [23] Lee YY, Iyer P, Torget RW. Dilute-acid hydrolysis of lignocellulosic biomass. *Adv Biochem Eng Biot* 1999;65:93–115.
- [24] Energy information Administration. International Energy Outlook 2011, Report Number:DOE/EIA-0484(2011) (<http://www.eia.doe.gov/oiaf/ieo/pdf/world.pdf>).
- [25] Balat M, Balat H. Recent trends in global production and utilization of bio-ethanol fuel. *Appl Energ* 2009;86:2273–82.
- [26] Sun Y, Cheng JY. Hydrolysis of lignocellulosic materials for ethanol production: a review. *Bioresour Technol* 2002;83:1–11.
- [27] Kim S, Dale BE. Global potential bioethanol production from wasted crops and crop residues. *Biomass Bioenerg* 2004;26:361–75.
- [28] Dhepe PL, Fukuoka A. Cellulose conversion under heterogeneous catalysis. *ChemSusChem* 2008;1:969–75.
- [29] Pandey A. Handbook of plant-based biofuels. 1st ed. Boca Raton: CRC Press; 2008.
- [30] Duran N, Esposito E. Potential applications of oxidative enzymes and phenoloxidase-like compounds in wastewater and soil treatment: a review. *Appl Catal B-Env* 2000;28(2):83–99.
- [31] Bonini C, D'Auria M, Ernanuele L, Ferri R, Pucciariello R, Sabia AR. Polyurethanes and polyesters from lignin. *J Appl Polym Sci* 2005;98(3):1451–6.
- [32] Depaoli MA, Furlan LT. Sugar-cane bagasse-lignin as photo-stabilizer for butadiene rubber. *Polym Degrad Stab* 1985;11(4):327–37.
- [33] Hayashi J, Kazehaya A, Muroyama K, Watkinson AP. Preparation of activated carbon from lignin by chemical activation. *Carbon* 2000;38(13):1873–8.
- [34] Wu YF, Zhang L, Cui YC. Synthesis of lignin-amine supported palladium catalysts for Heck reaction. *China Petrochem Technol* 2009;38(7):733–8.
- [35] Kelsey RG, Shafizadeh F. Enhancement of cellulose accessibility and enzymatic hydrolysis by simultaneous wet milling. *Biotechnol Bioeng* 2004;22:1025–36.
- [36] Mandels M, Hontz L, Nystrom J. Enzymatic hydrolysis of waste cellulose. *Biotechnol Bioeng* 2010;105:3–25.
- [37] Chang VS, Holtzapple MT. Fundamental factors affecting biomass enzymatic reactivity. *Appl Biochem Biotech* 2000;84-86:5–37.
- [38] Grohmann K, Bothast RJ. Saccharification of corn fiber by combined treatment with dilute sulphuric acid and enzymes. *Process Biochem* 1997;32:405–15.
- [39] Millett MA, Efland MJ, Caulfield DF. Influence of fine grinding on the hydrolysis of cellulosic materials - acid vs. enzymatic. *Adv Chem* 1979;181:71–89.
- [40] Chang MM, Chou TYC, Tsao GT. Structure, pretreatment and hydrolysis of cellulose. *Adv Biochem Eng Biot* 1981;20:15–42.
- [41] Kim SB, Lee YY. Diffusion of sulfuric acid within lignocellulosic biomass particles and its impact on dilute-acid pretreatment. *Bioresour Technol* 2002;83:165–71.
- [42] Kootstra AMJ, Beefink HH, Scott EL, Sanders JPM. Optimization of the dilute maleic acid pretreatment of wheat straw. *Biotechnol Biofuel* 2009;2:31–45.
- [43] Li CL, Knierim B, Manisseri C, Arora R, Scheller HV, Auer M, et al. Comparison of dilute acid and ionic liquid pretreatment of switchgrass: biomass recalcitrance, delignification and enzymatic saccharification. *Bioresour Technol* 2010;101:4900–6.
- [44] Silverstein RA, Chen Y, Sharma-Shivappa RR, Boyette MD, Osborne J. A comparison of chemical pretreatment methods for improving saccharification of cotton stalks. *Bioresour Technol* 2007;98:3000–11.
- [45] Bjerre AB, Olesen AB, Fernqvist T, Ploger A, Schmidt AS. Pretreatment of wheat straw using combined wet oxidation and alkaline hydrolysis resulting in convertible cellulose and hemicellulose. *Biotechnol Bioeng* 1996;49:568–77.
- [46] Ishii D, Tatsumi D, Matsumoto T. Effect of solvent exchange on the supra-molecular structure, the molecular mobility and the dissolution behavior of cellulose in LiCl/DMAc. *Carbohydr Res* 2008;343:919–28.
- [47] Song YB, Zhou JP, Zhang LN, Wu XJ. Homogenous modification of cellulose with acrylamide in NaOH/urea aqueous solutions. *Carbohydr Polym* 2008;73:18–25.
- [48] Okatova OV, Lavrenko PN, Cvetkov VN, Dautzenberg H, Philipp B. Viscometric and diffusion investigations in the cellulose/cadoxen/water system. *Acta Polym* 2003;40:297–301.
- [49] Ramos LA, Frollini E, Heinze T. Carboxymethylation of cellulose in the new solvent dimethyl sulfoxide/tetrabutylammonium fluoride. *Carbohydr Polym* 2005;60:259–67.
- [50] Feng L, Chen Z. Research progress on dissolution and functional modification of cellulose in ionic liquids. *J Mol Liq* 2008;142:1–5.
- [51] Weingärtner H. Understanding ionic liquids at the molecular level: facts, problems, and controversies. *Angew Chem Int Ed* 2007;47:654–70.
- [52] Moulthrop JS, Swatloski RP, Moyna G, Rogers RD. High-resolution ¹³C NMR studies of cellulose and cellulose oligomers in ionic liquid solutions. *Chem Commun* 2005;12:1557–9.
- [53] Swatloski RP, Spear SK, Holbrey JD, Rogers RD. Dissolution of cellulose with ionic liquids. *J Am Chem Soc* 2002;124:4974–5.
- [54] Zakrzewska ME, Bogel-yukaski E, Bogel-yukaski R. Solubility of carbohydrates in ionic liquids. *Energ Fuel* 2010;24:737–45.
- [55] Mosier N, Wyman C, Dale B, Elander R, Lee YY, Holtzapple M, et al. Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresour Technol* 2005;96:673–86.

- [56] Welton T. Ionic liquids in catalysis. *Coord Chem Rev* 2004;248:2459–77.
- [57] Tao FR, Song HL, Chou LJ. Hydrolysis of cellulose in SO(3)H-functionalized ionic liquids. *Bioresour Technol* 2011;102:9000–6.
- [58] King AW, Asikkala A, Mutikainen I, Järvi P, Kilpeläinen I. Distillable acid-base conjugate ionic liquids for cellulose dissolution and processing. *Angew Chem* 2011;123:6425–9.
- [59] Zavrela M, Brossa D, Funkea M, Büchsa J, Spiess AC. High-throughput screening for ionic liquids dissolving (ligno-)cellulose. *Bioresour Technol* 2009;100:2580–7.
- [60] Wang XJ, Li HQ, Cao Y, Tang Q. Cellulose extraction from wood chip in an ionic liquid 1-allyl-3-methylimidazolium chloride (AmimCl). *Bioresour Technol* 2011;102:7959–65.
- [61] Spronsen J, Amares Cardoso MA, Witkamp GJ, Jong W, Kroon MC. Separation and recovery of the constituents from lignocellulosic biomass by using ionic liquids and acetic acid as co-solvents for mild hydrolysis. *Chem Eng Process* 2011;50:196–9.
- [62] Brandt A, Ray MJ, To TQ, Leak D, Murphy RJ, Welton T. Ionic liquid pretreatment of lignocellulosic biomass with ionic liquid-water mixtures. *Green Chem* 2011;13:2489–99.
- [63] Jia SY, Cox BJ, Guo XW, Zhang ZC, Ekerdt JG. Cleaving the β -O-4 bonds of lignin model compounds in an acidic ionic liquid, 1-H-3-methylimidazolium chloride: an optional strategy for the degradation of lignin. *ChemSusChem* 2010;3:1078–84.
- [64] Amarasekara A, Owereh OS. Hydrolysis and decomposition of cellulose in Bronsted acidic ionic liquids under mild conditions. *Ind Eng Chem Res* 2009;48:10152–5.
- [65] Guo F, Fang Z, Tian XF, Long YD, Jiang LQ. One-step production of biodiesel from *Jatropha* oil with high-acid value in ionic liquids. *Bioresour Technol* 2011;102:6469–72.
- [66] Qi XH, Watanabe M, Aida TM, Smith Jr RL. Efficient catalytic conversion of fructose into 5-hydroxymethylfurfural in ionic liquids at room temperature. *ChemSusChem* 2009;10:944–6.
- [67] Qi XH, Watanabe M, Aida TM, Smith Jr RL. Efficient one-pot production of 5-hydroxymethylfurfural from inulin in ionic liquids. *Green Chem* 2010;12:1855–60.
- [68] Nanjing Forestry Institute. *Plant hydrolysis technology*. 1st ed. Beijing: Agricultural Press; 1961.
- [69] Saeman JF, Bubl JL, Harris EE. Quantitative saccharification of wood and cellulose. *Ind Eng Chem Anal Ed* 1945;17:35–7.
- [70] Camacho F, González-Tello P, Jurado E, Robles A. Microcrystalline-cellulose hydrolysis with concentrated sulphuric acid. *J Chem Technol Biotechnol* 1996;67:350–6.
- [71] Stevens CV, Deswarte FEI. *Introduction to chemicals from biomass*. 1st ed. John Wiley & Sons; 2008.
- [72] Nguyen QA, Tucker MP, Keller FA, Eddy FP. Two-stage dilute-acid pretreatment of softwoods. *Appl Biochem Biotechnol* 2000;84–86:561–76.
- [73] Kim KH, Tucker MP, Nguyen QA. Effects of pressing lignocellulosic biomass on sugar yield in two-stage dilute-acid hydrolysis process. *Biotechnol Prog* 2002;18:489–94.
- [74] Fang Z. *Complete dissolution and oxidation of organic wastes in water*. 1st ed. Germany: VDM Verlag; 2009.
- [75] Fang Z. *Rapid production of micro- and nano-particles using supercritical water*. 1st ed. Germany: Springer-Verlag; 2010.
- [76] Sasaki M, Fang Z, Fukushima Y, Adschiri T, Arai K. Dissolution and hydrolysis of cellulose in subcritical and supercritical water. *Ind Eng Chem Res* 2000;39:2883–90.
- [77] Fang Z, Fang C. Complete dissolution and hydrolysis of wood in hot water. *AIChE J* 2008;54:2751–8.
- [78] Fang Z. Noncatalytic fast hydrolysis of wood. *Bioresour Technol* 2011;102:3587–90.
- [79] Sasaki M, Kabyemela B, Malaluan R, Hirose S, Takeda N, Adschiri T, et al. Cellulose hydrolysis in subcritical and supercritical water. *J Supercrit Fluid* 1998;13:261–8.
- [80] Sasaki M, Adschiri T, Arai K. Kinetics of cellulose conversion at 25 MPa in sub- and supercritical water. *AIChE J* 2004;50:192–202.
- [81] Eriksson T, Börjesson J, Tjerneld F. Mechanism of surfactant effect in enzymatic hydrolysis of lignocellulose. *Enzym Microb Technol* 2002;31:353–64.
- [82] Hosseini SA, Shah N. Enzymatic hydrolysis of cellulose part II: Population balance modelling of hydrolysis by exoglucanase and universal kinetic model. *Biomass Bioenergy* 2011;35:3830–40.
- [83] Hosseini SA, Shah N. Modelling enzymatic hydrolysis of cellulose part I: population balance modelling of hydrolysis by endoglucanase. *Biomass Bioenergy* 2011;35:3841–8.
- [84] Zhang MJ, Su RG, Qi W, He ZM. Enhanced enzymatic hydrolysis of lignocellulose by optimizing enzyme complexes. *Appl Biochem Biotechnol* 2010;160:1407–14.
- [85] Palmqvist E, Hahn-Hägerdal B. Fermentation of lignocellulosic hydrolysates. II: inhibitors and mechanisms of inhibition. *Bioresour Technol* 2000;74:25–33.
- [86] Marques S, Alves L, Roseiro JC, Gírio FM. Conversion of recycled paper sludge to ethanol by SHF and SSF using *Pichia stipitis*. *Biomass Bioenergy* 2008;32:400–6.
- [87] Xue J, Chen HZ, Kadar Z. Optimization of microwave pretreatment on wheat straw for ethanol production. *Biomass Bioenergy* 2011;35:3859–64.
- [88] Chen WH, Tu YJ, Sheen HK. Disruption of sugarcane bagasse lignocellulosic structure by means of dilute sulfuric acid pretreatment with microwave-assisted heating. *Appl Energy* 2011;88:2726–34.
- [89] Mikkola JP, Kirilina A, Tuuf JC, Pranovich A, Holmbom B, Kustov LM, et al. Ultrasound enhancement of cellulose processing in ionic liquids: from dissolution towards functionalization. *Green Chem* 2007;9:1229–37.
- [90] Lan W, Liu CF, Yue FX. Ultrasound-assisted dissolution of cellulose in ionic liquid. *Carbohydr Polym* 2011;86:672–7.
- [91] Liao HD, Chen D, Yuan L, Zheng M, Zhu YH, Liu XM. Immobilized cellulase by polyvinyl alcohol/Fe(2)O(3) magnetic nanoparticle to degrade microcrystalline cellulose. *Carbohydr Polym* 2010;82:600–4.
- [92] Fang Z, Zhang F, Zeng HY, Guo F. Production of glucose by hydrolysis of cellulose at 423 K in the presence of activated hydrotalcite nanoparticles. *Bioresour Technol* 2011;102:8017–21.
- [93] Zhu SD, Wu YX, Yu ZN, Liao JT, Zhang Y. Pretreatment by microwave/alkali of rice straw and its enzymic hydrolysis. *Process Biochem* 2005;40:3082–6.
- [94] Ma H, Liu WW, Wu YJ, Yu ZL. Enhanced enzymatic saccharification of rice straw by microwave pretreatment. *Bioresour Technol* 2009;100:1279–84.
- [95] Krieger-Brockett B. Microwave pyrolysis of biomass. *Res Chem Intermed* 1994;20:39–49.
- [96] Wu YY, Fu ZH, Y DL, Xu Q, Liu FL, Lu CL, et al. Microwave-assisted hydrolysis of crystalline cellulose catalyzed by biomass char sulfonic acids. *Green Chem* 2010;12:696–700.
- [97] Possidonio S, Fidale LC, Seoud OAE. Microwave-assisted derivatization of cellulose in an ionic liquid: an efficient, expedient synthesis of simple and mixed carboxylic esters. *J Polym Sci Polym Chem* 2010;48:134–43.
- [98] Ooshima H, Aso K, Harano Y. Microwave treatment of cellulosic materials for their enzymatic hydrolysis. *Biotechnol Lett* 1988;5:289–94.
- [99] Kardos N, Luche JL. Sonochemistry of carbohydrate compounds. *Carbohydr Res* 2001;332:115–31.
- [100] Alviraa P, Tomas-Pejo E, Ballesterosa M, Negro MJ. Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: a review. *Bioresour Technol* 2010;101:4851–61.
- [101] Zhang YQ, Fu EH, Liang JH. Effect of ultrasonic waves on the saccharification processes of lignocellulose. *Chem Eng Technol* 2008;31:1510–5.
- [102] Lan W, Liu CF, Yue FX, Sun RC, Kennedy JF. Ultrasound-assisted dissolution of cellulose in ionic liquid. *Carbohydr Polym* 2011;86:672–7.
- [103] Tang A, Zhang H, Chen G, Xie G, Liang W. Influence of ultrasound treatment on accessibility and regioselective oxidation reactivity of cellulose. *Ultrason Sonochem* 2005;12:467–72.
- [104] Sun RC, Tomkinson J. Characterization of hemicelluloses obtained by classical and ultrasonically assisted extractions from wheat straw. *Carbohydr Polym* 2002;50:263–71.
- [105] Suslick KS, Price GJ. Applications of ultrasound to materials chemistry. *Annu Rev Mater Sci* 1999;29:295–326.
- [106] Mason TJ. Large scale sonochemical processing: aspiration and actuality. *Ultrason Sonochem* 2000;7:145–9.
- [107] Dolatowski ZJ, Stadnik J, Stasiak D. Applications of ultrasound in food technology. *Acta Sci Pol. Technol Aliment* 2007;6:89–99.
- [108] Bootsma JA, Shanks BH. Cellobiose hydrolysis using organic-inorganic hybrid mesoporous silica catalysts. *Appl Catal A-Gen* 2007;327:44–51.
- [109] Takagaki A, Tagusagawa C, Domen K. Glucose production from saccharides using layered transition metal oxide and exfoliated nanosheets as a water-tolerant solid acid catalyst. *Chem Commun* 2008;42:536–45.
- [110] Vigier KDO, Jérôme F. Heterogeneously-catalyzed conversion of carbohydrates. *Top Curr Chem* 2010;295:63–92.
- [111] Shimizu K, Satsum A. Toward a rational control of solid acid catalysis for green synthesis and biomass conversion. *Energy Environ Sci* 2011;4:3140–53.
- [112] Rinaldi R, Palkovits R, Schüth F. Depolymerization of cellulose using solid catalysts in ionic liquids. *Angew Chem* 2008;120:8167–70.
- [113] Lai DM, Deng L, Li J, Liao B, Guo QX, Fu Y. Hydrolysis of cellulose into glucose by magnetic solid acid. *ChemSusChem* 2011;4:55–8.
- [114] Degirmenci V, Uner D, Cinlar B, Shanks BH, Yilmaz A, Santen RA, et al. Sulfated zirconia modified SBA-15 catalysts for cellobiose hydrolysis. *Catal Lett* 2011;141:33–42.
- [115] Onda A, Ochi T, Yanagisawa K. Selective hydrolysis of cellulose into glucose over solid acid catalysts. *Green Chem* 2008;10:1033–7.
- [116] Qi XH, Watanabe M, Aida TM, Smith Jr RL. Catalytic conversion of cellulose into 5-hydroxymethylfurfural in high yields via a two-step process. *Cellulose* 2011;18:1327–33.
- [117] Pang JF, Wang AQ, Zheng MY, Zhang T. Hydrolysis of cellulose into glucose over carbons sulfonated at elevated temperatures. *Chem Commun* 2010;46:6935–7.
- [118] Lai DM, Deng L, Guo QX, Fu Y. Hydrolysis of biomass by magnetic solid acid. *Energy Environ Sci* 2011;4:3552–7.
- [119] Akiyama G, Matsuda R, Sato H, Takata M, Kitagawa S. Cellulose hydrolysis by a new porous coordination polymer decorated with sulfonic acid functional groups. *Adv Mater* 2011;23:3294–7.
- [120] Kobayashi H, Komanoya T, Hara K, Fukuoka A. Water-tolerant mesoporous-carbon-supported ruthenium catalysts for the hydrolysis of cellulose to glucose. *ChemSusChem* 2010;3:440–3.
- [121] Chang RHY, Jang J, Wu KCW. Cellulase immobilized mesoporous silica nanocatalysts for efficient cellulose-to-glucose conversion. *Green Chem* 2011;13:2844–50.
- [122] Tian J, Wang J, Zhao S, Jiang C, Zhang X, Wang X. Hydrolysis of cellulose by the heteropoly acid H₃PW₁₂O₄₀. *Cellulose* 2010;17:587–94.

- [123] Cheng MX, Shi T, Guan HY, Wang ST, Wang XH, Jiang ZJ. Clean production of glucose from polysaccharides using a micellar heteropolyacid as a heterogeneous catalyst. *Appl Catal B-Env* 2011;107:104–9.
- [124] Salman N, Rüscher CH, Buhl JC, Lutz W, Toufar H, Stöcker M. Effect of temperature and time in the hydrothermal treatment of HY zeolite. *Micropor Mesopor Mat* 2006;90:339–46.
- [125] Dimitrijevic R, Lutz W, Ritzmann A. Hydrothermal stability of zeolites: Determination of extra-framework species of H-Y faujasite-type steamed zeolite. *J Phys Chem Solids* 2006;67:1741–8.
- [126] Zhang Z, Zhao ZK. Solid acid and microwave-assisted hydrolysis of cellulose in ionic liquid. *Carbohydr Res* 2009;344:2069–72.
- [127] Hou A, Wang X, Wu L. Effect of microwave irradiation on the physical properties and morphological structures of cotton cellulose. *Carbohydr Polym* 2008;74:934–7.
- [128] Huang J, Jiang Y, Marthala VRR, Ooi YS, Weitkamp J, Hunger M. Concentration and acid strength of hydroxyl groups in zeolites La, Na-X and La, Na-Y with different lanthanum exchange degrees studied by solid-state NMR spectroscopy. *Micropor Mesopor Mat* 2007;104:129–36.
- [129] Pedrosa AMG, Souza MJB, Silva AOS, Melo DMA, Araujo AS. Effect of cerium, holmium and samarium ions on the thermal and structural properties of the HZSM-12 zeolite. *J Therm Anal Calorim* 2006;84:503–9.
- [130] Pedrosa AMG, Souza MJB, Silva AOS, Melo DMA, Araujo AS. Synthesis, characterization and catalytic properties of the cobalt and nickel supported on HZSM-12 zeolite. *Catal Comm* 2006;7:791–6.
- [131] Zhang YW, Zhou YM, Liu H, Wang Y, Xu Y, Wu PC. Effect of La addition on catalytic performance of PtSnNa/ZSM-5 catalyst for propane dehydrogenation. *Appl Catal A Gen* 2007;333:202–10.
- [132] Sugi Y, Kubota Y, Komura K, Sugiyama N, Hayashi M, Kim JH, et al. Shape-selective alkylation and related reactions of mononuclear aromatic hydrocarbons over H-ZSM-5 zeolites modified with lanthanum and cerium oxides. *Appl Catal A Gen* 2006;299:157–66.
- [133] Wang Y, Cui DM, Li QZ. Synthesis, characterization and influence parameters on the overgrowth of micro/mesoporous Y-zeolite-MCM-41 composite material under acidic conditions. *Micropor Mesopor Mat* 2011;142:503–10.
- [134] Min HK, Chidambaram V, Hong SB. Diethylated diphenylethane species: main reaction intermediates of ethylbenzene disproportionation over large-pore zeolites. *J Phys Chem C* 2010;114:1190–3.
- [135] Zhang L, Liu AL, Xie SJ, Xu LY. Organic template-free synthesis of ZSM-5/ZSM-11 co-crystalline zeolite. *Micropor Mesopor Mat* 2012;147:117–26.
- [136] Jia CJ, Liu Y, Schmidt W, Lu AH, Schüth F. Small-sized HZSM-5 zeolite as highly active catalyst for gas phase dehydration of glycerol to acrolein. *J Catal* 2010;269:71–9.
- [137] Inagaki S, Takechi K, Kubota Y. Selective formation of propylene by hexane cracking over MCM-68 zeolite catalyst. *Chem Commun* 2010;46:2662–4.
- [138] Bi J, Liu M, Song C, Wang X, Guo X. C₂–C₄ light olefins from bioethanol catalyzed by Ce-modified nanocrystalline HZSM-5 zeolite catalysts. *Appl Catal B Env* 2011;107:68–76.
- [139] Gagea BC, Lorgouilloux Y, Altintas Y, Jacobs PA, Martens JA. Bifunctional conversion of n-decane over HPW heteropoly acid incorporated into SBA-15 during synthesis. *J Catal* 2009;265:99–108.
- [140] Kamalakar G, Komura K, Sugi Y. Tungstophosphoric acid supported on MCM-41 mesoporous silicate: an efficient catalyst for the di-tert-butylation of cresols with tert-butanol in supercritical carbon dioxide. *Appl Catal A Gen* 2006;310:155–63.
- [141] Xie S, Liu K, Liu S, Liu Y, Zhang W, Xu L. The crystallization process of MCM-49/ZSM-35 composite zeolites in a mixed-amine system. *Chin J Catal* 2010;31:1071–6.
- [142] Prokešová P, Mintova S, Čejka J, Bein T. Preparation of nanosized micro/mesoporous composites via simultaneous synthesis of Beta/MCM-48 phases. *Micropor Mesopor Mat* 2003;64:165–74.
- [143] Schmidt H, Koch D, Grathwohl G, Colombo P. Micro-/macroporous ceramics from preceramic precursors. *J Am Ceram Soc* 2001;84:2252–5.
- [144] Yarlagadda P, Lund CRF, Ruckenstein E. Oligomerization of ethene and propene over composite zeolite catalysts. *Appl Catal* 1990;62:125–39.
- [145] Foo KY, Hameed BH. The environmental applications of activated carbon/zeolite composite materials. *Adv Colloid Interfac* 2011;162:22–8.
- [146] Shen Q, Zhang W, Hao Z, Zou L. A study on the synergistic adsorptive and photocatalytic activities of TiO₂-xN₂/beta composite catalysts under visible light irradiation. *Chem Eng J* 2010;165:301–9.
- [147] Tagusagawa C, Takagaki A, Iguchi A, Takanabe K, Kondo JN, Ebitani K, et al. Highly active mesoporous Nb-W oxide solid-acid catalyst. *Angew Chem Int Ed* 2010;49:1128–32.
- [148] Chidambaram M, Curulla-Ferre D, Singh AP, Anderson BG. Synthesis and characterization of triflic acid-functionalized mesoporous Zr-TMS catalysts: heterogenization of CF₃SO₃H over Zr-TMS and its catalytic activity. *J Catal* 2003;220:442–56.
- [149] Kondo JN, Yamashita T, Nakajima K, Lu D, Hara M, Domen K. Preparation and crystallization characteristics of mesoporous TiO₂ and mixed oxides. *J Mater Chem* 2005;15:2035–40.
- [150] Tagusagawa C, Takagaki A, Iguchi A, Takanabe K, Kondo JN, Ebitani K, et al. Synthesis and characterization of mesoporous Ta-W oxides as strong solid acid catalysts. *Chem Mater* 2010;22:3072–8.
- [151] Roggenbuck J, Schafer H, Tsoncheva T, Minchev C, Hanss J, Tiemann M. Mesoporous CeO₂: synthesis by nanocasting, characterisation and catalytic properties. *Microp Mesopor Mater* 2007;101:335–41.
- [152] Zhang F, Deng X, Fang Z, Zeng HY, Tian XF, Kozinski JA. Hydrolysis of crystalline cellulose over Zn-Ca-Fe oxide catalyst. *Petrochem Technol* 2011;40:43–8.
- [153] Zhang ZY, Zou RJ, Yu L, Hu JQ. Recent research on one-dimensional silicon-based semiconductor nanomaterials: synthesis, structures, properties and applications. *Crit Rev Solid State* 2011;36:148–73.
- [154] Yuan JY, Xu YY, Müller AHE. One-dimensional magnetic inorganic-organic hybrid nanomaterials. *Chem Soc Rev* 2011;40:640–55.
- [155] Luo H, Zou D, Zhou L, Ying T. Ionic liquid-assisted synthesis of transition metal oxalates via one-step solid-state reaction. *J Alloy Comd* 2009;481:12–4.
- [156] Zou D, Xu C, Luo H, Wang L, Ying T. Synthesis of Co₃O₄ nanoparticles via an ionic liquid-assisted methodology at room temperature. *Mater Lett* 2008;62:1976–8.
- [157] Sanz MT, Murga R, Beltran S, Cabezas JL. Autocatalyzed and ion-exchange-resin-catalyzed esterification kinetics of lactic acid with methanol. *Ind Eng Chem Res* 2002;41:512–7.
- [158] Uozumi Y, Shibatiomi K. Catalytic asymmetric allylic alkylation in water with a recyclable amphiphilic resin-supported P, N-chelating palladium complex. *J Am Chem Soc* 2001;123:2919–20.
- [159] Okada T, Harada M. Hydration of halide anions in ion-exchange resin and their dissociation from cationic groups. *Anal Chem* 2004;76:4564–71.
- [160] Qi XH, Watanabe M, Aida TM. Catalytic dehydration of fructose into 5-hydroxymethylfurfural by ion-exchange resin in mixed-aqueous system by microwave heating. *Green Chem* 2008;10:799–805.
- [161] Zheng HL, Guan CJ, Feng XL, Zhao CX. Synthesis of macroreticular p-(ω-sulfonic-perfluoroalkylated)polystyrene ion-exchange resin and its application as solid acid catalyst. *J Mol Catal A-Chem* 2006;247:19–26.
- [162] Hartler N, Hyllegren K. Heterogeneous hydrolysis of cellulose with high polymer acids. Part 3. The acid hydrolysis of cellulose with finely divided cation-exchange resin in the hydrogen form. *J Polym Sci* 1962;56:425–34.
- [163] Kim SJ, Dwiatmoko AA, Choi JW, Suh YW, Suh DJ, Oh M. Cellulose pretreatment with 1-n-butyl-3-methylimidazolium chloride for solid acid-catalyzed hydrolysis. *Bioresour Technol* 2010;101:8273–9.
- [164] Nilvebrant NO, Reimann A, Larsson S, Jönsson LJ. Detoxification of lignocellulose hydrolysates with ion-exchange resins. *Appl Biochem Biotechnol* 2001;91-93:35–49.
- [165] Abreu FR, Alves MB, Macêdo CCS, Zara LF, Suarez PAZ. New multi-phase catalytic systems based on tin compounds active for vegetable oil transesterification reaction. *J Mol Catal A Chem* 2005;227:263–7.
- [166] Qi XH, Watanabe M, Aida TM, Smith Jr RL. Efficient process for conversion of fructose to 5-hydroxymethylfurfural with ionic liquids. *Green Chem* 2009;11:1327–31.
- [167] Hegner J, Pereira KC, DeBoef B, Lucht BL. Conversion of cellulose to glucose and levulinic acid via solid-supported acid catalysis. *Tetrahedron Lett* 2010;51:2356–8.
- [168] Suganuma S, Nakajima K, Kitano M, Yamaguchi D, Kato H, Hayashi S, et al. Hydrolysis of cellulose by amorphous carbon bearing SO₃H, COOH, and OH groups. *J Am Chem Soc* 2008;130:12787–93.
- [169] Yamaguchi D, Kitano M, Suganuma S, Nakajima K, Kato H, Hara M. Hydrolysis of cellulose by a solid acid catalyst under optimal reaction conditions. *J Phys Chem C* 2009;113:3181–8.
- [170] Suganuma S, Nakajima K, Kitano M, Yamaguchi D, Kato H, Hayashi S, et al. Synthesis and acid catalysis of cellulose-derived carbon-based solid acid. *Solid State Sci* 2010;12:1029–34.
- [171] Santo VD, Liguori F, Pirovano C, Guidotti M. Design and use of nanostructured single-site heterogeneous catalysts for the selective transformation of fine chemicals. *Molecules* 2010;15:3829–56.
- [172] Hara M. Biomass conversion by a solid acid catalyst. *Energy Environ Sci* 2010;3:601–7.
- [173] Yang Z, Niu L, Ma Z, MaH Lei Z. Fabrication of highly active Sn/W mixed transition-metal oxides as solid acid catalysts. *Transit Met Chem* 2011;36:269–74.
- [174] Delaney P, McManamon C, Hanrahan P, Copley MP, Holmes JD, Morris A. Development of chemically engineered porous metal oxides for phosphate removal. *J Hazard Mater* 2011;185:382–91.
- [175] Fukuoka A, Dhepe PL. Catalytic conversion of cellulose into sugar alcohols. *Angew Chem Int Ed* 2006;45:5161–3.
- [176] Toda M, Takagaki A, Okamura M, Kondo JN, Hayashi S, Domen K, et al. Biodiesel made with sugar catalyst. *Nature* 2005;438:178.
- [177] Takagaki A, Toda M, Okamura M, Kondo JN, Hayashi S, Domen K, et al. Esterification of higher fatty acids by a novel strong solid acid. *Catal Today* 2006;116:157–61.
- [178] Zong MH, Duan ZQ, Lou WY, Smith TJ, Wu H. Preparation of a sugar catalyst and its use for highly efficient production of biodiesel. *Green Chem* 2007;7:434–7.
- [179] Lou WY, Zong MH, Duan ZQ. Efficient production of biodiesel from high free fatty acid-containing waste oils using various carbohydrate-derived solid acid catalysts. *Bioresour Technol* 2008;99:8752–8.
- [180] Shu Q, Zhang Q, Xu GH, Nawaz Z, Wang DZ, Wang JF. Synthesis of biodiesel from a model waste oil feedstock using a carbon-based solid acid catalyst: reaction and separation. *Fuel Process Technol* 2009;90:1002–8.
- [181] Fukuhara K, Nakajima K, Kitano M, Kato H, Hayashi S, Hara M. Structure and catalysis of cellulose-derived amorphous carbon bearing SO(3)H groups. *ChemSusChem* 2011;4:778–84.

- [182] Hokrolahi A, Zali A, Pouretedal AR, Mahdavi M. Carbon-based solid acid catalyzed highly efficient oxidations of organic compounds with hydrogen peroxide. *Catal Comm* 2008;9:859–63.
- [183] Nakajima K, Hara M. Environmentally benign production of chemicals and energy using a carbon-based strong solid acid. *J Am Ceram Soc* 2007;90:3725–30.
- [184] Yang L, Qi Y, Yuan X, Shen J, Kim J. Direct synthesis, characterization and catalytic application of SBA-15 containing heteropolyacid $H_3PW_{12}O_{40}$. *J Mol Catal A-Chem* 2005;229:199–205.
- [185] Su K, Li Z, Cheng B, Zhang L, Zhang M, Ming J. The studies on the Friedel–Crafts acylation of toluene with acetic anhydride over HPW/TiO₂. *Fuel Process Technol* 2011;92:2011–5.
- [186] Sai Prasad PS, Lingaiah N. Aluminium exchanged heteropoly tungstate supported on titania catalysts: the generation of Lewis acidity and its role for benzylation reaction. *J Mol Catal A-Chem* 2011;350:83–90.
- [187] Tian J, Fan CY, Cheng MX, Wang XH. Hydrolysis of cellulose over $C_5xH_{3-x}PW_{12}O_{40}$ (X = 1–3) heteropoly acid catalysts. *Chem Eng Technol* 2011;34:482–6.
- [188] Kozhevnikov IV, Sinnema A, Jansen RJJ. New acid catalysis comprising heteropoly acid on a mesoporous molecular-sieve MCM-41. *Catal Lett* 1995;30:241–52.
- [189] Okuhara T, Mizuno N, Misono M. Catalytic chemistry of heteropoly compounds. *Adv Catal* 1996;41:113–252.
- [190] Okuhara T, Mizuno N, Misono M. Catalysis by heteropoly compounds – recent developments. *Appl Catal A-Gen* 2001;222:63–77.
- [191] Okuhara T. Water-tolerant solid acid catalysts. *Chem Rev* 2002;102:3641–65.
- [192] Zieba A, Matachowski L, Gurgul J, Bielańska E, Drelinkiewicz A. Transesterification reaction of triglycerides in the presence of Ag-doped H(3)PW(12)O(40). *J Mol Catal A-Chem* 2010;316:30–44.
- [193] Kozhevnikov IV, Kloetstra KR, Sinnema A, Zandbergen HW, Bekkum H. Study of catalysts comprising heteropoly acid $H_3PW_{12}O_{40}$ supported on MCM-41 molecular sieve and amorphous silica. *J Mol Catal A-Chem* 1996;114:287–98.
- [194] Izumi Y, Haseve R, Urabe K. Catalysis by heterogeneous supported heteropoly acid. *J Catal* 1983;84:402–9.
- [195] Misono M. Unique acid catalysis of heteropoly compound (heteropolyoxometalates) in the solid state. *Chem Commun* 2001;13:1141–52.
- [196] Gill CS, Price BA, Jones CW. Sulfonic acid-functionalized silica-coated magnetic nanoparticle catalysts. *J Catal* 2007;251:145–52.
- [197] Nanda KK. Size-dependent melting of nanoparticles: hundred years of thermodynamic model. *Pramana* 2009;72:617–28.
- [198] Zimicza MG, Lamas DG, Larrondo A. Ce_{0.9}Zr_{0.1}O₂ nanocatalyst: influence of synthesis conditions in the reducibility and catalytic activity. *Catal Comm* 2011;15:68–73.
- [199] Zhang XC. Ionic liquids—from theoretical fundamentals to research advances. 1st ed. Beijing: Chemical Industrial Press; 2009.
- [200] Tian XY, Fang Z, Jian DXY, Sun XY. Pretreatment of microcrystalline cellulose in organic electrolyte solutions for enzymatic hydrolysis. *Biotechnol Biofuels* 2011;4:53.
- [201] Smith Jr RL, Fang Z. Properties and phase equilibria of fluid mixtures as the basis for developing green chemical processes. *Fluid Phase Equilibria* 2011;302:65–73.