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Insights into solid acid catalysts for efficient cellulose hydrolysis to glucose: progress, challenges, and future opportunities

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ABSTRACT

Solid acids as heterogeneous catalysts for cellulose hydrolysis have drawn increasing attention; however, current solid acids face challenges such as high catalyst loading (low catalytic activity), poor catalyst-substrate interaction, deficient hydrothermal stability, and unsatisfactory recyclability. This review critically discussed the recent efforts and progress in overcoming the issues of solid acids and developing high-performance solid acids for hydrolyzing cellulose. The key structural features of solid acids and their effects on the interactions with cellulose and cellulose hydrolysis were addressed in detail. Strategies and perspectives to enhance performance, hydrothermal stability and recyclability of solid acids were provided.

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Solid acid; cellulose; heterogeneous hydrolysis of cellulose; cellulose depolymerization; interaction of cellulose with catalyst

1. Introduction

The production of biofuels and biochemicals from renewable lignocellulosic biomass has the potential to release our current dependence on traditional fossil resources, reduce greenhouse gases, and improve energy security.[1–3] Glucose, produced from the hydrolysis of cellulose in lignocellulose, is an essential platform sugar, which can be transformed into valuable downstream chemicals (e.g. furfural, 5-hydroxymethylfurfural, levulinic acid) and renewable biofuels (e.g. bioethanol, biobutanol, and hydrocarbons).[4–9]

Glucose can be produced from cellulose by cleaving β-1,4-glycosidic bonds between glucose units via acid- or enzyme (cellulases)-catalyzed hydrolysis.[10] However, cellulose has a robust crystalline structure created by strong hydrogen bonding between equatorial hydroxyl groups and axial stacking between cellulose molecules (Figure 1), which makes cellulose insoluble in water and most organic solvents and resistant to mild chemical attack.[11,12] In addition, cellulose is physically trapped by hemicelluloses and lignin in a tough matrix of lignocellulose, which further decreases the cellulose accessibility to hydrolysis.[13–15] Therefore, it is still very challenging to cost- and energy-

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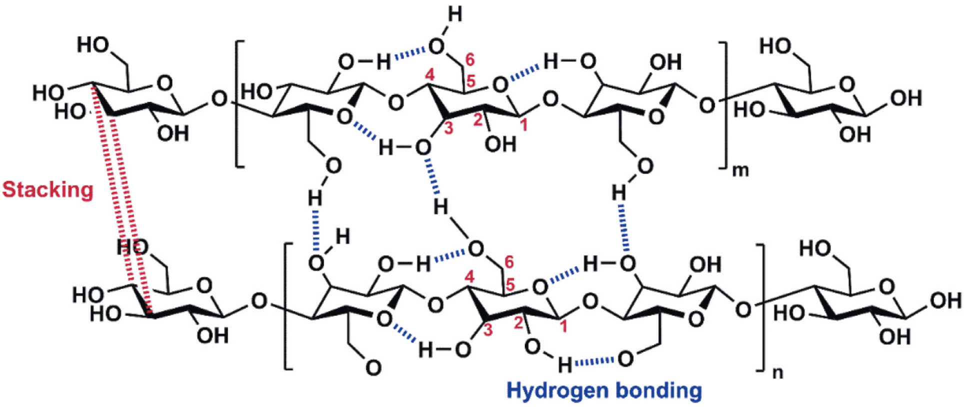

Figure 1. Hydrogen bonding and stacking between cellulose molecules.

effectively produce glucose via hydrolyzing cellulose in lignocellulosic biomass, which has been a key bottleneck to the industrial success of biorefineries based on the sugar platform.

Enzymes (cellulases) and homogeneous Brønsted acids (e.g. sulfuric and hydrochloric acids) are the most used catalysts for cellulose hydrolysis. Cellulases can selectively hydrolyze cellulose to glucose at moderate conditions (pH ~5 and temperature ~50 °C).[16] However, cellulases are currently expensive to produce and difficult to recycle, and enzymatic hydrolysis required energy- and cost-intensive pretreatment of lignocellulosic biomass to remove its recalcitrance for a satisfactory glucose yield.[15,17,18] Overall, enzymatic hydrolysis is currently economically unfavorable and still faces challenges in commercial success. Homogeneous acids such as H_2SO_4 and HCl are inexpensive and effective catalysts for cellulose hydrolysis.[19] However, the acid-catalyzed hydrolysis had the issues of sugar-acid separation, equipment corrosion, acid recovery, and wastewater treatment.[10,20] In addition, the acids promote undesirable sugar degradation to hydroxymethylfurfural, furfural, and levulinic acid.[21,22]

To address the issues of acid- and cellulase-catalyzed cellulose hydrolysis, solid acid catalysts for cellulose hydrolysis have received increasing attention recently. Solid acids usually have a solid framework with surface acidic sites (Lewis or Brønsted acid sites), which can catalyze the hydrolysis of cellulose. In general, solid acids are less expensive and more thermally stable than cellulases, and typically less corrosive and friendlier to the environment than liquid acids. Moreover, solid acids are expected to be easier to recover from hydrolyzate and reuse for next batch hydrolysis than liquid acids. Solid acids reported for cellulose hydrolysis include metal oxides, H-form zeolites, sulfonated carbons, supported metal catalysts, heteropoly acids, porous polymer-based catalysts, C/Si nanocomposites, and bifunctional solid acids. The fabrication, structure properties, hydrolysis performance, and reusability of representative solid acid catalysts recently reported for cellulose hydrolysis are summarized in **Table 1**.

A great deal of achievements has been made in synthesizing high-performance solid acid catalysts, understanding the catalytic mechanisms, and improving hydrothermal stability and recyclability in cellulose hydrolysis during the last 20 years.[11,12,53–57] However, solid acids still have many unknowns and issues before successful application in cellulose hydrolysis. For example, the overall performance and glucose yield of the solid acids in cellulose hydrolysis is not as satisfactory as expected. Most existing solid acids need an extremely high mass ratio of catalyst to substrate (c.a. 1:1) to achieve a satisfactory glucose yield. Selectivity is another issue of solid acids. The solid acids catalyze not only cellulose hydrolysis to glucose but also glucose dehydration to 5-hydroxymethylfurfural and other side-products, in particular at high temperature that is usually required to accelerate the hydrolysis of cellulose by solid acids. In addition, it has not been fully understood how solid acids interact/bind with cellulose substrates and hydrolysis intermediates (glucose, cellobiose, and oligoglucan) and why the solid acids show different affinity/adsorption toward different substrates, which are very important in designing solid acids and improving their performance in hydrolyzing cellulose. Hydrothermal stability (leaching of SO_3H group) and recyclability of solid acids remain big challenges. The recalcitrant nature of lignocellulosic biomass makes it more challenging than pure cellulose to hydrolyze by solid acids. First, lignocellulosic feedstock needs extensive size reduction (such as grinding), which is cost- and energy-intensive operation, to achieve satisfactory hydrolysis by solid acids. Second, lignin forms a physical “shield” around cellulose to retard cellulose hydrolysis by solid acids. In addition, the lignin residue behind cellulose hydrolysis makes the recycling of solid acids more difficult.

This review is to critically discuss the progress in solid acids for cellulose hydrolysis in response to the issues and challenges identified above. Previous studies indicated that catalytic acid sites, surface area and porous structure, interactions with cellulose, hydrothermal stability, and recyclability, as summarized in Figure 2, are the key structural features and properties of solid acids that crucially affect their performance in hydrolyzing cellulose. We will critically review the recent progress and effort in designing and fabricating solid acids to address the issues and improve the performance of solid acids in cellulose hydrolysis. Special attention will be paid to the strategies and attempts that enhance and improve the affinity and interaction with cellulose, hydrothermal stability, and recyclability of solid acids. The catalytic mechanisms and the structure-performance relationship of solid acids will be discussed. Perspectives on the design and fabrication of solid acids for future studies are provided.

Table 1. Comparison of fabrication, structure properties, hydrolysis performance and reusability of solid acid catalysts for cellulose hydrolysis.

			Acid density (mmol/g)		Porosity		Substrate
Type	Solid acid	Fabrication	SO_3H	Total[a]	SA_{BET} (m^2/g)	D_A (nm)	
H-form zeolites	HY-zeolite	Zeolite, Si/Al = 4	-	1.36	-	0.74	Avicel
	H-Beta (25)	Zeolite, Si/Al = 25		0.88	-	0.67	Avicel
	H-Beta (75)	Zeolite, Si/Al = 75	-	0.18	315	-	ball-milled Avicel
Metal oxide	$HNbMoO_6$	Layered transition metal oxide $HNbMoO_6$ obtained from Li form by a proton-exchange reaction	-	1.9	5	-	Avicel
Supported metal	Ru/CMK-3	Ruthenium supported mesoporous carbon	2 wt% Ru		1100	3.8	ball-milled Avicel
Inorganic-organic composite	Si_mC_n-SO_3H	Sulfonated Si/C nanocomposite	0.25		124	6.9	ball-milled Avicel
Heteropoly acid	$H_3PW_{12}O_{40}$	Prepared by sodium tungstate, H_3PO_4, and HCl (aq.)	2.63 mol/L H^+		-	-	ball-milled Avicel
SO_3H-based polymers	PCP-SO_3H	Porous coordination polymer with SO_3H	-		1.8	1915	ball-milled Avicel
	Amberlyst-15	Polystyrene-based cation exchange resin with SO_3H	4.8	-	-	-	Avicel
			4.6	-	36	36	Avicel
	Nafion NR50	Perfluoro-sulfonated ionomer	0.9	-	-	-	Avicel
Sulfonated carbonaceous solid acids	$CH_{0.61}O_{0.57}S_{0.05}$	Hydrothermal carbonized glucose (180 °C, 4 h), sulfonated with H_2SO_4 (200 °C, 12 h)	2.15	-	0.5		Avicel
	$CH_{0.62}O_{0.54}S_{0.05}$	Sulfonation (with fuming H_2SO_4, 80 °C, 10 h) of carbonized Avicel (450 °C, 5 h, N_2)	1.9	4.3	2	-	Avicel
	AC-SO_3H	Activated carbon sulfonated with H_2SO_4 (150 °C, 16 h), hydrothermally pretreated (200 °C, 3 h)	0.44	1.63	803	-	ball-milled Avicel
	AC-N-SO_3H-250	HNO_3 pretreated activated carbon was sulfonated with H_2SO_4 at 250 °C for 24 h	0.44	2.23	762	-	ball-milled Avicel
	CMK-3-SO_3H	Sulfonated ordered mesoporous carbon	0.63	2.39	412	-	ball-milled Avicel
	SO_3H-3DOm	Sulfonated three-dimensional ordered mesoporous carbon	0.5	1.3	1191	28.1	mixed cellobiose and oligomers
Unsulfonated carbonaceous solid acids	K26	KOH treated coke powder carbonized at 700 °C, washed with water, 1 M HCl and boiling water	-	0.85	2270	-	mix-milled K26 and Avicel
	MSC-T4	Oxidation of nanoporous carbon with NaOCl (25 °C, 24 h, pH 4-5)	-	2.2	2015	-	Avicel
	ACOH	Activated charcoal carbonized at 200 °C for 24 h, then oxidized with H_2O_2 at 85 °C for 1 h	-	0.78	634	-	ball-milled Avicel
	E-carbon	Air-oxidized *Eucalyptus* (biomass): 25-300 °C by 5 min and 300 °C for 1 h	-	2.1	-	-	mix-milled *Eucalyptus* and E-carbon

(*Continued*)

Table 1. (Continued).

Type	Solid acid	Fabrication	Acid density (mmol/g)		Porosity		Substrate
			SO_3H	Total[a]	SA_{BET} (m^2/g)	D_A (nm)	
Biomass-based sulfonated carbonaceous solid acids	LCSA-623	Lignin carbonized at 623 K for 6 h, ground to 150 mesh, then sulfonated with H_2SO_4 at 150 °C for 6 h	0.8	4.1	-	-	H_3PO_4 pretreated Avicel
	$LPC\text{-}SO_3H$	Co-carbonization of lignin, H_3PO_4 and alkali at 450 °C for 1.5 h, then sulfonated with H_2SO_4 under N_2 at 180 °C for 12 h	0.88	3.52	488.4	2.30	Avicel
	$LAHC\text{-}SO_3H$	Hydrothermal treated lignin (with acrylic acid, 240 °C, 10 h), sulfonated with H_2SO_4 (180 °C, 12 h)	1.58	5.48	1.6	-	Avicel
	$BC\text{-}SO_3H\text{-}1$	Bamboo powder and H_2SO_4 was carbonized at 80 °C for 3 h, then sulfonated with oleum at 80 °C for 2 h under N_2	1.88	4.64	-	-	Avicel
	CSA	Carbonized corncob hydrolysis residue (450 °C, 5 h, N_2), sulfonated with fuming H_2SO_4 (120 °C, 10 h)	1.42	1.76	1	-	Corncob
Bifunctional solid acids with cellulose-binding groups	$CP\text{-}SO_3H^c$	Sulfonating chloromethyl polystyrene with sulfanilic acid	0.0067	-	-	-	Avicel
	Porous polymer bearing $B(OH)_2$ and SO_3H	Friedel-Crafts polymerization of aromatic monomer with a boronic acid group, then sulfonated with H_2SO_4 and fuming H_2SO_4 at 80 °C for 24 h	2.2	-	736	3.32	ball-milled Avicel
	Porous polymer bearing Cl and SO_3H	Friedel-Crafts polymerization of aromatic monomer with chloride, then sulfonated with H_2SO_4 and fuming H_2SO_4 at 80 °C for 24 h	0.97	-	14	5.97	Avicel
	40-CCSA	Co-carbonized starch and polyvinyl chloride (450 °C, 10 h, N_2), sulfonated with 98% H_2SO_4 (150°C, 6 h, N_2)	0.832	(-Cl 6.55 mmol/g)	-	-	Cellobiose
	MPCSA-80	Co-carbonized cellulose, polyvinyl chloride and polyethylene (500 °C, 6 h), sulfonated with 98% H_2SO_4 (150 °C, 6 h)	1.15	3.08	4.18	-	H_3PO_4 pretreated Avicel
Magnetically recoverable solid acids	$Fe_3O_4\text{-}SBA\text{-}SO_3H$	Magnetic Fe_3O_4 nanoparticles embedded in mesoporous silica via sol-gel method	1.09	-	464	4.8	Avicel
	$MNPs@SiO_2\text{-}SO_3H$	Magnetic $CoFe_2O_4$ embedded silica nanoparticles, sulfonated by oxidizing thiol groups with H_2O_2	0.5	-	-	-	Avicel
	$Fe_3O_4@C\text{-}SO_3H$	Magnetic core-shell $Fe_3O_4@C$ nanoparticles were prepared by hydrothermal carbonization of $FeCl_3$, glucose, and urea, followed by sulfonation with 16 mL/g H_2SO_4 (60 °C, 24 h).	-	1.3	-	-	Avicel

Type	Catalyst/substrate (mass ratio)	Solvent	Temp. (°C)	Time (h)	TRS yield^d (%)	Glucose yield (%)	Stability & Recyclability	Ref
H-form zeolites	0.5	ionic liquid [BMIm]Cl	130	2	84.3	50.0	Reused for 5 cycles without obvious activity loss	[23]
	0.5	ionic liquid [BMIm]Cl	130	2	-	41.5	-	[23]
	1.1	water	150	24	17.8	11.2	-	[24]
Metal oxide	2:1	water	130	12	8.5	0.8	-	[25]
Supported metal	0.15	water	230	24	46.8	34.2	Separated by centrifugation and reused for 3 cycles without obvious activity loss	[26]
Inorganic-organic composite	1	water	150	24	51	42	Reused for 3 cycles (catalyst filtrated and dried), activity only decreased for the first run (SO_3H leaching)	[27]
Heteropoly acid	3 mL/ 60 mg substrate	water^b	100	2	98.4	68.1	Extracted by diethyl ether and reused for 7 cycles without obvious activity loss	[28]
SO_3H-based polymers	8	water^b	120	3	5.3	1.4	Reused for 13 times without obvious activity loss	[29]
	12	water	100	3	-	-	-	[30]
	0.2	ionic liquid [BMIm]Cl	100	5	26	11	-	[31]
	12	water	100	3	-	-	-	[30]
Sulfonated carbonaceous solid acids	0.6	ionic liquid [BMIm]Cl	110	4	72.7	-	Reuse for 5 cycles (120°C, total 5 h), TRS yield decreased from 61% to 55%	[32]
	12	water	100	3	64	4	Recovered by decantation, reused for 25 cycles (100 °C, total 150 h) without obvious activity loss	[33]
	1.1	water	150	24	42.5	40.5	Filtered catalyst reused for 3 runs without obvious activity loss	[24]
	1.1	water	150	24	74.3	62.6	-	[34]
	1.1	water	250	24	94.4	74.5	-	[34]
	0.67	water	120	2	1.5 mol glucose/ H^+/h		Hydrothermally treated (200 °C) for 10 days, SO_3H density decreased from 0.89 to 0.31 mmol/g	[35]
Unsulfonated carbonaceous solid acids	0.15	water	180	0.3	91	20	Recovered K26 and Avicel were mixed-milled again and reused for 4 runs with 0.012% HCl (total sugar yield maintained at >80%)	[36]
	13	water	150	24	-	36	-	[37]
	1.1	water	150	24	26	2	-	[38]
	0.15	water	215	0.3	-	31	Hydrolysis residue *Eucalyptus* was oxidized again to prepare E-carbon, then mix-milled with *Eucalyptus* for continuous hydrolysis	[39]
Biomass-based sulfonated carbonaceous solid acids	2	water	150	2	46	-	Hydrolysis yield decreased about 10% after reused for 3 cycles	[40]
	4	water	180	3	50.8	-	-	[41]

(*Continued*)

Table 1. (Continued).

Type	Catalyst/substrate (mass ratio)	Solvent	Temp. (°C)	Time (h)	TRS yield[d] (%)	Glucose yield (%)	Stability & Recyclability	Ref
	0.6	ionic liquid [BMIm]Cl water	130	2	75.4	-	Reuse for 5 cycles (130°C, total 10 h), TRS yield decreased from 75.4% to 68.1%	[42]
	0.5	water[b]	90	1	-	16.71	-	[43]
	1	water[b]	140	20	54	35	CSA recovered and regenerated, reused for 3 times, glucose yield was 32.7%, 31.3%, and 32.9% respectively	[44]
Bifunctional solid acids with cellulose-binding groups	2.5	water	120	10	-	93	Catalyst filtered and reused for 3 runs without obvious activity loss	[45]
	4	water	120	24	-	94.9	Catalyst filtered and reused for 4 runs, glucose yield decreased after the first run (94.6% to 79.8%)	[46]
	8	water	140	48	-	65.1	Catalyst filtered and reused for 4 runs, glucose yield decreased from 50.8% to 17.2% (SO_3H leaching)	[47]
	2	water	120	6	94.2	44.76	CSSA recovered by decantation and reused for 3 cycles, 10-25% Cl was leached and TRS yield decreased from 94.2% to 90%	[48]
	2	water	150	6	58.3	-	MPCSA-80 reused for 3 cycles and TRS yield decreased to 56.4%	[49]
Magnetically recoverable solid acids	1	water	150	3	-	26	Fe_3O_4-SBA-SO_3H recovered by magnet field, regenerated with H_2SO_4 and reused for 3 runs without obvious activity loss	[50]
	1	water	150	3	30.2	7.0	MNPs@SiO_2-SO_3H could be recycled with the magnet and reused for 3 times (glucose yield 59%, 50%, 63% for cellobiose hydrolysis at 120 °C, 9 h)	[51]
	3	water	140	12	48.6	25.3	Fe_3O_4@C-SO_3H recovered by an external magnet and reused for 3 cycles (140 °C, total 36 h), acid density decreased from 1.30 mmol/g to 1.10 mmol/g	[52]

[a] total acid density of sulfonic acid, phenolic hydroxyl and carboxylic acid groups

[b] microwave irradiation

[c] cellulase-mimetic bifunctional solid acid bearing chloride as a cellulose-binding group and sulfonic acid as cellulose-hydrolytic group

[d] yield of total reducing sugar

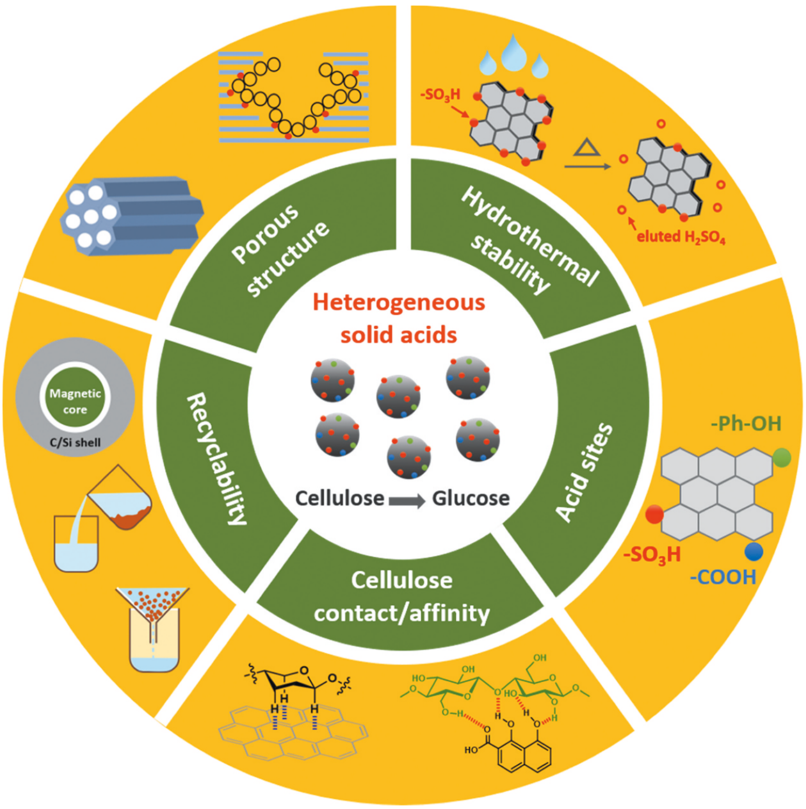

Figure 2. Key features affecting the performance of solid acids in hydrolyzing cellulose.

2. Acidic sites of solid acids for cellulose hydrolysis

The acidic sites are essential for solid acids to effectively hydrolyze cellulose to glucose. Most solid acids bear Brønsted acid groups like strong sulfonic acid (SO_3H) and/or weak carboxylic acid (COOH) as catalytic sites, as shown in Figure 3. Some solid acids such as H-form zeolites and metal oxides possess not only strong Brønsted acidity but also effective Lewis acidity for cellulose hydrolysis. However, the Lewis acid sites are usually unstable and inactive in water due to the formation of Lewis acid-base adducts by water coordination,[25,59] as further discussed in Section 2.5 and 5.1.

2.1. Strong and weak Brønsted acid sites

2.1.1. Strong SO_3H group and catalytic activity

Sulfonic acid (SO_3H) is a strong acidic group that can provide proton for hydrolyzing β-1,4 glycosidic bonds of cellulose. Many polymer-based solid acids (such as Amberlyst-15 and Nafion NR50), inorganic solid acids (such as sulfonated silica), and carbon-based solid acids use SO_3H as a strong Brønsted acidic site.[30,31,33,60,61] Among which, sulfonated carbon catalysts are the most

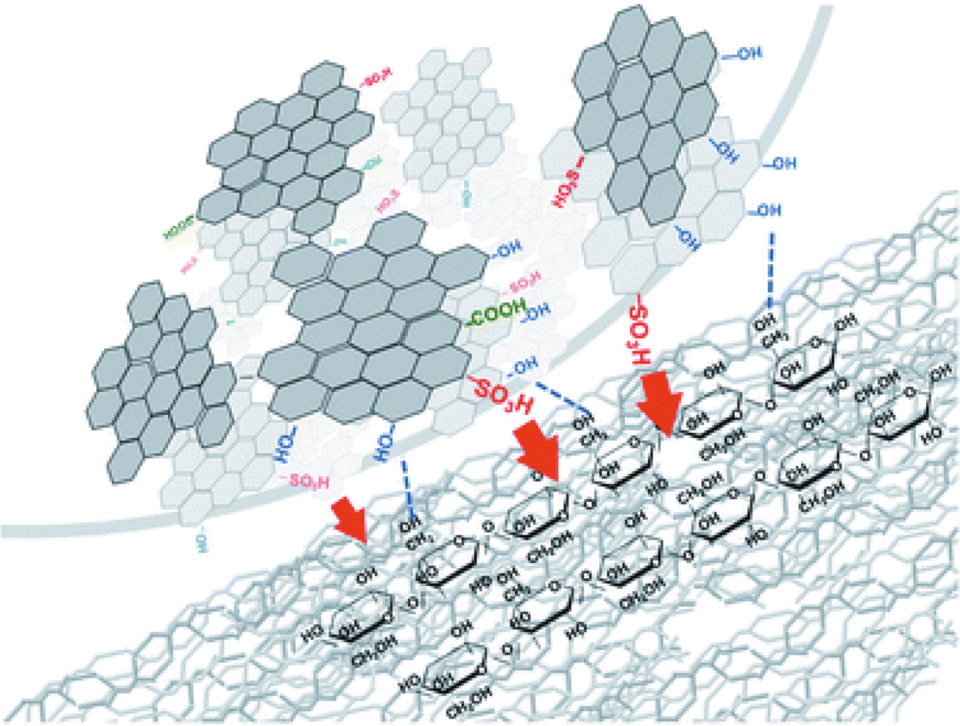

Figure 3. Illustration of cellulose adsorption and hydrolysis by sulfonated carbon catalyst bearing SO_3H, COOH, and phenolic OH groups (Reproduced with permission.[58] Copyright 2010 the Royal Society of Chemistry).

studied solid acids because they have remarkable catalytic activity for cellulose hydrolysis. For example, sulfonated CMK-3 (an ordered mesoporous carbon) had a total acid density of 2.39 mmol/g (SO_3H 0.63 mmol/g) and was able to hydrolyze ball-milled cellulose to glucose by 74.5% at 150 °C within 24 h.[34] Moreover, sulfonated carbon catalysts can be readily fabricated by sulfonating carbonized natural polymers, such as cellulose, starch, lignin, and lignocellulosic biomass.[39–41,62]

Conceptually, carbonaceous solid acids with more SO_3H acidic sites are prone to have better performance in cellulose hydrolysis. The catalytic activity of solid acids can be evaluated by turnover number (TON) or turnover frequency (TOF) of strong SO_3H acidic sites.[43] TON is defined as the total quantity of substrate hydrolyzed per active acidic site and TOF refers to the turnover per unit time. Hara *et al* reported that the TOF of SO_3H groups in a graphene-based solid acid was about 20 times those in conventional solid acids like Amberlyst-15 and almost reached that of H_2SO_4.[30] However, it was found that the SO_3H density was not directly proportional to the catalytic activity of solid acid for hydrolyzing cellulose.[63,64] The carbonization of biomass could produce carbon precursors with abundant sites for sulfonation, and sulfonation reaction was proposed to occur preferably from the surface of the carbon frame to the internal carbon layers.[63] After the carbon surface was completely sulfonated, additional SO_3H groups would be introduced to internal layers of the carbon, which was less accessible to cellulosic substrates and thus contributed less to the overall catalytic activity of the resultant solid acid. Therefore, the distribution and location of SO_3H groups matters, and it is the surface acidic sites that are more active for a hydrolysis reaction.[37] The accessibility of internal SO_3H groups was also affected by the carbonization conditions of the carbon catalyst. For example, the carbon catalyst prepared at mild carbonization temperature (ca. 723 K) had SO_3H groups on the surface of carbon sheets with poor cross-linking, which allowed unhindered access of cellulose to the SO_3H groups. In contrast, in the carbon catalyst obtained at high carbonization temperature (≥823 K), SO_3H groups were surrounded and blocked by highly cross-linked aromatic carbon sheets, which prevented the access of cellulose and thus these internal SO_3H groups were not effective in cellulose hydrolysis.[64, 65]

A concern of the SO_3H group is that its strong acidity can catalyze the dehydration of glucose to 5-hydroxymethylfurfural and further decomposition to levulinic acid and formic acid.[12] Sievers *et al* studied the cellobiose hydrolysis by sulfonated activated carbon catalyst (functionalized with both strong SO_3H and weak acid groups) and found that the carbon catalyst with a high fraction of strong SO_3H groups resulted in a high conversion rate of cellobiose but low selectivity of glucose, while that with more weak acid sites exhibited high glucose selectivity but lower conversion rate.[66] Therefore, the density of surface SO_3H groups and hydrolysis conditions should be carefully tuned to ensure high cellulose hydrolysis but limited glucose degradation.

2.1.2. Weak acid sites and catalytic activity

It was demonstrated that solid acids without strong SO_3H but with only weak acidic sites such as carboxylic acid group (COOH) can hydrolyze the β-1,4 glycosidic bonds of cellulose.[36,67,68] Similarly, the weak acid groups inside the catalytic domain of cellulases are responsible for the catalytic activity of cellulases in hydrolyzing glycosidic bonds of cellulose.[69,70] Onda *et al* found that compared with the sulfonated activated carbon (AC-SO_3H), the untreated activated carbon (AC) also showed a low catalytic activity for cellulose hydrolysis because of the acidic surface functional groups (hydroxyl and carboxyl groups).[24] Fukuoka *et al* reported a similar observation that the alkali-activated carbon K26 (unacidified) was able to hydrolyze ball-milled cellulose by 60% and yield 36% glucose in distilled water because of the weak acid groups (phenols and carboxylic acids).[36] Besides, the mesoporous carbon CMK-3 with a small number of weak acid groups (0.41 mmol/g) was able to hydrolyze amorphous cellulose by 14%.[26] The mesoporous carbon MSC-30 functionalized with the carboxylic acid, phenolic hydroxyl, and lactone groups (total acidity 2.2 mmol/

g) showed a good ability to hydrolyze Avicel and gave a glucose yield of 67.2%.[37] Removing the weak acid groups by heating at 673–1273 K reduced the catalytic activity of the solid acid, confirming that the weak acid groups were the active sites for cellulose hydrolysis.[36] It was found that there was a correlation (not directly proportional) between the phenolic hydroxyl groups on carbonaceous solid acid and the glucose yield from cellulose hydrolysis.[36,68] All these findings indicate that the weak-acid sites can hydrolyze cellulosic substrates. Besides, they also play a critical role in the adsorption of cellulosic substrates to solid acids (further discussed in section 4.3.1), which is essential for the effective hydrolysis of cellulose.

2.2. Fabrication strategies to incorporate acid sites

2.2.1. Sulfonation to incorporate SO_3H into solid acids

For efficient and fast cellulose hydrolysis, a high density of surface SO_3H groups is always desirable when fabricating solid acids through a proper sulfonation reaction. During the sulfonation, other than the electrophilic substitution to introduce SO_3H, oxidation may also occur and introduce weak acidic groups like COOH and OH onto the solid acids. In 2005, Hara and coworkers proposed the sulfonation of incompletely carbonized natural products (e.g. glucose and cellulose) with sulfuric acid (H_2SO_4) at elevated temperatures.[30,33,71] The resultant solid acid (from partially carbonized glucose) consisted of amorphous carbon sheets bearing a high density of SO_3H, COOH, and OH groups. The density of SO_3H was determined by elemental analysis of sulfur content, and XPS analysis confirmed that all sulfur atoms were in SO_3H groups.[65] It was reported that sulfonation with the vapor from fuming H_2SO_4 at 550 °C in a closed autoclave could incorporate 1.2 mmol/g SO_3H groups (total acidity 1.3 mmol/g) into mesoporous carbon CMK-3, which was more effective than concentrated H_2SO_4.[72] Besides, sulfonation could be realized by reducing diazonium salt (4-benzene-diazoniumsulfonate) with hypophosphorous acid under mild condition.[73,74] In this method, SO_3H-bearing aryl radicals were generated and then covalently attached to carbonaceous materials. The resultant ordered mesoporous carbon CMK-5-SO_3H had an acid density of 1.93 mmol/g.[73] Other than post-grafting sulfonation, sulfonated carbon catalysts could also be prepared by one-step carbonization of carbon precursor with SO_3H groups such as benzene sulfonic acid and naphthalene sulfonic acid. Hara *et al.* reported that heating naphthalene in H_2SO_4 at 473–573 K could introduce 4.9 mmol/g SO_3H into the resultant carbon-based solid acid.[75] The less-corrosive *p*-toluenesulfonic acid (TsOH) was also used for solid acid fabrication as a precursor.[62,76,77] For example, the thermal treatment of TsOH with D-glucose at 180 °C in a sealed autoclave could produce a carbonaceous solid acid with 1.3 mmol/g SO_3H.[76]

Aside from sulfonation reagent, sulfonation conditions also affect the introduction of SO_3H groups on solid acids. Zhang *et al* studied the effect of temperature on the sulfonation of activated carbon with H_2SO_4 and found that the SO_3H density and surface hydrophilicity of activated carbon increased with sulfonation temperature.[34] The activated carbon (nitric acid pretreated) sulfonated at 250 °C had the highest acidity (total acidity 2.23 mmol/g with 0.44 mmol/g SO_3H) and achieved a glucose yield 62.6% when hydrolyzing cellulose at 150 °C for 24 h. If the sulfonation temperature was further increased, the porous structure of solid acid collapsed, and the sulfonated moieties even decomposed.[34] It was found that the reactivity toward sulfonation was affected by the carbonization degree of starting carbon materials.[64,78] For example, the SO_3H density of cellulose-derived carbonaceous solid acid decreased from 1.8 to 0.89 mmol/g as the carbonization temperature increased from 400 to 550 °C.[64] One possible explanation was that the carbon precursor prepared at high carbonization temperature (≥550 °C) had no COOH and phenolic OH groups, which led to more sp^2 cross-linking between the carbon sheets. The densely cross-linked carbon sheets prevented the incorporation of sulfonation reagents into the carbon bulk, therefore resulting in fewer SO_3H groups.[64,65,78] The optimal carbonization temperature was found to be around 400 °C for glucose and microcrystalline cellulose, which resulted in 0.7 and 1.8 mmol/g SO_3H groups, respectively. It was also proposed that the co-existence of COOH and OH groups increase the sulfonation efficiency.[55] For example, oxidizing the carbon precursor with nitric acid or hydrogen peroxide to introduce COOH and OH groups could increase the SO_3H density of the resultant sulfonated carbon catalysts.[34,79] This was probably because the hydrophilic COOH and OH groups favored the immobilization of SO_3H groups on the hydrophobic carbon surface via forming covalent bonds or hydrogen bonds.

2.2.2. Incorporation of weak acid sites into solid acids

The incorporation of weak acid sites could occur concomitantly during the sulfonation of solid acids. Under the sulfonation condition, carbonaceous solid acids usually underwent oxidation to form weak acid sites such as COOH, phenolic OH, ketone, lactone, etc.[33,64] Alternatively, specific oxidation or pre-oxidation process could be used to introduce various oxygen-containing sites into solid acids.[34,37,38] Commonly used oxidants include oxidizing gases (e.g. air, oxygen, and ozone) and solutions (e.g. nitric acid (HNO_3), hydrogen peroxide (H_2O_2), and hypochlorite (HOCl)). The type and content of weak acidic groups introduced are largely dependent on the oxidizing agent/condition and carbon source of the solid acids. It was reported that biomass-derived solid acid fabricated from air oxidation of eucalyptus had 2.1 mmol/g carboxyl group.[39] It was also found that carboxyl groups were preferably formed over phenol and lactone by air oxidation at high temperatures. Oxidation with HNO_3 was a highly efficient process and led to mainly carboxyl groups on the surface of a carbonaceous solid acid.[34,80,81] H_2O_2 and HOCl are milder oxidants and usually resulted in carboxyl, phenolic OH, and lactone groups.[37,82] It was observed that the oxidation of activated carbon in the liquid phase selectively generated COOH groups, while the oxidation in the gas phase formed mainly OH and C = O groups.[83] Moreover, hydrothermal carbonization (~130-250 °C) in presence of water could introduce abundant weak acidic groups (OH, Ar-OH, C = O, and COOH) into the carbon materials (*i.e.* hydrochar).[68,84–86]

2.2.3. Characterization techniques of acid sites

The total acid density of solid acids is usually characterized by Boehm potentiometric titration, $TPD\text{-}NH_3$ (temperature-programmed desorption of ammonia), or cation-exchange analysis. Boehm titration was found to be the best method for finely powdered carbons, which use bases with different strengths (e.g. NaOH, $NaHCO_3$, Na_2CO_3) to neutralize the surface acidic sites to determine total acid density.[30,36] $TPD\text{-}NH_3$ is another widely used method to estimate acid sties density of solid acids.[34] Because the molecular size of NH_3 is very small, it can penetrate the internal pores of solid acids. As a result, the result from $TPD\text{-}NH_3$ is usually larger than that from Boehm titration, which only determines the surface acid sites. By combing these two methods, the acid sites located in internal pores of solid acids can be calculated. The temperature-programmed desorption (TPD) method was used to quantify the surface functional oxygen-containing groups on activated carbons by detecting CO and CO_2 as a result of decomposition at different temperatures.[83] In a cation-exchange analysis, the density of (SO_3H +COOH) and (SO_3H+COOH+OH) was estimated by cation-exchanging with Na^+ in aqueous NaOH or NaCl solution, respectively, to afford a proportion of different functional groups.[33] The SO_3H density can be estimated from the sulfur content by elemental analysis[46,47] and X-ray photoelectron spectroscopy (XPS).[30,33] The number of weak acid sites could be calculated by the difference of total acid density and SO_3H density. Alternatively, ^{13}C nuclear magnetic resonance (NMR) could be used to analyze weak acid sites like COOH and OH as well.[30,45]

2.3. Catalytic mechanism of Brønsted acidic sites

Regardless of what catalysts are used in cellulose hydrolysis, the breakdown of β-1,4 glycosidic bonds is essentially catalyzed by an acid (proton). For example, the protons from ionization of homogeneous acids (e.g. HCl, H_2SO_4) or weakly acidic sites in the catalytic domain of cellulases are all able to catalyze cellulose hydrolysis. The mechanism of solid acid-catalyzed hydrolysis of cellulose (using cellobiose as a model) in water is illustrated in Figure 4.

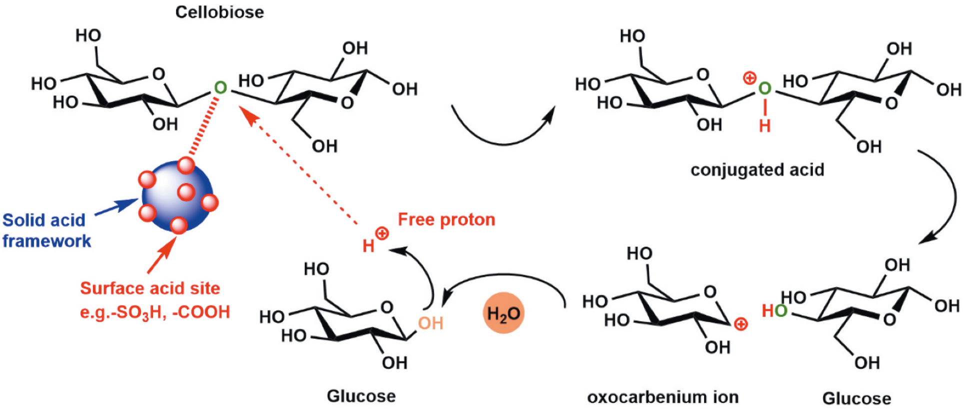

Figure 4. Illustration of cellulose hydrolysis by a solid acid with surface Brønsted acid sites in water.

Initially, the solid acid approaches and collides with cellobiose, which enables the surface Brønsted acid sites to attack the oxygen atom of the β-1,4 glycosidic bond, forming a conjugate acid. The following cleavage of the C-O bond and breakdown of the conjugated acid releases glucose and forms an oxocarbenium ion intermediate. Then, after a rapid addition of water, another glucose and a free proton are liberated. The free protons in hydrolyzate as well as the solid acid continue hydrolyzing β-1,4 glycosidic bonds of cellulose. Like other acids, solid acid hydrolyzed cellulose both from the chain ends and by a random attack from the middle,[30] although it was reported that cellulose hydrolysis by homogeneous acid could preferably succeed from its ends.[87] The initial contact/affinity between solid acid and cellulose (discussed in section 4.3) and the presence of water are all indispensable for effective hydrolysis of cellulose.

Weak acid sites like phenol OH ($pK_a = 9.9$) might be not acidic enough to directly hydrolyze cellulose but their presence as well as other oxygen-containing groups like ketone and lactone in solid acids could improve the affinity of solid acid to cellulose and oligoglucan through hydrogen bonding and thus provide a synergistic effect in cellulose hydrolysis (Figure 5).[12,30,33,38,67] Mesoporous carbon CMK-3 was able to hydrolyze amorphous cellulose partially because of the favorable interaction between cellulose and the acidic groups (carboxyl and phenolic groups, 0.41 mmol/g) on the carbon surface.[26] It was found that salicylic acid, which has adjacent COOH and OH groups, were more effective in hydrolyzing cellobiose than other acids where functional groups are further apart.[88] These observations suggested that the synergistic effect is more pronounced when oxygenated groups are juxtaposed adjacent because the functional groups can form a hydrogen bond with the oxygen of β-1,4 glycosidic bond and increase the probability of neighboring acid group COOH or SO_3H to attack the β-1,4 glycosidic bonds. It was observed that the affinity to cellulose of the weak acidic groups on the carbonaceous solid acid was critical for the

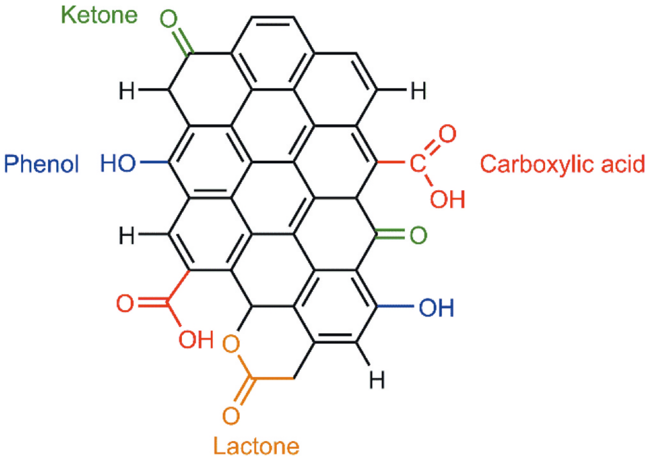

Figure 5. Schematic illustration of weak acidic groups in carbonaceous solid acid.

effective hydrolysis of cellulose because the adsorption/association could increase the contact between cellulose and solid acid, which is usually limited in a solid-solid catalysis system.[30]

2.4. Leaching and deactivation of SO_3H under hydrothermal condition

The stability of the SO_3H group under hydrothermal condition remains a big issue of solid acid catalysts.[47,74,89] SO_3H groups are prone to leach under hydrothermal conditions mainly because the C-S bond tends to undergo acid-catalyzed hydrolysis (de-sulfonation).[90] The leaching extent is dependent on the temperature of cellulose hydrolysis. Usually, high temperature (100 °C or higher) is required to obtain a satisfactory glucose yield. The stability of SO_3 H groups can be evaluated by hydrothermally treating solid acids in hot water and then analyzing the change in SO_3H groups. It was reported that the SO_3 H-based resin Amberlyst-15 had poor hydrothermal stability and lost 1.7 mmol/L SO_4^{2-} after hydrolyzing cellulose at 150 °C for 24 h.[24] In another study, the SO_3H density of activated carbon-based solid acid decreased from 0.58 to 0.35, 0.30, and 0.20 mmol/g after hydrothermal treatment at 150, 200, and 225 °C, respectively.[81] Shanks *et al* found that solid acids fabricated from sulfonation of incompletely carbonized carbohydrates, hydrothermal carbon, and dehydration-sulfonation of glucose all lost a significant amount of their sulfur (>90%) after repeated hydrothermal treatment at 160 °C.[91] Other than SO_3H leaching, proton leaching caused by ion exchange with cationic minerals could also lead to the deactivation of solid acids.[90] It was found that ionic liquid deactivated sulfonated resin Amberlyst-15 through the ion-exchange with the cation of the ionic liquid.[92] When hydrolyzing lignocellulosic biomass, the metals present in the ash of biomass could also lead to the deactivation of strong acidic sites via ion exchange, but this was not observed for weak-acid sites on some reported carbon catalysts.[68,93,94]

The deactivation (de-sulfonation) mechanism of carbonaceous solid acids under hydrothermal conditions has been extensively studied. Shanks *et al* studied the hydrothermal stability of several sulfonated carbon catalysts and found that the rate of sulfur loss was considerable during initial water exposure and then generally slowed down with successive treatments.[91] The initial sulfur loss was mainly caused by the leaching of polycyclic aromatic hydrocarbons bearing SO_3H groups (aryl-SO_3H). This phenomenon was also confirmed by other studies that the most labile SO_3H groups were removed quickly by hydrothermal pretreatment and the remaining ones became stable under the hydrothermal condition.[81,90,95,96] The aryl-SO_3H groups were more susceptible to leaching than alkyl-SO_3H groups (SO_3H bonds to furan-carbon) because the alkyl-SO_3H did not undergo de-sulfonation.[97] The de-sulfonation of aryl-SO_3H groups was affected by the electron-donating or -withdrawing substituents on the benzene ring. The activated aryl-SO_3H with high electron density at ortho or para position (e.g. ortho-hydroxyl or para-benzoxy) were de-sulfonated readily in hot water at 130 or 180 °C, while the unsubstituted or the deactivated aryl-SO_3H (e.g. carboxy-substituted) were not prone to desulfonation even exposed at 180 °C.[90] Therefore, carbon materials carbonized at a lower temperature would have more deactivating substituents (e.g., carboxylic acid and lactone) and tend to have better stability and catalytic activity for cellulose hydrolysis.[64,83] To avoid leaching of SO_3H groups, it was suggested to functionalize solid acids with weak acid groups such as COOH and OH. These weak acid sites are more stable, but they are less acidic and thereby usually much slower to hydrolyze cellulose than the strong SO_3H groups.

To address the deactivation and leaching of acid sites, regeneration strategies such as re-sulfonation and ion-exchange are developed to restore the catalytic activity of solid acids.[75,90,98] After catalyzing cellulose hydrolysis, a solid acid could be re-sulfonated in concentrated sulfuric acid to regenerate strong acidic sites, which ensured the solid acid could be reused for multiple runs of cellulose hydrolysis.[75] It was observed that the performance of some regenerated solid acids was better than the fresh ones. However, what made the difference was not fully understood. The development of an efficient and economic regeneration process should be investigated in future research.

2.5. Other catalytic sites of solid acids

In addition to Brønsted acid sites, Lewis acid sites were also investigated for cellulose hydrolysis. For example, as lanthanide (III) ions can maintain

Lewis acidity in aqueous solutions, Ishida et al reported that lanthanum (III) chloride effectively catalyzed the degradation of cellulose in the water at 250°C.[99] The yield of total water-soluble products reached a maximum of 54.2 wt% at 150 s, but glucose yield was only 5.8 wt%, with the dominant degradation product being 5-hydroxymethyl-2-furaldehyde (HMF) (19.2 wt%). It was reported that mesoporous niobium-tungsten ($Nb_x W_{(10-x)}$) oxides were excellent solid acid catalysts for Friedel–Crafts alkylation, hydrolysis, and esterification reactions. The Nb-W oxides have both Brønsted and Lewis acid sites, which are tunable by changing the Nb-W ratio (more W gives Brønsted acid sites). For example, replacing Nb^{5+} by higher-valence W^{6+} in a tungsten-enriched sample (e.g., Nb_3W_7 oxide) formed strong Brønsted acid sites, thereby improving the performance in hydrolyzing cellobiose.[59] Domen *et al* found that layered niobium molybdate ($HNbMoO_6$) and niobium-titanium ($HTiNbO_5$) were able to catalyze cellulose hydrolysis, but the glucose yield was very low (only 0.4%), and most of the products were cello-oligosaccharides,[25] which was probably attributed to the relatively low Brønsted acidity of the niobium oxides.[59] Fukuoka *et al* incorporated transition metal ruthenium (Ru) into mesoporous carbon materials (CMKs) and obtained supported metal Ru/CMK-3, which was a water-tolerant and reusable catalyst for cellulose hydrolysis.[26] The acidic species of Ru, the large surface area, and highly oxygen-functionalized surfaces of CMKs (containing high-density weak-acid sites) contributed to the good performance of Ru/CMK-3 in cellulose hydrolysis.

It was believed that cellulose hydrolysis in water is catalyzed predominantly by Brønsted acid sites,[87,100] but the findings above indicated that Lewis acid sites on solid acids are capable of cleaving β-1,4 glycosidic bonds. Therefore, incorporation of Lewis acid sites into solid acids is a strategy to increase the total acidity toward efficient cellulose hydrolysis. Shimizu *et al* studied the effects of Brønsted and Lewis acidities on the catalytic activity and selectivity of heteropoly acids ($H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$) and polyvalent transition metal salts of $PW_{12}O_{40}{}^{3-}$ in cellulose hydrolysis.[101] It was found that for Brønsted acids (both mineral and the heteropoly acids), stronger Brønsted acidity was more favorable for cleaving β-1,4 glycosidic bonds in cellulose and cellobiose. For Lewis acids (the salts), the rate of cellulose hydrolysis increased with Lewis acidity of the cations, but the selectivity was the highest at moderate Lewis acidity with the metals such as Sn^{4+} and Ru^{3+}. A Lewis acid potentially possesses both Lewis acidity originated from the metal cation as electron pair acceptor and Brønsted acidity generated from the dissociation of coordinated water under the polarizing effect of the cation. The underlying mechanism of Lewis acid sites hydrolyzing cellulose and their synergetic effect with Brønsted acid sites in cellulose hydrolysis is of interest and importance in future research.

3. Surface area and porous structure of solid acids

3.1. Correlation to hydrolysis performance

The performance of solid acids in cellulose hydrolysis is not only related to their functional acidic sites but also other properties, such as surface area and porous structure. Traditional SO_3H-bearing resin Amberlyst-15 had SO_3H density up to 4.8 mmol/g. However, its performance in cellulose hydrolysis was poorer than the carbon material bearing SO_3H (1.9 mmol/g), COOH (0.4 mmol/g), and phenolic OH (2.0 mmol/g). An important reason behind was that the specific surface area of Amberlyst-15 was only about 50 m^2/g that was mostly attributed to the external macropores. The surface area, average pore diameter, and pore volume of solid acids are generally characterized by N_2 adsorption according to the Brunauer-Emmett-Teller (BET) method. As will be discussed in the next section, micropores are not as useful and desirable as mesopores for solid acids for cellulose hydrolysis. Many carbonaceous solid acids prepared from carbonization and sulfonation of natural polymers (e.g. sugars, cellulose, starch, and lignocellulosic biomass) had a low BET surface area (usually less than 5 m^2/g) due to their nonporous structure, and their catalytic performance in cellulose hydrolysis was usually unsatisfactory.[43,63,75,78] In contrast, solid acids with the larger surface area associated with porous structure had higher catalytic activity in the hydrolysis of cellulose.[26,29,102–104] For example, Zhang *et al* reported that sulfonated activated carbon AC-N-SO_3H-250 with relatively low acid density (SO_3H 0.44 mmol/g) but high BET surface area (762 m^2/g) achieved a glucose yield of 62.6% when hydrolyzing cellulose at 150 °C for 24 h, which was better than the cellulose-derived carbon with high acid density but very low surface area.[34] Moreover, sulfonated ordered mesoporous carbon material CMK-3 showed excellent catalytic activity in hydrolyzing cellulose, because of large surface area and mesopores .[34,72] These results indicated that a large surface area and mesoporous structure play a crucial role in the effective hydrolysis of cellulose by solid acids. The observations are in agreement with the hypothesis that the hydrolysis could occur inside the pores of solid acids, and thereby solid acid with higher surface area and porous structure would provide more available acidic sites for the hydrolysis of cellulose.[11,34] Moreover, the porous structure of solid acids would allow hydrolysis intermediates (e.g., gluco-oligosaccharides and cellobiose) to enter the pores and interact with the active acidic sites inside the pores. Besides, the mesoporous channels facilitate the mass transfer of hydrolysis intermediates and products, thus increasing the reaction rate of cellulose hydrolysis.[105,106] Therefore, solid acids with large surface area and porous structure tend to perform better in cellulose hydrolysis compared to those with a small surface area.

3.2. Function of mesopores and micropores

The porous properties (pore diameter and volume) of solid acids play a critical role in the catalytic hydrolysis of large molecules like cellulose.[73,102,107] Pores are classified into three groups: microporous (pore size <2 nm), mesoporous (2–50 nm), and macroporous (>50 nm) ones. Many studies indicated that solid acid catalysts with mesoporous structure had higher catalytic activity and better performance in cellulose hydrolysis than those with micropores, which is presumably attributed to the larger surface area associated with mesopores, better accessibility of the acidic sites inside the pores to cellulosic substrates, and easier mass transfer of reactants and products.[55,57,72,108] For example, microporous H-form zeolites with Brønsted acid sites such as H-beta (75) and H-ZSM (45) (SA_{BET} 105 m^2/g and 124 m^2/g) were able to catalyze the hydrolysis of cellulose, but the glucose yield was relatively low .[24] Mesoporous sulfonated activated carbon AC-SO_3H (SA_{BET} 806 m^2/g) showed better catalytic activity.[24] Similarly, sulfonated CMK-3 (an ordered mesoporous carbon) with 0.63 mmol/g SO_3H gave 94.4% cellulose conversion and 74.5% glucose yield when hydrolyzing ball-milled cellulose at 150°C for 24 h.[34] Mesoporous carbon materials such as CMK with high specific surface area (usually >1,000 m^2/g) were also chosen as the carbon support for metal solid acids such as Ru/CMK-3 and Ni/MMC (macro-mesoporous carbon) to improve their catalytic activity by preventing aggregation of metal atoms and improving their dispersibility.[26,103] Besides, Katz *et al* found that mesoporous carbon nanoparticle (MCN) could adsorb up to 30% (by mass) soluble long-chain β-1,4 glucans (model compound for cellulose), while the graphene-type carbon nanopowder (CNP) that lacks internal mesopores only adsorbed less than 1% glucans under similar condition.[109] A following-up study by Katz *et al* further confirmed the importance of the internal porosity for glucan adsorption in mesoporous carbon materials and found that the glucan adsorption systematically increased with the magnitude of exposed carbon mesoporous surface and the mesopore size, and the micropores in the range of 5 – 8 Å in diameter were too small for glucan adsorption.[110]

However, recent studies by Katz *et al* demonstrated that soluble long-chain β-1,4 glucans could be rapidly adsorbed into larger micropores in the range of 10 – 15 Å of the zeolite-templated carbon (ZTC) catalyst up to 80% of the ZTC mass, and the adsorbed glucan was readily hydrolyzed into glucose with high yield (73%) after treatment at 180°C for 3 h.[111,112] Post surface functionalization to introduce additional carboxylic acid groups on ZTC could bring the cellulose hydrolysis up to 87%.[112] It was surprising but confirmed that even though the β-1,4 glucan had a radius of gyration several fold-larger than the micropore diameter, the glucan adsorption occurred within internal ZTC micropores rather than on the external surface. Similar phenomena were observed in the diffusion

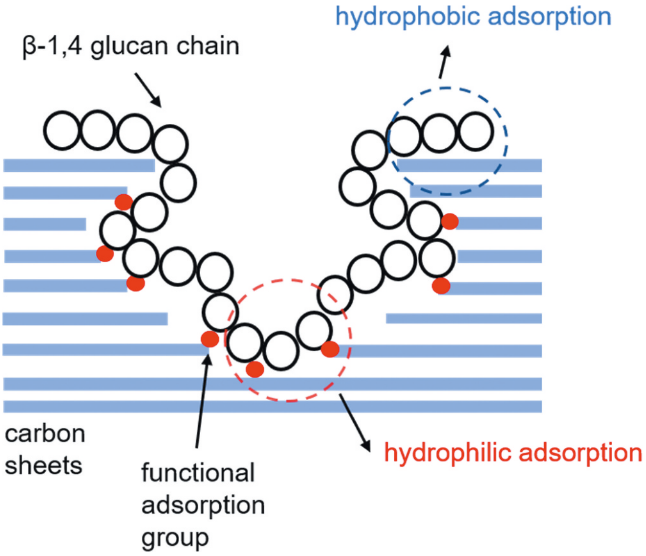

Figure 6. Schematic illustration of constrained β-1,4 glucan chain adsorbed in confined mesopores of a carbonaceous solid acid. [38]

of flexible polymer strands into porous membrane via conformational change.[113] In contrast to the observations above, the new findings demonstrated micropores might have a functional advantage over mesopores for the glucan adsorption and depolymerization on porous carbon catalysts, which opens the door to new approaches and opportunities for designing and fabricating porous solid acids for cellulose hydrolysis and conversion.

The β-1,4 glucan adsorption on carbon catalyst is driven enthalpically by the cumulative effect of a multitude of weak CH–π interactions between the glucan strand and graphitic domains on the carbon surface and entropically by the release of bound water from the hydrophobic carbon surface upon glucan strand adsorption.[111] Once the glucan is adsorbed on the interior surface of the carbon material, the adsorption-driven conformational rearrangement would occur, which would allow glucan strands to diffuse into the interior pores of the carbon nanoparticles. When the glucan was adsorbed into the confined porous domain, driven by the hydrophobic CH-π interaction and/or hydrophilic OH-H hydrogen bonding (further discussed in section 4.3.3), a significant mechanical strain would be exerted on the glucan chain that in principle promoted the hydrolysis of β-1,4 glycosidic bonds by weak acid sites to relieve the strain.[111] The hydrophobic and hydrophilic interactions between glucan and carbon catalyst for cellulose adsorption and hydrolysis are schematically presented in Figure 6.

3.3. Porous structure control during fabrication of solid acids

As discussed in previous sections, sulfonated mesoporous carbons with large surface areas exhibited good catalytic activity for cellulose hydrolysis. Hence, how to control the porous structure during the fabrication of a solid acid is of great importance and research interest. Solid acids with mesoporous structure can be obtained by the sulfonation of mesoporous carbon materials, which can be synthesized with the assistance of pore-forming agents or templates, either by a hard templating method involving sacrificial silica scaffolds or by a soft templating method using surfactants or amphiphilic block copolymers.[55,82,114] Traditional hard template synthesis generally involves the impregnation of a rigid silica template with an appropriate carbon precursor, followed by high-temperature carbonization and subsequent removal of the hard template (see Figure 7). For example, mesoporous carbon CMK series were fabricated by replicating a mesoporous silica template like SBA-15 and MCM-41.[114,116] After proper sulfonation, mesoporous carbon was functionalized with SO_3H groups and became a highly active catalyst for cellulose hydrolysis and other acid-catalyzed reactions.[34,72,73]

More recently, the soft-templating technique using surfactants or amphiphilic block copolymers was developed .[114,117,118] Triblock copolymers Pluronic F127 (PEO_{106}-PPO_{70}-PEO_{106}) and Pluronic P123 (PEO_{20}-PPO_{70}-PEO_{20}) are typical soft templates that contain both hydrophobic PO segment and hydrophilic EO segment, which can self-assemble to micelle structure.[117,119] The soft-templating synthesis is illustrated in Figure 8a. The hydrophilic EO segment interacted with the OH groups of phenolic resin phloroglucinol (carbon precursor) through hydrogen bonding and self-assembled to a miscible shell, while the hydrophobic PO segment aggregated to an immiscible domain, which was responsible for directing mesopores in the resultant carbon. The phenolic resin with a high density of hydroxyl group that enhanced hydrogen bonding was critical for the preferential self-assembly of carbon precursor with PEO-PPO-PEO copolymers.[114,117] Later, lignin

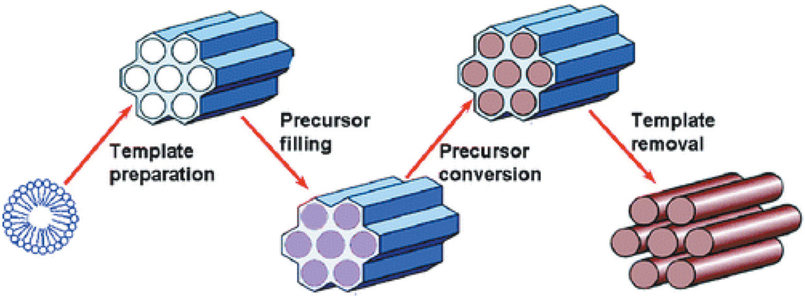

Figure 7. Schematic illustration of mesoporous carbon by hard-template method (Reproduced with permission.[115] Copyright 2008 American Chemical Society).

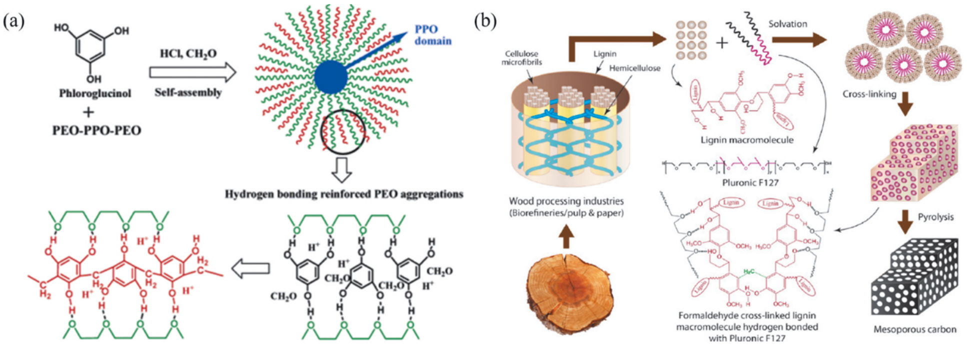

Figure 8. Scheme of mesoporous carbon via soft-templating synthesis from different carbon precursors (a) phloroglucinol (Adapted with permission.[117] Copyright 2006 American Chemical Society) (b) lignin (Adapted with permission.[120] Copyright 2013 American Chemical Society).

with an abundance of aliphatic and phenolic hydroxyl groups was used as a low-cost carbon precursor to fabricate mesoporous carbon.[120,121] Similarly, lignin was solvated with Pluronic F127 surfactant and then self-assembled to core-shell micelles, followed by pyrolysis to obtain the mesoporous carbon (Figure 8b). The resultant lignin-derived mesoporous carbon had a BET surface area of 418 m^2/g and a mesopore volume of 0.34 cm^3/g.[120] Subsequent physical and chemical activation with CO_2 and KOH could further enhance the BET surface and total pore volume of the lignin-derived mesoporous carbon to 1148 m^2/g and 1.0 cm^3/g, respectively.[121]

Other than hard/soft templating synthesis, there are other methods to synthesize mesoporous solid acids. For example, Clark *et al* synthesized a series of mesoporous carbon materials by pyrolysis of expanded mesoporous starch without the need of a templating agent.[122] The amylose and amylopectin chains within the starch granules could assemble into an organized nanoscale lamellar structure and further form mesoporous structure in the expanded starch. After subsequent sulfonation with H_2SO_4, a highly active solid acid was produced for various acid-catalyzed reactions.[123] Pan *et al* developed a facile two-step strategy to synthesize polymeric solid acids.[46,47] The aromatic monomer (e.g. benzyl chloride, phenylboronic acid) and external cross-linker formaldehyde dimethyl ether was used to synthesize the porous polymer backbone via Friedel-Crafts alkylation, followed by sulfonation to introduce SO_3H groups as catalytic sites for cellulose hydrolysis. Friedel-crafts polymerization was proven to be effective in synthesizing polymers with desirable mesopores and large surface area.[124] The resultant polymeric solid acids were able to effectively hydrolyze cellulose, which is presumably attributed to the large surface area from the mesoporous structure of the solid acids (average pore diameter 2.55–6.03 nm).

While much progress has been made in the synthesis of mesoporous carbons, the chemical modification of mesoporous carbon is relatively difficult because of the chemical inertness of carbon materials.[82] During the fabrication of carbonaceous solid acids, harsh conditions were usually required for sulfonation and/or oxidation to introduce functional acidic sites on carbon surfaces. However, this could cause a partial structural collapse of mesopores and result in an observed drop in surface area and pore volume.[24,34] It is crucial to carefully control modification conditions for incorporating functionalities without altering the mesoporosity/microporosity of the solid acid catalysts. It was reported that the post-synthetic modification by oxidants like H_2O_2, HNO_3, or NaOCl could successfully introduce weak acid sites to the surface of carbon materials without pore collapse.[37,112]

4. Strategies to enhance contact and affinity of solid acids to cellulose substrate

Although a lot of efforts have been made to improve the catalytic activity of solid acids for cellulose hydrolysis, the performance of most existing solid acids is still not comparable to that of liquid acids and cellulases. The main reason for the unsatisfactory performance of solid acids is the insufficient contact/interaction between the solid acids and cellulose, which is partially due to the poor affinity of solid acids to cellulose. Besides, the crystalline nature of cellulose makes it more difficult to access and hydrolyze by the solid acids. Therefore, this section discusses major strategies to enhance the contact and affinity between insoluble cellulose and solid acids[31,45–47,57,125] and the adsorption/interaction mechanism between solid acids and both insoluble cellulose and soluble intermediates, [35,111,126] which are crucial to the design and fabrication of solid acids with improved hydrolysis performance.

4.1. Milling pretreatment

As discussed in the introduction, the strong hydrogen bonding between equatorial hydroxyl groups and tight axial packing between the cellulose chains make cellulose highly crystalline and difficult to hydrolyze by solid acids. Many studies observed a significant increase in hydrolysis efficiency when ball-milled cellulose was used as a substrate for solid acids instead of microcrystalline cellulose because ball-milling pretreatment effectively destroying cellulose crystallinity in addition to reducing cellulose particle size (increasing surface area).[24,27,28,34] Inspired by this, Kobayashi *et al* developed a mix-milling technique where cellulose and catalyst were ball-milled together to enhance the contact of the solid acid catalyst and cellulose.[36] As shown in Figure 9, the dry mix-milling process crushed crystalline cellulose into smaller amorphous particles by the impact of hard alumina balls and thoroughly mixed the amorphous cellulose with a carbonaceous solid acid catalyst.[56] This method enhanced the physical contact between cellulose and

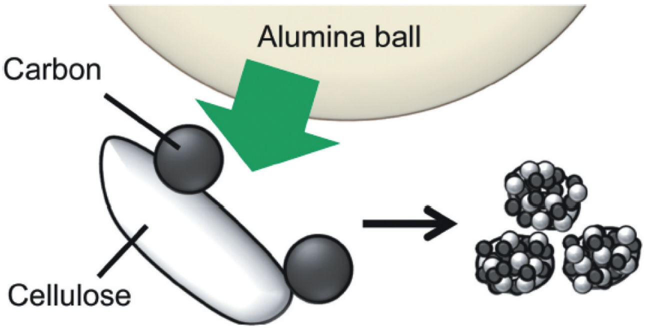

Figure 9. Schematic of mix-milling (Reproduced with permission.[56] Copyright 2018 the Chemical Society of Japan).

the carbon catalyst and therefore gave a high cellulose conversion rate of 93%. Although ball milling pretreatment can effectively improve the cellulose hydrolysis by solid acid, it is not only energy-intensive but also a time-consuming process.

4.2. Homogenous hydrolysis

To enhance the interaction between solid acids and cellulose, hydrolysis in cellulose solvents such as ionic liquids was explored, in which cellulose was dissolved and then hydrolyzed by solid acids.[32,42] The dissolution of cellulose disrupted the crystalline structure and made the β-1,4 glycosidic bonds more accessible for hydrolysis.[127] It was reported that Amberlyst 15 (a sulfonated resin) could hydrolyze cellulose to cello-oligomers in 1-butylmethylimidazolium ([BMIm]Cl) at 100 °C.[31] Cai *et al* found that H-form zeolites were able to effectively hydrolyze cellulose in ionic liquids, [23] but the water had to be gradually added because it is required for cellulose hydrolysis. However, the addition of water could cause cellulose precipitation because water is a non-solvent of cellulose. Moreover, the ionic liquid could affect the performance (catalytic activity) of solid acids. It was found that Amberlyst 15 was deactivated in ionic liquid because of the leaching of SO_3H groups through the ion-exchange with the cation of the ionic liquid.[92] The ionic liquid could affect the catalytic activity of supported metal catalysts as well by leaching metal species.[57] Besides, many ionic liquids are currently expensive, and their recovery is still challenging in industrial applications.

It was also found that microwave irradiation can effectively promote the solid acid-catalyzed cellulose hydrolysis.[43,44,128] The microwave could weaken and break the hydrogen bonding between cellulose chains, which made cellulose more accessible for hydrolysis.[129] It was believed that the microwave radiation enhanced the collision between cellulose and solid acid, thereby facilitating the heterogeneous hydrolysis of cellulose.[43] As observed in other applications, the microwave could enhance many reactions, but mechanisms are not fully understood. The industrial large-scale application of microwave irradiation is still very challenging, as it is a very energy-intensive process.

4.3. Interactions between cellulose and solid acids

The hydrolysis of cellulose by a solid acid requires sufficient interaction, adsorption, and contact between the solid acid and the substrates, including solid cellulose and soluble intermediates such as oligo-glucan and cellobiose. Otherwise, the active acidic sites of the solid acid are unable to access glycosidic bonds to complete the hydrolysis. To enhance the interaction between cellulose and solid acid, a strategy is to improve the physical contact of cellulose with solid acid, for example, by the mix-milling discussed above. Another strategy is to decorate solid acids with affinity and capability to "attach" or "bind" cellulose. It was reported that the β-1,4 glucan immobilized on SiO_2 and Al_2O_3 through ether bonds could be hydrolyzed by the surface OH groups of the oxides, but the free cellulose could not,[67] suggesting that even weak acids were able to hydrolyze cellulose as long as they could closely interact with cellulose. Hydrogen bonding and CH-π interaction are the two important mechanisms for solid acids to adsorb glucan.

4.3.1. Hydrogen bonding

Hara and coworkers found that the amorphous carbon-based solid acid bearing high densities of SO_3H, COOH, and phenolic OH groups could effectively adsorb and hydrolyze soluble long-chain β-1,4 glucan (cellohexaose with 6 glucose units) (Figure 3), while sulfonated resins bearing only SO_3H group (Amberlyst 15 and Nafion NR50) was ineffective to hydrolyze the glucan due to the lack of the close interaction (adsorption) between the resins and the glucan.[30,33,58] Adsorption study indicated that phenolic OH and COOH are capable of adsorbing β-1,4 glucan (phenolic OH are dominant adsorption sites), while SO_3H is not.[30] It was proposed that strong polarized OH-H hydrogen bonds were formed between glycosidic bonds of cellulose and OH groups in the carbon catalyst, which was responsible for the adsorption of cellohexaose on the carbon. Such hydrogen bonds were stronger than the inter- and intra-molecular hydrogen bonds of cellulose, so the β-1,4 glycosidic bonds of cellulose could be preferably associated with the active acidic sites of the catalyst for hydrolysis.[58] Therefore, the good performance of the carbonaceous solid acid was attributed to the synergistic effect of phenolic OH and COOH as adsorption sites to associate with cellulose and strong SO_3H groups as effective acidic sites to hydrolyze cellulose.[30]

Fukuoka *et al*[12,36,88] and Katz *et al*[37,68] reported that carbon materials bearing weak acids (carboxylic acid, phenolic hydroxyl, and lactone groups) could effectively catalyze the hydrolysis of cellulose. They claimed that the functional groups were responsible not only for hydrolyzing cellulose but also for adsorbing cellulose via hydrogen bonding with the hydroxyl group of cellulose. The hydrogen bonding increased the probability of the acid sites attacking the β-1,4 glycosidic bond (Figure 10a), which was demonstrated by density functional theory (DFT) studies.[88]

The importance of the hydrogen bonding between the OH groups on solid acids and glycosidic bonds of cellulose was also demonstrated by Katz and coworkers.[67,98] They grafted β-1,4 glucan strands (derived from cellulose) on SiO_2 and Al_2O_3 surface through ether bonds between cellulose-OH and Si-OH or Al-OH and studied the effect of surface OH density (4.6 and 17 OH/nm^2 for silica and alumina, respectively) on the hydrolysis of grafted β-1,4 glucan. It was observed that the hydrolysis rate of the glucan increased linearly with the surface OH density. They believed that hydrogen bonding formed between the OH group on the solid acids and the oxygen of β-1,4 glycosidic bonds that are juxtaposed adjacent to the surface, which activated the β-1,4 glycosidic bonds for hydrolysis by the OH groups on SiO_2 and Al_2O_3 surface.[98,130]

4.3.2. CH-π interaction

Katz *et al* systematically investigated the adsorption of cellobiose, cellotriose, and long-chain β-1,4 glucans on mesoporous carbon nanoparticles (MCN) and confirmed that the MCN had preferential adsorption of glucans with longer chain (up to 40 glucose units) because the free energy of adsorption monotonically decreased with increasing glucan chain length (at least 0.4 kcal/mol for each glucose unit).[109] As the decrease in the free energy of adsorption was relatively small, compared to the strength of a hydrogen bond,[131] it was suggested that the hydrophilic interactions of cellulose with the oxygen-

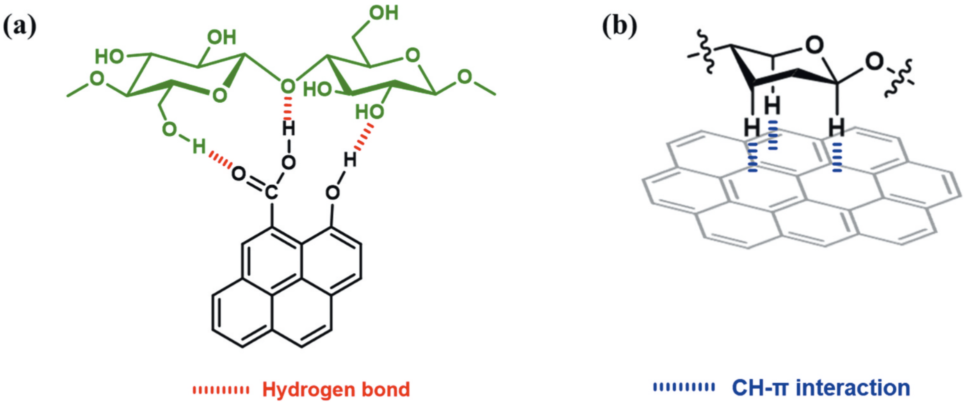

Figure 10. Schematic illustration of cellulose adsorption on solid acid catalyst via (a) hydrogen bonding and (b) CH-π interaction (Adapted and modified with permission.[12] Copyright 2018 American Chemical Society).

containing functional groups were not responsible for the adsorption of cellulose.[38] Fukuoka *et al* also claimed that adsorption occurred at hydrophobic sites on the carbon surface and that hydrophilic groups were not involved.[126] They treated the microporous carbon K26 at high temperature to remove the hydrophilic oxygen functional groups (mostly phenolic OH and COOH), but it turned out the heat-treated carbon had very similar K_{ads} (adsorption equilibrium constant) with the untreated K26 in cellobiose adsorption. Additionally, it was found that the K_{ads} of β-glucans on the carbons increased exponentially with increasing DP (degree of polymerization). Since each glucose unit has two or three axial CH groups on each side of the glucose plane, it was believed that the hydrophobic interaction between axial CH groups and the π electrons of the carbon graphene sheets (CH-π hydrogen bonding) was the main driving force for the adsorption.[109,126] Besides, the entropic release of bound water from the hydrophobic carbon surface to gain a higher degree of freedom also favored the adsorption in addition to the CH-π hydrogen bonding,[126] as the original conformation and mobility of water molecules are restricted to maintain traditional hydrogen-bonding networks, which are entropically disfavored. Fan *et al* demonstrated that the adsorption of glucan oligomers on three-dimensionally ordered mesoporous carbon catalysts was enthalpically and entropically favored, and the adsorption capacity increased with the chain length of the glucans.[35] The longer glucan oligomers had more efficient packing on the carbon surface, and thus the quantity of adsorbed longer glucan was more than that of shorter glucan oligomers and glucose. These findings indicated that hydrophobic rather than hydrophilic interaction was one of the possible driving forces for the adsorption of cellulose on carbon catalysts. It was proposed that van der Waals forces, including CH-π interaction between the axial hydrophobic C-H groups of cellulose chain and π electrons in the polyaromatic rings of the carbon structure, contributed a significant fraction to the adsorption driving force (Figure 10b). The CH-π interaction is similar to that between cellulase (cellulose-hydrolyzing enzymes) and cellulose, in which cellulase is adsorbed on cellulose through the carbohydrate-binding sites of cellulase that consists of hydrophobic aromatic amino acid residues.[132,133]

4.3.3. Cellulase-mimetic bifunctional solid acid catalysts

The cellulose hydrolysis by solid acids usually requires very high catalyst loading to substrate because of the ineffective interactions between solid acids and cellulosic substrate. In contrast, cellulases are highly active in hydrolyzing cellulose because they have a dedicated substrate-binding domain for associating themselves to cellulose surface and a catalytic domain responsible for hydrolyzing β-1,4 glycosidic bonds of cellulose. To improve the interaction/binding between solid acids and cellulose, a concept of cellulase-mimetic solid acid was proposed to introduce an additional cellulose-binding

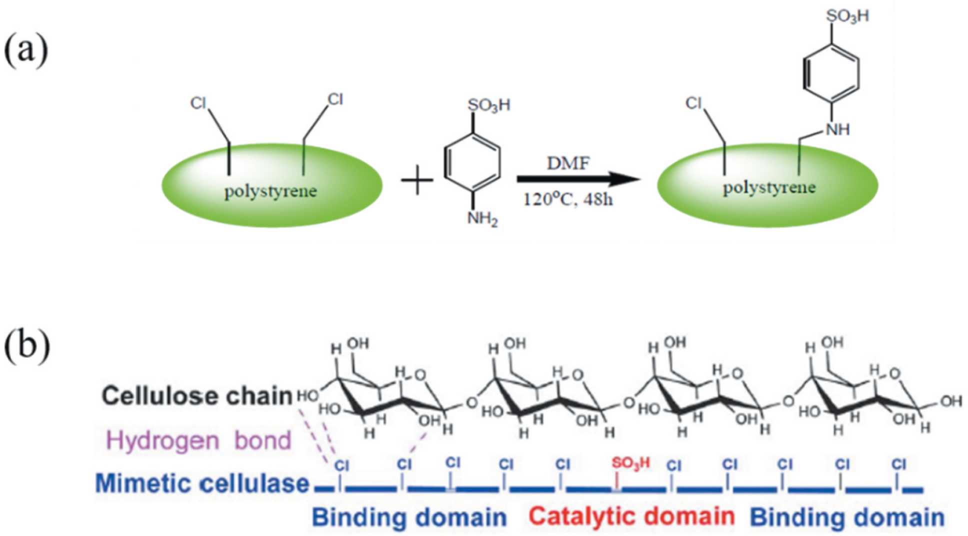

Figure 11. (a) Fabrication and (b) hydrolysis mechanism of cellulase-mimetic bifunctional solid acid (Adapted with permission.[45] Copyright 2012 The Royal Society of Chemistry)

group and fabricate a bifunctional solid acid. For example, Shuai and Pan fabricated a sulfonated chloromethyl polystyrene resin (CP) as bifunctional solid acid (CP-SO$_3$H) for cellulose hydrolysis (Figure 11a).[45] The chlorides (-Cl) on the solid acid functioned as cellulose-binding groups (CBGs) by forming hydrogen bonds with hydroxyls of cellulose and also facilitated disrupting the inter- and intra-hydrogen bonds within cellulose, while sulfonic acid groups (-SO$_3$H) as catalytic domain were responsible for hydrolyzing β-1,4 glycosidic bonds of cellulose (Figure 11b). Because of the substrate-binding ability of CP-SO$_3$H, it showed significantly higher catalytic activity than sulfuric acid and other solid acids at equivalent acid loading, hydrolyzing cellulose by up to 93% under relatively mild conditions (120 °C, 10 h). Moreover, the apparent activation energy for cellulose hydrolysis by CP-SO$_3$H was much lower than that by sulfuric acid. This is why the CP-SO$_3$H was able to hydrolyze cellulose at a lower temperature, which would avoid or reduce the undesirable glucose degradation occurring at high temperatures.

The idea of incorporating chloride as a cellulose-binding group in solid acids was adopted in many follow-up studies. For example, carbon-based solid acid was fabricated by co-carbonization of starch and polyvinyl chloride (PVC) for cellulose hydrolysis so that the chloride groups derived from PVC functioned as adsorption sites for cellulose. It was found that 10–25% chloride of the catalyst leached after three runs in cellulose hydrolysis.[48] A double-adsorption functional carbon-based solid acid with chloride and hydroxyl groups was fabricated from pyrolysis of polyethylene (PE) and polyvinyl chloride (PVC) from plastic wastes.[49] The strong electronegative Cl groups and high-density phenolic OH group both contributed to the adsorption of cellulose. A recent study questioned the role of chloride groups to form a hydrogen bond with cellulose and demonstrated that the C-Cl bonds were readily hydrolyzed to C-OH under the cellulose hydrolysis condition and released HCl. They claimed the released HCl is more likely to contribute to the improved performance of bifunctional solid acid in hydrolyzing cellulose.[134]

Later, a two-step strategy was developed to fabricate porous polymeric solid acid with bifunctionality, synthesis of the porous polymeric backbone from aromatic monomers with desirable cellulose-binding groups (e.g., phenylboronic acid) by Friedel-Crafts polymerization followed by sulfonation of resultant polymer to introduce sulfonic groups as cellulose-hydrolytic groups (Figure 12a).[46] For example, a resultant bifunctional solid acid with 0.09 mmol/g $B(OH)_2$, 2.20 mmol/g SO_3H, and 736 m^2/g BET surface area gave a glucose yield of 94.6% after 48-h hydrolysis of Avicel at 120°C, while Amberlyst 15 with 4.9 mmol/g SO_3H and 53 m^2/g BET surface area but without cellulose-binding group only yielded 7.7% glucose. The good catalytic activity of the cellulase-mimetic solid acid toward cellulose hydrolysis was attributed to the boronic acid group as cellulose-binding domain and the large surface area from the mesoporous structure of the solid acid. The reason why boronic acid can function as an effective cellulose-binding group is that it can form a reversible five-element ester ring with two adjacent hydroxyl groups of cellulose and thus associate cellulose to the catalytic sites to complete the hydrolysis reaction (Figure 12b).[46] The cellulase-mimetic solid acid bearing both $B(OH)_2$ and SO_3H showed a significant decrease in glucose yield (94.6% to 74.6%) after recycling four times in cellulose (Avicel) hydrolysis, which was primarily attributed to SO_3H leaching. Bifunctional solid acid with chloride as a cellulose-binding group was also fabricated by the two-step strategy from the aromatic monomers with a chloride group such as chlorobenzene.[47] Numerous follow-up studies fabricated bifunctional solid acid catalysts using the same two-step strategy for applications in different catalytic reactions.[135–

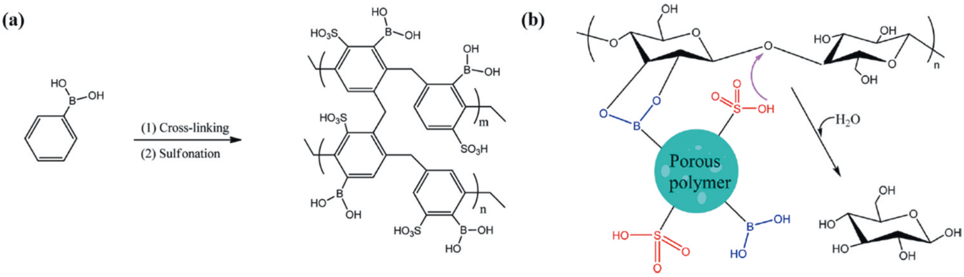

Figure 12. (a) Two-step fabrication and (b) hydrolysis mechanism of mesoporous cellulase-mimetic bifunctional solid acid bearing boronic and sulfonic acids (Adapted with permission.[46] Copyright 2016 American Chemical Society)

138] For example, Zhang *et al* fabricated SO_3H-functionalized highly cross-linked porous polymer from benzene and found the solid acid was active in the catalytic dehydration of biomass-derived carbohydrates into 5-hydroxymethyl furfural.[135] Wang *et al* synthesized porous polymeric solid acids from dichloromethyl monomers (e.g., *α*,*α*'-dichloro-*p*-xylene), followed by post-sulfonation to introduce acid sites.[136] The resultant solid acids had a large surface area (>1000 m^2/g) with narrow dispersed pores (~2 nm) and showed good catalytic activity in acid-catalyzed Friedel-Crafts alkylation and Beckmann rearrangement reactions.

Cellulase-mimetic bifunctional solid acid with a dedicated cellulose-binding domain is conceptual progress toward developing effective solid acid catalysts for cellulose hydrolysis. Inspired by cellulases, the introduction of cellulose-binding functionality to the solid acid enhanced the interaction/binding between cellulose and solid acid, which is a major limitation of traditional monofunctional solid acids. To further improve the performance of cellulase-mimetic solid acid, attention should be paid to selecting more effective and stable cellulose-binding groups, increasing the density of cellulose-hydrolytic /binding sites, manipulating porous structure, and improving the recyclability of cellulase-mimetic solid acids.

5. Hydrothermal stability and recyclability of solid acids

5.1. Hydrothermal stability of solid acids

Water is required for cellulose hydrolysis, and it is also the most common reaction media for cellulose hydrolysis. The cellulose hydrolysis by solid acids is usually conducted at elevated temperature (c.a.100–200 °C) for long reaction time to achieve a satisfactory glucose yield. However, the stability of solid acids under such harsh hydrothermal conditions becomes a major concern, under which partial leaching or deactivation of acidic sites (discussed in 2.4) and even the hydrolysis of the framework of solid acids could occur.[53] This would negatively affect the reusability of the solid acids, which is supposed to be a major advantage of solid acids over homogenous acids. In principle, solid acids with higher hydrophobicity tend to be more hydrothermally stable because they are more resistant to water. However, it should be kept in mind that water as a medium is crucial in cellulose hydrolysis, and surface wettability of solid acid is required to ensure the access of water to the catalyst surface. Therefore, when designing and synthesizing solid acids, surface hydrophobicity and hydrophilic acidic sites must be carefully balanced to maximize their performance in cellulose hydrolysis and good stability for recycling and reuse.

The reported solid acids such as zeolites, sulfonated metal oxides, SO_3H-functionalized silica, sulfonated carbon, and SO_3H-based porous polymer, have various frameworks and structures, which result in different degrees of hydrophobicity and hydrothermal stability. For example, the hydrothermal stability of H-form zeolites was strongly dependent on their framework types.[23,24,128] H-ZSM-5 zeolite was reported to be relatively stable in hot water between 150 and 200 °C, while zeolite Y was less stable, dependent on the Si/Al ratio.[139] Zeolites with a high Si/Al ratio generally have relatively higher hydrophobicity and thus better hydrothermal stability and catalytic activity in cellulose hydrolysis.[24,53] Zeolites tended to undergo dealumination under hydrothermal conditions, leading to the reduction of accessible acid sites as well as the micropore volume, which would negatively affect the catalytic activity and reusability of the zeolites.[139,140]

Metal oxides with Lewis acid sites are generally unstable and tend to evolve to metal hydroxides in water.[141] Niobic acid ($Nb_2O_5 \cdot nH_2O$), prepared by amorphous niobium oxide with incorporated water ($Nb_2O_5 \cdot nH_2O$), was found to be a water-tolerant heterogeneous Lewis acid catalyst.[142,143] The Lewis site NbO_4 rapidly combined with water to NbO_4-H_2O, but it could still catalyze the dehydration of glucose to 5-(hydroxymethyl)furfural. However, due to the lack of Brønsted acid sites, niobic acid was proved to be inefficient in hydrolyzing β-1,4 glycosidic bonds in cellulose.[30] Later, layered transition-metal oxide $HNbMoO_6$ with strong acidity and water tolerance was developed for cellulose hydrolysis.[25,144] Its unique 2D-layered nanostructure facilitated the intercalation of oligosaccharides, cellobiose, and water into the strong acidic interlayer gallery (the strong Brønsted acid sites ascribed to the bridging hydroxyl groups between Nb^{5+} and Nb^{5+}) and the mass transfer of resultant glucose off the catalyst.[25] The total yield of glucose and cellobiose was about 8.5% from the hydrolysis of cellulose at 403 K for 12 h.[25] The $HNbMoO_6$ was recoverable by washing with water and acetone to remove the residues within the interlayer, and no change in crystal structure or activity was observed after three reuse cycles.[25]

Solid acids with an inorganic framework such as SO_3H-functionalized mesoporous silica usually had low hydrothermal stability because their hydrophilic frameworks were prone to be hydrolyzed by eluted H_2SO_4 from the leaching of acidic sites.[53,145] In contrast, carbonaceous solid acids with hydrophobic carbon network showed better hydrothermal stability and generally had a good performance in cellulose hydrolysis.[33,72,73] A study on the cellulose hydrolysis in the water at 150 °C for 24 h by various solid acids revealed that the sulfonated activated carbon (AC-SO_3H) had significantly higher catalytic activity and glucose selectivity than the tested H-form zeolites, which was presumably attributed to its hydrophobic and stable graphene planes and strong acidic SO_3H groups.[24] Sulfated zirconia (ZrO_2) and Amberlyst 15 (ion-exchange resin with SO_3H) had low hydrothermal stability, eluting H_2SO_4, which led to more by-products from glucose degradation. In addition to sulfonated activated carbon, carbonaceous solid acids fabricated by sulfonation of incompletely carbonized natural polymers (e.g. sugars, starch, and cellulose) also showed good hydrothermal stability. For example, only 6 μmol of SO_3H groups (ca. 1%) was eluted as H_2SO_4 after the treatment at 100 °C for 150 h.[33] The hydrothermal stability of hydrophobic carbon-based solid acids could be further improved by increasing the degree of cross-linking in their framework, for example, by increasing the carbonization temperature during the fabrication. As carbonization temperature increased, the resultant carbon precursor transformed from small loose polycyclic aromatic carbon sheets to larger densely cross-linked graphitic carbon rings, which prevented water from incorporation into the carbon bulk.[41,97] Besides, the highly cross-linked carbon had low reactivity toward sulfonation, so SO_3H and other hydrophilic groups (phenolic OH and COOH) were much lower in the resultant solid acid, leading to lower affinity to hydrophilic molecules.[36] Therefore, the carbon-based solid acid carbonized at higher temperatures had fewer hydrophilic functional groups and a more hydrophobic framework, which helped to maintain their stability under hydrothermal conditions. However, on the other hand, because of the low density of acid sites and the poor and limited accessibility of hydrophilic reactants to the tightly cross-linked carbon sheets, the catalytic activity of the solid acids carbonized at high temperature was usually lower than that of those obtained at low temperature in cellulose hydrolysis.

5.2. Strategies to recycle solid acids from lignocellulose hydrolysis

5.2.1. Challenges in the recycling of solid acids

One issue of homogeneous acids is the difficulty in their separation and recovery from the hydrolyzate. In contrast, heterogeneous solid acid could be easily separated from cellulose hydrolyzate by filtration or centrifugation[30,58,59] and then reused in cellulose hydrolysis on the premise that the solid acid maintained catalytic activity. For example, Hara *et al* reported that more than 99% carbon catalyst was recovered from the hydrolyzate by simple decantation, and the recovered catalyst showed no activity decrease after 25 reuses for cellulose hydrolysis.[33] In the case of pure cellulose hydrolysis, the solid acid along with residual cellulose could be directly recycled and reused in the next batch without separation. However, when hydrolyzing real lignocellulosic biomass, lignin along with unhydrolyzed cellulose and even humins derived from the degradation of sugars would make the recycle of solid acids more challenging. Hara *et al* claimed that carbon catalysts could be readily separated from lignin in the hydrolyzate of eucalyptus by decantation, as the sedimentation rates of lignin and dense carbon particles differed substantially.[33] Fukuoka *et al* developed a self-contained system to prepare carbon catalysts from eucalyptus wood for hydrolyzing the wood, which realized a facile loop of catalyst preparation and recycling (Figure 13).[39] A carbon-based solid acid (E-carbon, with 2.1 mmol/g

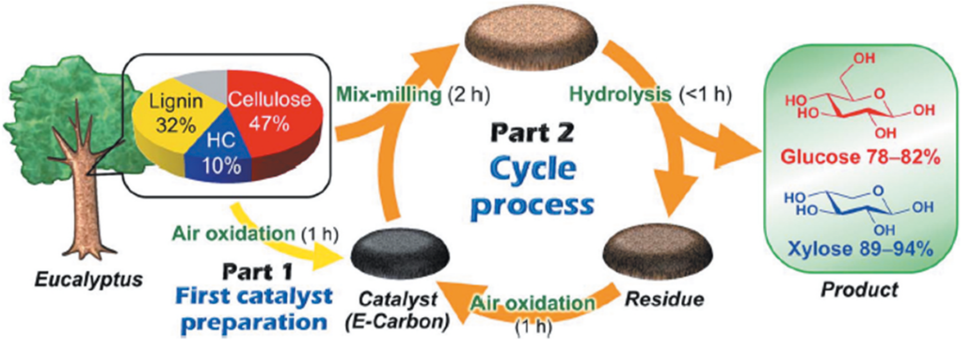

Figure 13. Schematic representation of a self-contained system using *Eucalyptus* as both catalyst source and biomass substrate (Reproduced with permission.[39] Copyright 2016 the Royal Society of Chemistry).

carboxylic groups) was produced from eucalyptus by air oxidation and then used to hydrolyze eucalyptus to produce glucose and xylose. After the hydrolysis, the solid residue consisting of the catalyst and insoluble ingredients (mainly lignin) was transformed back to regenerate the catalyst by the same air oxidation. This strategy creatively leveraged the contamination of lignin for the preparation of catalysts and achieved efficient recycling of solid acid in the hydrolysis of real lignocellulosic biomass.

5.2.2. Magnetic solid acids to facilitate recycling

A feasible way to recycle solid acids is to synthesize magnetic solid acids, which could be easily separated from hydrolysis residues with an external magnetic field. Magnetic solid acids could be fabricated by incorporating magnetic nanoparticles such as iron (Fe), nickel (Ni), or cobalt (Co) into solid acid catalysts, assuming that these magnetic components should not interfere with other functionalities (e.g. acidity and mesoporosity) of solid acids.[82] For example, Fu *et al* synthesized a magnetic solid acid catalyst (Fe_3O_4-SBA-SO_3 H) by incorporating magnetic Fe_3O_4 nanoparticles into sulfonated ordered mesoporous silica SBA-15.[50,146] The magnetic solid acid gave a glucose yield of 26% from hydrolyzing microcrystalline cellulose and total reducing sugar yield of 45% from corncob, respectively. The used Fe_3O_4-SBA-SO_3H could be easily separated from the reaction mixture by a permanent magnet, and both mesoporous structure and the magnetic of the solid acid were retained after three repeated hydrolysis experiments (3 cycles), indicating that Fe_3O_4-SBA-SO_3H was stable under the hydrothermal condition. Similarly, Ebitani *et al* reported that SO_3H-appended magnetic silica nanoparticles were capable of hydrolyzing disaccharides (sucrose and cellobiose) and polysaccharides (starch and cellulose) with facile magnetic separation.[51] The catalyst was fabricated by embedding magnetic $CoFe_2O_4$ cores in silica and followed by oxidation of thiol groups to strong acidic SO_3H groups. The $CoFe_2O_4$-

embedded silica nanoparticle acid catalyst had good dispersion in water and better interaction with cellulose, but the acid density of the magnetic solid acid was low (0.5 mmol/g), thereby only yielding 7.0% glucose after hydrolyzing microcrystalline cellulose at 150 °C for 3 h.

A common concern of magnetic solid acids is the stability of magnetic nanoparticles in the acidic environment during cellulose hydrolysis. These metallic nanoparticles embedded in solid acids are in high surface energy and prone to leaching under aqueous acidic conditions. Strategies to "protect" and maintain the magnetism of solid acids are critical for the success of magnetic solid acids in cellulose/lignocellulose hydrolysis. For example, entrapping metallic nanoparticles within mesoporous or graphene-like carbon shells could effectively prevent the leaching or aggregation. Lu *et al* fabricated carbon-shell protected cobalt nanoparticles via pyrolysis of monodispersed cobalt nanoparticles (freshly prepared) with excessive Pluronic surfactant P_{123} at 1000°C.[52] P_{123} not only prevented the agglomeration of cobalt nanoparticles but also acted as the carbon source for surface coating. In the resultant magnetic material Co@C-1, cobalt nanoparticles were completely embedded in curved and layered graphite structures with 5–10 graphitic sheets, which resembled larger fullerene cages. No cobalt nanoparticles were leached after Co@C-1 was immersed in excessive nitric acid (53 wt%) at room temperature for one month, which demonstrated that magnetic cobalt nanoparticles were protected in carbon-shells from acid erosion.[147] Similarly, Zhang *et al* reported a magnetically recyclable catalyst Fe_3O_4@C-SO_3H prepared by sulfonating magnetic core-shell Fe_3O_4@C nanocomposite in concentrated sulfuric acid.[52] The carbon-encapsulated Fe_3O_4@C composite was synthesized by hydrothermal carbonization of the mixture of $FeCl_3$, glucose, and urea, which produced amorphous carbon shells (about 10 nm, from carbonization of glucose) with Fe_3O_4 core (100–200 nm, formed from the reduction of Fe^{3+} by glucose under the alkaline condition from the decomposition of urea).[148] Glucose was chosen as the carbon source because the functional groups (such as OH and $C = O$) on the surface of the resultant carbon shells could facilitate subsequent sulfonation to incorporate acid sites.[149] The prepared catalyst Fe_3O_4@C-SO_3H had an acid density of 1.30 mmol/g and gave a cellulose conversion of 48.6% with 52.1% glucose selectivity after 12 h cellulose hydrolysis at 140°C, but the performance was not as good as the reported regular sulfonated carbon catalysts without magnetization. The catalyst Fe_3O_4@C-SO_3H could be effectively recovered in a magnetic field. The saturation magnetization of reused Fe_3O_4@C-SO_3H slightly dropped in the first run and no further decrease was observed in the second and the third run. The good stability of magnetic Fe_3O_4@C-SO_3H nanoparticles was mainly attributed to the carbon shell, which prevented the magnetic Fe_3O_4 cores from elution during hydrolysis reaction.

6. Conclusive remarks and outlooks

Significant progress has been made during the last decades in the design, fabrication, and application of solid acids as catalysts for cellulose hydrolysis. It was understood that the performance of solid acid catalysts in cellulose hydrolysis is a combined outcome of structural properties of both solid acid and cellulose and the efficient contact/interaction between the solid acid and cellulose. In general, solid acids with a high density of functional acid sites, a large surface area associated with mesopores, and strong affinity and close contact to cellulose tend to have high catalytic activity toward cellulose hydrolysis. Many efforts have successfully improved the performance of solid acids in hydrolyzing cellulose through, for example, incorporating more acid sites, creating mesoporous structure, and enhancing the cellulose-solid acid interaction/contact by mix-milling, dissolving cellulose, and introducing cellulose-binding sites into solid acids. In addition, a better understanding has been achieved of the interactions between cellulose and solid acids, which include hydrophilic hydrogen bond, hydrophobic CH-π interaction, and dedicated cellulose-binding groups. Magnetic solid acids have been fabricated to facilitate the separation and recycling of solid acids, but the stability of the magnetic particles (e.g. Fe_2O_3 and Fe_3O_4) under acidic and hydrothermal conditions needs improvement.

Future research on solid acid catalysts for cellulose hydrolysis should address the major problems and challenges identified above, in particular, low catalytic activity, poor hydrothermal stability, inefficient interactions between solid acids and solid cellulose, and unsatisfactory recyclability. The following areas are of great interest and full of opportunities.

(1) Solid acids with high specific catalytic activity are highly desired. Introducing high-density, multiple, and hydrothermally stable acid sites is a general approach to enhance catalytic activity. Dedicated cellulose-binding /adsorbing functionality is a successful strategy to enhance the interactions of a solid acid with cellulose. The dispersion and synergetic effects of the multi functionalities are crucial to the performance of the solid acids.

(2) There is an increasing interest in exploring new methods and new precursors to synthesize solid acids with high surface area, mesopores, and high-density acid sites. For example, porous polyaromatic hydrocarbons (polypyrrole, polynaphthalene, and polystyrene) are expected to be promising precursors of solid acids, because the aromatic skeletons facilitate the introduction of high-density sulfonic acid groups. Lignin could be a unique carbon precursor for solid acids. This not only provides a low-cost carbon source but also potentially alleviates the separation and recycling of solid acids because

the mixture of used solid acids and hydrolysis residues (mainly lignin) could be directly transformed into next-batch solid acid without separation. The mesoporous structure has been proven to be crucial for solid acids, but the function of mesopores during cellulose hydrolysis retains unclear, which should be further studied. Hydrothermal carbonization with an appropriate template is a promising and efficient strategy to fabricate carbon-based solid acids with a controllable mesoporous structure. Considering the potential environmental impact/hazard of solid acids, such as heavy metal-containing solid acids, biodegradable, and less hazardous materials/precursors are desirable for the fabrication of solid acids.

(3) Further understanding of the interactions between solid acids and cellulose, such as the relative affinity to and selective adsorption of substrate (cellulose), intermediates (oligoglucan and cellobiose), and product (glucose) on solid acids, is fundamentally and practically important in designing and fabricating substrate-philic solid acids to enhance the contact and interaction between cellulose and solid acids. For example, atomic force microscopy (AFM) and quartz crystal microbalance (QCM) can be utilized to study the relative affinity of intermediates (soluble oligosaccharides and cellobiose) and product (glucose) on solid acids and to investigate the function and performance of the dedicated cellulose-binding groups, which are expected to have a preferable affinity to cellulose over glucose. In the hydrolysis of lignocellulosic biomass by solid acid, the interaction between solid acid and lignin is not well understood, which may impact cellulose hydrolysis by the nonproductive interaction/adsorption, similar to that between lignin and cellulases.

(4) It is highly desirable to synthesize hydrothermally stable and easily recyclable solid acids for cellulose hydrolysis. It is a challenging work to protect SO_3 H groups of solid acids from leaching at high temperatures. An alternative strategy is to hydrolyze cellulose at a lower temperature, but this needs a higher solid acid load and longer hydrolysis time. A solid acid with ultra-high catalytic activities is a potential solution to this issue. An innovative recycling strategy is highly desirable. Magnetic solid acids are promising for easy recycling, but their stability in the acidic and hydrothermal environment needs further improvement. An alternative strategy is to fabricate carbonaceous solid acid particles with lower density than water, cellulose, and lignin, so the solid acid could be separated easily from the hydrolyzate and the residual lignocellulosic biomass (unhydrolyzed cellulose and lignin) by centrifugation such as using a cyclone separator. For solid acid regeneration, fast, facile, and inexpensive methods for regenerating solid acids such as re-sulfonation and ion-exchange are greatly needed.

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