

Introducing hydroxyl groups as cellulose-binding sites into polymeric solid acids to improve their catalytic performance in hydrolyzing cellulose

Qiang Yang^{a,b}, Xuejun Pan^{a,*}

^a Department of Biological Systems Engineering, University of Wisconsin-Madison, 460 Henry Mall, Madison, WI, 53706, United States

^b Department of Chemical and Paper Engineering, Western Michigan University, Kalamazoo, MI, 49008, United States

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ABSTRACT

Effective hydrolysis of cellulose to glucose is a crucial step to produce fuels and chemicals from lignocellulosic biomass. Solid acids are promising alternatives of cellulases and homogenous acids for hydrolyzing cellulose. In this study, porous polymeric solid acids bearing hydroxyl and sulfonic acid groups were fabricated for cellulose hydrolysis in water through the low-cost Friedel-Crafts “knitting” polymerization of hydroxyl-containing aromatic monomers followed by sulfonation. The synthesized bifunctional solid acids could effectively hydrolyze microcrystalline cellulose (Avicel) to glucose by as high as 93 % at 120 °C within 48 h and ball-milled Avicel by 98 % at 120 °C in 24 h. The evidence from this study indicated that the outstanding catalytic performance of the solid acids was attributed to the porous structure (large surface area) and the presence of the hydroxyl (cellulose-binding group) in the solid acids.

1. Introduction

With increasing consumption and concomitant depletion of fossil reserve, ever-increasing attention has been attracted to obtaining fuels and chemicals from renewable, sustainable, and inedible lignocellulosic biomass that consists mainly of cellulose, hemicellulose, and lignin (Bond, Alonso, Wang, West, & Dumesic, 2010; Chhedha, Huber, & Dumesic, 2007; Gürbüz et al., 2013; Kunkes et al., 2008). Cellulose is a polymer of anhydroglucose units linked by the β -1,4 glycosidic bond, and is the most abundant natural polymer on earth. Glucose has been consensually considered as a future feedstock for producing liquid fuels, such as ethanol and butanol, and platform chemicals, including sorbitol, lactic acid, 1,3-propanediol, 5-hydroxymethylfurfural, and levulinic acid (Bermejo-Deval et al., 2012; Gunther et al., 2012; Luo, Wang, & Liu, 2007; Moliner, Román-Leshkov, Labinger, & Davis, 2010; Ordonsky, van der Schaaf, Schouten, & Nijhuis, 2012; Ruppert, Weinberg, & Palkovits, 2012; Yong, Zhang, & Ying, 2008; Yoo, Zhang, & Pan, 2017) through sugar-platform based technologies. Effective hydrolysis of cellulose to glucose is, therefore, a crucial step and a prerequisite to produce the fuels and the chemicals from lignocellulosic biomass.

Tremendous efforts have been devoted to exploring efficient catalysts for hydrolyzing cellulose to glucose in an aqueous medium. Cellulolytic enzymes (cellulases) and homogenous mineral acids (e.g.,

sulfuric acid) are the dominant catalysts to cleave the β -1,4 glycosidic bonds of cellulose for hydrolysis (Akiyama, Matsuda, Sato, Takata, & Kitagawa, 2011; Lai, Deng, Guo, & Fu, 2011; Pang, Wang, Zheng, & Zhang, 2010; Vyver, Geboers, Jacobs, & Sels, 2011; Huang & Fu, 2013; Zeng & Pan, 2021). Cellulases are highly selective and can hydrolyze cellulose under mild conditions, but they are still facing technical and economic challenges in activity, cost, robusticity, hydrolysis rate, and recyclability. Mineral acids have exceptional catalytic activity and low cost, but they have issues such as poor selectivity (sugar degradation), equipment corrosion, wastewater treatment, and poor recyclability. To address the issues of cellulases and homogeneous acids, heterogeneous solid acids (such as metal oxides, H-form zeolites, sulfonated carbons, supported metal catalysts, porous polymer-based catalysts, and C/Si nanocomposites) have drawn increasing attention as alternative catalysts for cellulose hydrolysis (Zeng & Pan, 2021). In general, solid acids are less expensive and more thermally stable than cellulases, and less corrosive and more environmentally friendly than mineral acids. Besides, the solid acids are potentially easier to recycle than cellulases and homogeneous acids. However, the solid acids are usually not as effective as mineral acids and cellulases in hydrolyzing cellulose and therefore need high catalyst loading, mainly because of the solid nature of the solid acids, which limits their close interaction with the solid cellulose substrate (Zeng & Pan, 2021). Another issue of solid acids is the leaching

* Corresponding author.

E-mail address: xpan@wisc.edu (X. Pan).

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of acid sites under hydrothermal conditions, which affects their lifetime and recyclability.

Many strategies have been taken to improve the catalytic performance of the solid acids in hydrolyzing cellulose, for example, increasing the density of acid sites, synthesizing highly porous solid acids with a large surface area, and improving the affinity (interaction) between solid acids and cellulose. Many efforts have been made to enhance the solid acid-cellulose interaction, such as reducing the size of cellulose substrate and solid acids by milling (Kobayashi & Fukuoka, 2018), dissolving cellulose in a solvent for homogeneous hydrolysis (Cai, Li, Wang, Xu, & Zhang, 2012; Guo, Qi, Li, & Smith, 2012; Wu, Li, Pan, & Chen, 2020), and introducing cellulose-binding sites into solid acids (Shen et al., 2014; Shuai & Pan, 2012; Yang & Pan, 2016a, 2016b; Tyufekchiev et al., 2018; Yuan et al., 2019). The idea of introducing cellulose-binding sites into solid acids was inspired by the nature of two-domain cellulases that have a cellulose-binding domain to attach the cellulases to cellulose and a cellulose-hydrolyzing domain to cleave the glycosidic bond. It has been proved that the functional groups such as chlorine and boronic acid on solid acids could improve their performance in hydrolyzing cellulose because of increased associations between the solid acids and cellulose via hydrogen bond or reversible covalent bond (Shuai & Pan, 2012; Yang & Pan, 2016a, 2016b). It was also observed that the hydroxyl groups on the carbon-based solid acids from incompletely carbonized biomass such as sugars, cellulose, and starch promoted the cellulose hydrolysis (Hu, Smith, Lou, & Zong, 2014; Suganuma et al., 2008; Wu et al., 2010; Zhang et al., 2012).

In a previous study (Shuai & Pan, 2012), we demonstrated that the vinyl polymer bearing both chloride and sulfonic acid groups showed a much better ability to hydrolyze cellulose than that bearing only the sulfonic acid group. Other groups synthesized similar halide-bearing polymeric solid acids and investigated the function of the halide groups in cellulose hydrolysis (Tyufekchiev et al., 2018; Woodward et al., 2018; Yuan et al., 2019). In a following-up study, we synthesized a chloride-bearing bifunctional and highly porous polymeric solid acid from chloride-containing aromatic monomers via the Friedel-Crafts “knitting” polymerization followed by sulfonation (Yang & Pan, 2016a), in which chloride functioned as the cellulose-binding group, and sulfonic acid as the cellulose-hydrolyzing group. The primary advantage of the Friedel-Crafts polymerization is to allow synthesizing the solid acids with desirable functional groups as well as porous structure (larger surface area). It turned out that the chloride-bearing solid acid was much more active than that without the chloride in hydrolyzing microcrystalline cellulose. However, a previous study (Tyufekchiev et al., 2018) suggested that the chloride-enhanced catalytic ability be probably (at least partially) attributed to the proton released from the hydrolysis of chloride, and meanwhile, the resultant hydroxyl groups from the chloride hydrolysis serve as cellulose-binding sites. This became the key working hypothesis of the present study that hydroxyl groups can function as cellulose-binding sites to enhance the solid acid-cellulose interaction and thereby improve the catalytic performance of solid acids in hydrolyzing cellulose. In another study (Yang & Pan, 2016b), we synthesized the boronic acid-bearing solid acids using the same Friedel-Crafts polymerization. Since boronic acid groups can form reversible covalent bonds with cellulose hydroxyl groups to improve the solid acid-cellulose interaction, the boronic acid-bearing solid acids performed excellently in hydrolyzing cellulose (up to 95 % hydrolysis at 48 h). However, the boronic acid-containing aromatic monomers were less abundant and more expensive for synthesizing the polymeric solid acids, compared to the chloride- or hydroxyl-containing ones.

Therefore, inspired by the previous studies and observations above, we explored to fabricate high-performance bifunctional porous polymeric solid acids from more abundant and inexpensive hydroxyl-containing aromatic monomers in the present study. The resultant solid acids bearing hydroxyl and sulfonic acid groups as cellulose-binding and cellulose-hydrolyzing sites, respectively, were

investigated for hydrolyzing microcrystalline cellulose in water.

2. Experimental section

2.1. Materials

Toluene, sulfuric acid, and fuming sulfuric acid (with 20 % free SO₃) were bought from Fisher Scientific. Phenol, benzyl alcohol, 3-phenyl-1-propanol, 3-phenylphenol, 1-naphthalene methanol, 2,3-dihydroxy naphthalene, 1,2-bi-2-naphthol, 1-pyrenemethanol, anhydrous iron (III) chloride, 1,2-dichloroethane, formaldehyde dimethyl acetal, and glucose were purchased from Alfa Aesar. Avicel cellulose with a degree of polymerization (DP) of 160 was obtained from Sigma-Aldrich. The DP was determined using a viscosity method. In brief, the viscosity of cellulose solution in cupriethylenediamine as a solvent was measured using a capillary viscometer, as described in the Technical Association of Pulp and Paper Industry (TAPPI) standard method T230 om-08. The DP was then calculated using the following equation, $DP^{0.905} = 0.75 \times (954 \log[\eta] - 325)$, where $[\eta]$ is the viscosity in mPa·s (Negri, Jimenez, Hill, & Francis, 1998). All chemicals were used as received. Amberlyst 15 was bought from Mallinckrodt. Cellulase with the activity of 70 FPU (filter paper unit)/g and β -glucosidase with the activity of 250 CBU (cellobiohydrolase unit)/g were generously provided by Novozymes (Franklinton, NC).

2.2. Synthesis of porous polymeric solid acids bearing hydroxyl and sulfonic acid

Porous polymers with hydroxyl groups as the precursor of the solid acids were synthesized with a nearly 100 % yield (based on the aromatic monomers consumed during the polymerization) according to our previously reported method (Yang & Pan, 2016a, 2016b). Typically, hydroxyl-containing aromatic monomer (0.04 mol) was dissolved (or dispersed) in anhydrous 1,2-dichloroethane (30 mL) in a 250-mL flask with a condenser. Then, formaldehyde dimethyl acetal (0.12 mol) and anhydrous iron chloride (0.12 mol) were added to the flask. The reaction was carried out at 45 °C for 5 h and then continued at 80 °C for 21 h under stirring. The formed precipitate was dispersed in methanol, thoroughly rinsed with methanol, and then extracted in Soxhlet with methanol for 24 h. The resultant porous polymer was dried under vacuum. The polymer was then sulfonated with a mixture of concentrated sulfuric acid and fuming sulfuric acid to introduce sulfonic acid. Briefly, the polymer (8 g) was dispersed in a mixture of sulfuric acid (100 mL) and fuming sulfuric acid (20 mL) in a 250-mL flask with a condenser. The sulfonation reaction was carried out at 80 °C for 24 h under stirring. The sulfonated polymer was separated by centrifugation, thoroughly rinsed with deionized water until the pH of filtrate reached about 7, and then dried under vacuum.

2.3. Ball-milling of cellulose

The ball-milling of Avicel was conducted on a Retsch planetary PM 100 ball mill. Avicel cellulose (5 g) was milled for 2 h in a stainless steel vial with 10 ZrO₂ balls at room temperature.

2.4. Hydrolysis of cellulose by the porous polymeric solid acids bearing hydroxyl and sulfonic acid

The conditions for cellulose hydrolysis were chosen according to our previous studies (Shuai & Pan, 2012; Yang & Pan, 2016a, 2016b). Typically, the synthesized solid acid (0.2 g) and Avicel or ball-milled Avicel cellulose (50 mg) were mixed with deionized water (2 mL) in a 6-mL Teflon vial (Saville, USA). The hydrolysis experiment was carried out at 120 °C under a strong magnetic stirring (1,150 rpm). When the reaction was completed, the mixture was filtrated and washed with deionized water. Glucose in the filtrate was determined with the

high-performance ion chromatography (HPIC) method, as described below.

2.5. Enzymatic hydrolysis of cellulose

Enzymatic hydrolysis of Avicel at 2% concentration was carried out at 50 °C in sodium acetate buffer (50 mM, pH 4.8, 40 mL) with tetracycline chloride (2 mg) as antibiotics on a shaking incubator (Thermo Fisher Scientific, Model 4450, Waltham, MA) at 150 rpm. Cellulase loading was 5 FPU/g cellulose, and β -glucosidase loading was 10 CBU/g cellulose, respectively. Aliquots (0.5 mL) were taken at specified intervals for the glucose analysis using the HPIC method below.

2.6. Characterization and analysis

Brunauer-Emmett-Teller (BET) surface area of the porous solid acids was determined according to the nitrogen adsorption method on an Autosorb-1 surface area analyzer (Quantachrome Instruments, Boynton Beach, Florida). Attenuated total reflectance meso-Fourier transform infrared (ATR-FTIR) spectra were recorded on a PerkinElmer Spectrum 100 Series FT-IR spectrophotometer with a universal ATR sampling accessory (Waltham, MA). Sulfonic acid content was determined by the conductometric titration method. Elemental analysis was performed on a PerkinElmer 2400 Series II Elemental Analyzer 2400. Glucose was analyzed on a high-performance ion chromatography (HPIC) system (ICS-3000, Dionex, Sunnyvale, CA) equipped with an integrated amperometric detector and CarboPac™ PA1 guard and analytic columns at an eluent (water) flow rate of 0.7 mL/min. Glucose yield (%) was calculated from the determined glucose in the hydrolysate as a weight percentage of the theoretically available glucose in Avicel.

$$\text{Glucose yield (\%)} = \frac{\text{Detected glucose in hydrolysate (g)}}{\text{Avicel (g)} \times 1.11} \times 100\%$$

3. Results and discussion

3.1. Synthesis and characterization of porous polymeric solid acids bearing hydroxyl and sulfonic acid

As shown in Scheme 1, porous polymeric solid acids (PPSAs) bearing hydroxyl and sulfonic acid groups were synthesized in two steps: 1) synthesis of porous polymeric precursors with hydroxyl group through the Friedel-Crafts "knitting" polymerization of the aromatic monomers with hydroxyl, including phenol (M1), benzyl alcohol (M2), 3-phenyl-1-propanol (M3), 3-phenylphenol (M4), 1-naphthalene methanol (M5), 2,3-dihydroxy naphthalene (M6), 1,2-bi-2-naphthol (M7), and 1-pyrene-methanol (M8), and 2) sulfonation of the porous polymeric precursors synthesized in step 1 to introduce the sulfonic acid group. The sulfonation of the polymeric precursors was completed through the electrophilic aromatic substitution reaction. The sulfur trioxide generated from fuming sulfuric acid acted as an electrophile agent.

The hydroxyl-containing aromatic monomers were carefully selected with varied structures in aromatic backbones (benzene, naphthalene, bi-2-naphthol, and pyrene) and substituents (hydroxyl, hydroxymethyl, propanol, and phenyl) to investigate the effect of the monomer structure

(e.g., the type and location of hydroxyl and the aromatic backbone) on the synthesis, properties, and performance of the polymeric solid acids. For comparison, toluene (M9) was used to synthesize a porous polymeric solid acid without hydroxyl. The resultant porous polymeric solid acids PPSA1-PPSA9 are listed in Table 1.

Morphological properties (surface area, total volume of pore, and average diameter of pore) of the obtained polymeric solid acids were analyzed with the Brunauer-Emmett-Teller (BET) method. The BET surface area (S_{BET}), total volume of pore (V_{total}), and average diameter of pore (D_{A}) are summarized in Table 1. Nitrogen adsorption-desorption isotherms of the porous polymeric solid acids were collected at -196.1 °C (Fig. 1). The PPSA samples exhibited the type IV characteristic hysteresis loops, according to the classification of International Union of Pure and Applied Chemistry (IUPAC) (Sing et al., 1985; Thommes et al., 2015). However, PPSAs 3, 6, 8, and 9 showed the unclosed hysteresis loops, while PPSAs 1, 2, 4, 5, and 7 had closed ones, which is likely associated with the difference in their porous structure (Sing et al., 1985; Thommes et al., 2015). The unclosed hysteresis loops were also observed for other porous polymers that were synthesized using the Friedel-Crafts polymerization (Liu, Wang, Shen, Ju, & Yuan, 2015, 2020; Rozyyev et al., 2019). It turned out that all the solid acids had mesoporous structure with an average pore diameter in the range of 2.55–6.19 nm (Table 1). However, the polymeric solid acids varied substantially in surface area, although they were synthesized under the same conditions following the same procedure. For example, PPSA2, PPSA3, PPSA4, PPSA7, and PPSA8 had a much larger surface area (162–683 m²/g) than PPSA1, PPSA5, and PPSA6 (16–73 m²/g), respectively.

The difference in surface area between the solid acids might be attributed to the reactivity of the aromatic monomers toward the Friedel-Crafts knitting polymerization (Dawson et al., 2012; Li et al., 2011; Yang & Pan, 2016a, 2016b). High reactivity in the knitting polymerization (i.e., the cross-linking by formaldehyde dimethyl acetal) could lead to a more porous polymer and therefore a larger surface area.

Table 1

Textural properties of sulfonated porous polymeric solid acids with or without hydroxyls as catalysts for cellulose hydrolysis.

Catalyst	SO ₃ H (mmol/g) ^a	OH (mmol/g) ^b	S _{BET} (m ² /g) ^c	V _{total} (cm ³ /g) ^d	D _A (nm) ^e
PPSA1	1.48	4.1	35	0.06	6.19
PPSA2	1.40	3.3	683	0.49	2.85
PPSA3	2.42	2.4	162	0.10	2.57
PPSA4	2.81	2.1	412	0.49	4.76
PPSA5	1.35	2.9	16	0.03	6.13
PPSA6	1.26	4.3	73	0.02	4.28
PPSA7	1.36	2.6	605	0.39	2.55
PPSA8	2.19	1.8	488	0.33	2.74
PPSA9	0.78	–	411	0.28	2.71
AM ^f	4.90	–	53	0.40	30.0

^a Determined with the conductometric titration method.

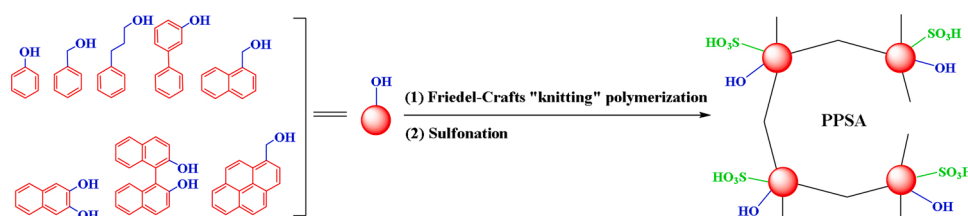
^b Determined via elemental analysis.

^c Calculated from the nitrogen adsorption isotherm using the Brunauer-Emmett-Teller (BET) method.

^d Calculated at P/P₀ = 0.9994.

^e Based on the Barrett-Joyner-Halenda (BJH) method.

^f Amberlyst 15.



Scheme 1. Illustration of synthesis of porous polymeric solid acids (PPSAs) with hydroxyl and sulfonic acid groups.

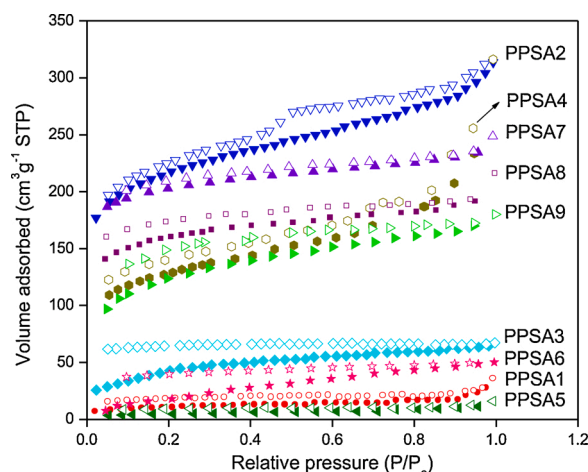


Fig. 1. Nitrogen adsorption (closed)/desorption (open) isotherms at -196.1°C of porous polymeric solid acids (PPSAs) bearing hydroxyl and sulfonic acid groups.

The reactivity of the substituted aromatic monomers is affected by the steric, resonance, and inductive effects of the substituents. The substituents of the aromatic monomers used in this study included hydroxyl, hydroxymethyl, propanol, and phenyl. These substituents activate the aromatic ring by increasing the electron density on the ring through a resonance donating effect. The activation effect of the substituents decreases in the order of hydroxyl, hydroxymethyl, propanol, and phenyl. The fusion of benzene rings also affects the reactivity of the aromatics, and the fused-ring aromatics are typically more reactive than single-ring aromatics.

The degree of knitting polymerization is also dependent on the number of available positions on the aromatic ring. Theoretically, the mono-substitution benzenes (M1, M2, and M3), the mono-substitution biphenyl (M4), bi-2-naphthol (M7), and pyrene (M8) can provide 5, 9, 12, and 9 positions for the knitting polymerization, respectively; while the mono-substitution (M5) and double-substitution (M6) naphthalenes have 7 and 6 positions, respectively. However, the available positions on the aromatic rings are not equally reactive. Due to the activation effect of substituents, the ortho- and para- positions to the substituents on the benzene ring are usually more reactive.

Therefore, under the same reaction conditions, the mono-substitution benzenes (M1, M2, and M3) with a smaller number of available positions were expected to result in the polymers with a smaller surface area, though they might have higher reactivity. Surprisingly, only the phenol-derived PPSA1 had a small surface area of $35\text{ m}^2/\text{g}$, while the PPSA3 from 3-phenyl-1-propanol had a large surface area of $168\text{ m}^2/\text{g}$, and the PPSA2 from benzyl alcohol had the largest surface area of $683\text{ m}^2/\text{g}$. As expected, bi-2-naphthol (M7) and pyrene (M8) with higher reactivity and a larger number of available positions ended up with the solid acids (PPSA7 and PPSA8) having a larger surface area (605 and $488\text{ m}^2/\text{g}$, respectively). However, the naphthalenes (M5 and M6) with higher reactivity and a mediate number of available positions resulted in a much smaller surface area (16 and $73\text{ m}^2/\text{g}$, respectively) of the corresponding polymers (PPSA5 and PPSA6). It should be noted that polymers with a much larger surface area were synthesized in previous studies through the Friedel-Crafts knitting polymerization from phenol ($400\text{ m}^2/\text{g}$, Li et al., 2011) and 1-naphthalene methanol and 2,3-dihydroxy naphthalene (538 and $333\text{ m}^2/\text{g}$, respectively, Dawson et al., 2012), respectively. The variations in the surface area of the polymers synthesized from the same monomers via the same method might be caused by the inconsistency between labs in synthesis conditions and experimental methods. However, this may not harm the objective of this study to understand the correlation between surface area and catalytic performance in cellulose hydrolysis of the

solid acids. As shown in Table 1, the surface areas of the synthesized solid acids fell in a wide range from $16\text{ m}^2/\text{g}$ to $683\text{ m}^2/\text{g}$.

The presence of sulfonic acid groups in the synthesized solid acids was verified by ATR-FTIR (Fig. S1 in Supporting Information). Two characteristic peaks of the sulfonic acid were visible at 1162 cm^{-1} ($\text{SO}_3\text{-H}$ stretching) and 1035 cm^{-1} ($\text{O}=\text{SO}=\text{}$ stretching), respectively (Li et al., 2014). The density of the sulfonic acid group in the solid acids was determined by the conductometric titration method, and the results are reported in Table 1. The results showed that PPSA1, PPSA2, PPSA5, PPSA6, and PPSA7 had lower densities of sulfonic acid ($1.26\text{--}1.48\text{ mmol/g}$), while PPSA3, PPSA4, and PPSA8 had higher densities of sulfonic acid ($2.19\text{--}2.81\text{ mmol/g}$). The variation in sulfonic acid density should result from the reactivity and available positions on the benzene rings of the polymeric precursors toward the sulfonation. Mechanistically, the sulfonation only introduced the sulfonic acid group no other oxygenates (such as carboxylic acid) into the solid acids. This was verified by the ATR-FTIR spectra of the solid acids, in which the characteristic peak of carboxylic acid at 1700 cm^{-1} was not observed.

The ATR-FTIR spectra also verified the presence of hydroxyl groups in the polymeric solid acids (the band at $3600\text{--}3000\text{ cm}^{-1}$). The density of the hydroxyl group in the solid acids was estimated by elemental analysis, assuming that the oxygen in the solid acids was only from the hydroxyl and sulfonic acid groups. The results in Table 1 showed that the content of the hydroxyl groups in the solid acids fell in a range of $1.8\text{--}4.3\text{ mmol/g}$. The density of the hydroxyl group in the solid acids depends not only on the hydroxyl density of the corresponding aromatic monomers but also on the degree of knitting polymerization that added mass to the polymers by introducing methylene. In general, the monomers with higher densities of the hydroxyl group, if less knitted by the methylene, would result in higher densities of the hydroxyl group in the resultant polymers. For example, the aromatic monomers M1 and M6 have higher densities of the hydroxyl group (10.6 and 12.5 mmol/g , respectively), and they were less knitted by the methylene, which was verified by their lower surface areas (35 and $73\text{ m}^2/\text{g}$, respectively). As a result, the PPSA1 and PPSA6 had higher densities of the hydroxyl group. Like other polymers synthesized using the Friedel-Crafts “knitting” polymerization (Fu, Jia, Li, & Liu, 2017; Liu et al., 2019), the PPSAs synthesized in this study were expected to be amorphous polymers.

3.2. Hydrolysis of cellulose by the porous polymeric solid acids bearing hydroxyl and sulfonic acid

The synthesized porous bifunctional solid acids were evaluated as heterogeneous catalysts to hydrolyze microcrystalline cellulose (Avicel) in an aqueous medium. They were compared with sulfonated porous polymers without hydroxyl group, sulfuric acid, and cellulolytic enzymes in hydrolyzing the cellulose. Amberlyst 15 (AM), a widely investigated commercial sulfonated polymer, and a synthesized sulfonated porous polymer from toluene were chosen as the references without hydroxyl group. To select appropriate application conditions (temperature and catalyst loading), PPSA2 was preliminarily investigated as an example. The results (Fig. S2 in Supporting Information) indicate that the PPSA2 performed well in hydrolyzing cellulose at 120°C and 48 h with a mass ratio of the catalyst to cellulose 4. Therefore, all the following cellulose hydrolysis tests in this study were carried out at 120°C with a mass ratio of the solid acid to cellulose 4, unless stated otherwise. It should be noted that the conditions selected might not be the optimal ones for the solid acids, and they were adapted just for comparing the performance of different solid acids under the same conditions. Sulfuric acid (SA) and cellulolytic enzymes (cellulase and β -glucosidase) were investigated as the homogenous catalysts for comparison. The loading of sulfuric acid was $12\text{ mmol proton (H}^+)/\text{g cellulose}$, which is higher than those ($3.12\text{--}11.24\text{ mmol proton/g cellulose}$) of the PPSA1-PPSA9. The loadings of cellulase and β -glucosidase were $5\text{ FPU (filter paper unit)/g cellulose}$ and $10\text{ CBU (cellobiohydrolase unit)/g cellulose}$, respectively, which were considered as economic enzyme

loadings in practice. The sulfuric acid-catalyzed hydrolysis was carried out at 120 °C, while the enzymatic hydrolysis was performed at 50 °C (the optimal performance temperature of the enzymes) (Yang and Pan, 2012).

The time-dependent hydrolysis profiles of cellulose catalyzed by different catalysts are presented in Fig. 2. Amberlyst 15 could not effectively hydrolyze the cellulose, despite its high sulfonic acid density (4.9 mmol/g). Only approximately 7.4 % and 7.7 % cellulose were hydrolyzed in 24 and 48 h, respectively. The poor performance of Amberlyst 15 was attributed to its low surface area (50 m²/g) and inefficient interaction with cellulose because there was no hydroxyl as a cellulose-binding group in Amberlyst 15. Under the same conditions, PPSA9 only hydrolyzed the cellulose by 3.8 % and 4.1 % in 24 and 48 h, respectively. PPSA9 with a larger surface area (411 m²/g) did not have a hydroxyl group either and had a lower sulfonic acid density (0.78 mmol/g) than Amberlyst 15. Therefore, the poor performance of PPSA9 should be attributed to its lower sulfonic acid density than the Amberlyst 15.

The bifunctional polymeric solid acids bearing both hydroxyl and sulfonic acid groups showed much better performance in cellulose hydrolysis than the two solid acids without the hydroxyl group above. For example, the PPSA2, PPSA4, PPSA7, and PPSA8 could hydrolyze cellulose by approximately 40 % in 24 h and over 70 % in 48 h, respectively. In particular, the PPSA7 and PPSA8 hydrolyzed cellulose by 83.1 % and 92.6 % in 48 h, respectively. Their remarkable hydrolysis performance should be primarily attributed to (1) the presence of hydroxyl as a cellulose-binding functional group that helped enhance the close contact between the solid acids and cellulose via hydrogen bonding and (2) the larger surface area (over 400 m²/g) of the catalysts that exposed more catalytic sites to cellulose. The PPSA3 also had an impressive glucose yield (63.5 %) at 48 h, despite only 22.7 % at 24 h. The performance difference between the PPSA2 and PPSA3 suggested that the larger surface area was likely more important than more sulfonic acid groups, as PPSA2 had fewer sulfonic groups but a larger surface area and better performance in hydrolyzing cellulose than PPSA3 (Table 1 and Fig. 2). However, when correlating the glucose yield with the content of hydroxyl and sulfonic acid groups in the solid acids, as shown in Fig. S3 in Supporting Information, the data points are very scattering, and no direct correlation was concluded between the glucose yield and sulfonic acid content or hydroxyl group content. This is obviously not true. The reason for the poor correlation is that the solid acid-catalyzed cellulose hydrolysis is a heterogeneous reaction, and the performance of the solid

acids in catalyzing cellulose hydrolysis is dependent on multiple factors (surface area, hydroxyl, and sulfonic group). In the hydrolysis experiments shown in Fig. S3, the solid acids were compared based on the same mass loading on cellulose. In other words, when looking at the effect of sulfonic group on the cellulose hydrolysis, hydroxyl and/or surface area was not fixed, and vice versa.

The solid acids with smaller surface areas, such as PPSA5 (16 m²/g) and PPSA6 (73 m²/g), gave significantly lower glucose yields. For example, the PPSA5 achieved only 22.9 % glucose yield in 24 h and 23.8 % in 48 h, respectively. These results suggested that a higher surface area be critical for a heterogeneous acid catalyst to achieve a better hydrolysis performance. As shown in Fig. 3, the glucose yield was positively correlated to the surface area of the catalysts in this study. An exception was the PPSA1 that performed worse than the PPSA5, although the former had a larger surface area (35 vs. 16 m²/g), more sulfonic acid groups (1.48 vs. 1.35 mmol/g), and more hydroxyl groups (4.1 vs. 2.9 mmol/g) than the latter, respectively, suggesting that other properties such as the locations and distributions of hydroxyl and sulfonic groups in the catalysts influenced the catalytic performance as well. As shown in Scheme 1, when designing the catalysts and selecting the aromatic monomers, one of the considerations was to investigate the effect of hydroxyl location/type and the ring structure of aromatics on the performance of the resultant polymeric catalysts. However, no conclusive results were observed in the present study.

For comparison, the hydrolysis results of cellulose by sulfuric acid and cellulolytic enzymes are also shown in Fig. 2. The glucose yield achieved by sulfuric acid was 14.0 % at 24 h and 38.2 % at 48 h, respectively. Some of the synthesized polymeric solid acids (PPSA5, PPSA6, and PPSA9) had similar performance to sulfuric acid, while other solid acids (PPSA2, PPSA3, PPSA4, PPSA7, and PPSA8) achieved a much higher glucose yield than sulfuric acid at both 24 h and 48 h despite the higher acid (proton) loading of the latter, which is because the solid acids provided a higher local proton concentration on the interface of cellulose and solid acids (Yang & Pan, 2016a, 2016b). In other words, at the same acid (proton) loading on cellulose, homogeneous sulfuric acid formed a uniform but dilute acid concentration in the solution, while the solid acids concentrated their acidic sites on the surface and therefore had a higher local acid concentration when reacting with cellulose. The PPSAs were comparable to or even better than the sulfonated activated carbon catalysts previously reported in hydrolyzing cellulose with the highest 74.5 % glucose yield (Pang et al., 2010).

Cellulolytic enzymes (cellulase and β -glucosidase) achieved a glucose yield of 51.9 % and 65.0 % at 24 and 48 h, respectively. The enzymatic hydrolysis followed a typical concave-down exponential

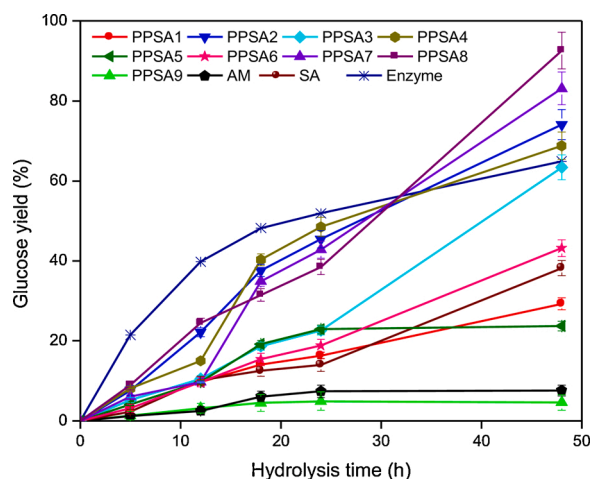


Fig. 2. Time-dependent hydrolysis profiles of Avicel cellulose by different catalysts (acid hydrolysis conditions: catalyst (0.2 g) or sulfuric acid (SA) (16 μ L, equivalent to 0.6 mmol H⁺), Avicel (50 mg), water (2 mL), 120 °C; enzymatic hydrolysis conditions: 2% consistency of Avicel, acetate buffer (50 mM, pH 4.8), cellulase (5 FPU/g cellulose) and β -glucosidase (10 CBU/g cellulose, 50 °C).

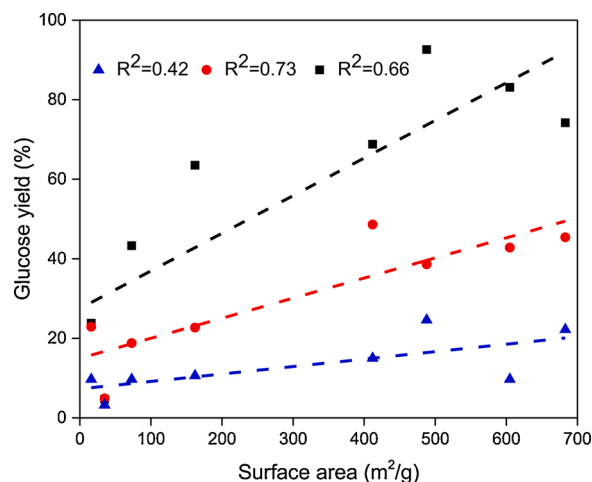


Fig. 3. Correlation between glucose yield (%) (blue: at 12 h, red: at 24 h, black: at 48 h) and surface area (m²/g).

pattern, i.e., the cellulolytic enzymes quickly hydrolyzed cellulose within the first 24 h, and then the enzymatic hydrolysis rate began slowing down beyond 24 h due to the accumulation of the produced glucose in the reaction system, which is the so-called end-product inhibition. As a result, the glucose yield increased only by 13.1 % during the second 24 h. However, the solid acid-catalyzed hydrolysis of cellulose followed a relatively linear profile, and the hydrolysis rate did not decline with time. For example, the PPSA2, PPSA7, and PPSA8 surpassed the enzymes in glucose yield after 30-h hydrolysis, though they were less productive in the first 30 h than the enzymes.

The poor hydrothermal stability (declining in catalytic activity) caused by the leaching of sulfonic acid in an aqueous medium at high temperature is a common issue of sulfonated solid acids. The reusability of two synthesized polymeric solid acids (PPSA7 and PPSA8), which were identified as the best in hydrolyzing cellulose, were preliminarily evaluated regarding their hydrothermal stability. To this end, the used catalyst along with unhydrolyzed cellulose from the previous batch of hydrolysis was recovered by vacuum filtration; after thoroughly rinsed with deionized water to remove hydrolysis products, fresh cellulose and water were added to maintain the same starting cellulose loading and consistency for the next batch of hydrolysis. As shown in Fig. 4, the performance of both solid acids declined after each cycle, indicating that the leaching did occur. For example, the glucose yields achieved by the PPSA7 and PPSA8 at 48 h decreased from 83.1 % and 92.6 %–78.0 % and 65.1 % after four cycles, respectively. However, the overall catalytic performance of PPSA8 declined faster and more than that of PPSA7. To quantify the extent of the leaching, the density of sulfonic acid of the PPSA7 and PPSA8 was monitored. It was found that after four cycles, the sulfonic density of PPSA7 and PPSA8 decreased from 1.36 and 2.19 to 0.38 and 0.50 mmol/g, respectively. Surprisingly, the PPSA7 and PPSA8 lost 72 % and 77 % sulfonic acid after four cycles, respectively, but their performance in hydrolyzing cellulose did not drop in the same proportion. For example, only a 5.1 % drop in the glucose yield was observed for the PPSA7 after the four cycles, though the glucose yield dropped by 27.5 % for the PPSA8. These results and observations suggested that the PPSA7 be more stable in catalytic activity than the PPSA8. The better stability (or greater tolerance toward the leaching) of the PPSA7 was probably attributed to its larger surface area and higher density of hydroxyl group (Table 1), which offset the negative impact on overall catalytic activity caused by the leaching of sulfonic groups. In other words, the hydroxyl groups as the cellulose-binding functional group and the larger surface area promoted the contact between the catalyst and cellulose, which helped retain the overall catalytic activity of the solid acids at the reduced level of sulfonic acid groups. In practice, the leached catalytic activity due to the loss of sulfonic acid groups could be

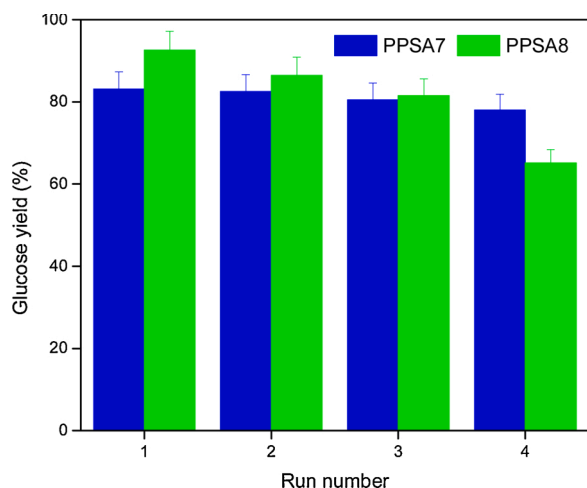


Fig. 4. Reusability of porous organic polymers bearing hydroxyl and sulfonic acid groups (PPSA7 and PPSA8).

restored by resulfonating the recovered solid acids.

The positive correlation between the surface area and catalytic performance of the polymeric solid acids observed above verified the importance of the interaction or effective contact between the solid catalysts and the solid substrate. To further demonstrate the effect of the interaction, the Avicel was ball-milled to reduce the size (increase the surface area) of the substrate. As shown in Fig. 5, the ball-milled cellulose was hydrolyzed faster with a significantly higher glucose yield by all the catalysts, compared to the unmilled one. For example, the PPSA5 and PPSA9, which hydrolyzed unmilled cellulose by only 16.4 % and 22.9 % in 48 h, hydrolyzed 73.8 % and 60.5 % of the milled cellulose in 24 h, respectively. The PPSA7 achieved a 98 % glucose yield at 24 h on the ball-milled cellulose, which was more than doubled the yield on the unmilled cellulose (42.6 %). Moreover, the solid acids bearing hydroxyl except for PPSA1 and PPSA8 reached a higher glucose yield at 24 h on the milled cellulose than that at 48 h on the unmilled cellulose. Sulfuric acid was also able to hydrolyze the milled cellulose by 55.9 % in 24 h. However, the PPSA1 and Amberlyst 15 were still the most ineffective catalysts in hydrolyzing the ball-milled cellulose due to their small surface area. In addition, the XRD analysis of the cellulose before and after the ball-milling (Fig. S4 in Supporting Information) indicated that the crystalline structure of the cellulose was disrupted by the ball-milling treatment, which was certainly another reason on top of reduced particle size (increased surface area) why milled cellulose was readily hydrolyzed.

The effect of temperature on the hydrolysis of the ball-milled cellulose catalyzed by the PPSA2 was investigated. As shown in Fig. 6, elevating temperature enhanced the cellulose hydrolysis like other reactions. To further understand the good performance of the synthesized polymeric solid acids in hydrolyzing cellulose, the apparent activation energy of the cellulose hydrolysis catalyzed by the PPSA2 was estimated (Fig. S5 in Supporting Information) from the 3-temperature data in Fig. 6. The apparent activation energy for the hydrolysis of milled cellulose at 110–130 °C was 97 kJ/mol.

In summary, the cellulose hydrolysis results above clearly indicated that the porous polymeric solid acids bearing both hydroxyl and sulfonic acid groups performed much better than those bearing only sulfonic acid groups, suggesting that the hydroxyl group played an important role in improving the performance of the solid acids. The hydroxyl improved the catalytic performance of the solid acids in different ways. First, the hydroxyl on the surface of the solid acids could form a hydrogen bond with the hydroxyl of cellulose and thus bring the catalysts and cellulose close to each other, which is analog to the function of the cellulose-binding domain of cellulases that attaches the enzymes on cellulose. As a result, the solid acids had a better contact with cellulose, which therefore facilitates the sulfonic acid groups to access and then cleave

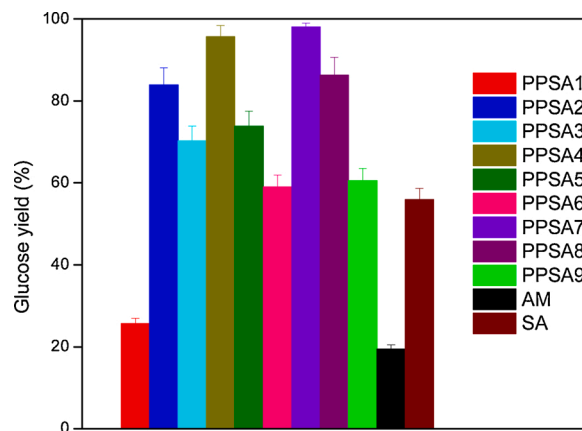


Fig. 5. Hydrolysis of 2-h milled cellulose at 24 h by different catalysts (hydrolysis conditions: catalyst (0.2 g) or sulfuric acid (16 μ L, equivalent to 0.6 mmol H^+), milled Avicel (50 mg), water (2 mL), and 120 °C).

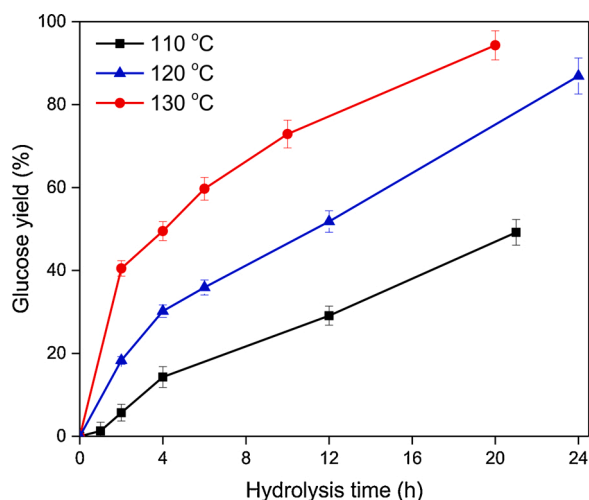


Fig. 6. Effect of temperature on hydrolysis of milled cellulose catalyzed by porous organic polymer bearing hydroxyl and sulfonic acid groups (hydrolysis conditions: porous organic polymer (PPSA2, 0.1 g), ball-milled cellulose (0.02 g), water (1 mL), and 110–130 °C).

the glycosidic bonds of cellulose. It was reported that the hydroxyl groups on the surface of the sulfonated amorphous carbon could form hydrogen bonds with cellulose and enhance the overall catalytic activity of the carbon (Suganuma et al., 2008; Zeng & Pan, 2021). Secondly, the phenolic hydroxyl on some of the solid acids synthesized from the monomers with hydroxyl groups on benzene rings (such as M6 and M7) could directly hydrolyze cellulose (Zeng & Pan, 2021), which was probably a reason why PPSA7 had better catalytic activity and better hydrothermal stability than other solid acids. Besides, it is possible but needs verification through a further study that the solid acids might be able to loosen or disrupt the crystalline structure of cellulose by breaking the intermolecular hydrogen bonds of cellulose through forming new hydrogen bonds with the cellulose, which was probably one of the reasons why the hydroxyl-bearing solid acids could efficiently hydrolyze the highly crystalline Avicel (microcrystalline cellulose).

Compared to other cellulose-binding groups (chloride and boronic acid) in the bifunctional cellulase-mimetic solid acids investigated in our previous studies (Yang & Pan, 2016a, 2016b), the hydroxyl performed much better than chloride and as well as the boronic acid. For example, the best glucose yields from the hydrolysis of unmilled microcrystalline cellulose at 48 h catalyzed by the chloride-, boronic acid-, and hydroxyl-bearing solid acids were 63 % (Yang & Pan, 2016a), 95 % (Yang & Pan, 2016b), and 93 % (Fig. 2), respectively. In terms of the working mechanisms of these cellulose-binding groups, chloride and hydroxyl associated with cellulose through hydrogen bonding, while boronic acid through reversible covalent bonding. In addition to forming hydrogen-bonding with cellulose, the chloride could release proton to the solution when hydrolyzed under hydrothermal conditions, which complemented the overall performance of the chloride-bearing sulfonated solid acids (Tyufekchiev et al., 2018). Besides, the hydroxyl formed from the chloride hydrolysis could function as a cellulose-binding group of the solid acid.

Interestingly, the best chloride- and boronic acid-bearing solid acids were synthesized both from naphthalene monomers, 1-chloromethyl naphthalene (Yang & Pan, 2016a) and naphthalene-1-boronic acid (Yang & Pan, 2016b), respectively, but the hydroxyl-bearing solid acid from 1-naphthalene methanol (PPSA5) performed poorly (Fig. 2), which was probably attributed to its small surface area (16 m²/g, Table 1), compared to the large surface areas (679 m²/g (Yang & Pan, 2016a) and 730 m²/g (Yang & Pan, 2016b), respectively) of the chloride- and boronic acid-bearing solid acids. Differently, the best hydroxyl-bearing solid acids (PPSA7 and PPSA8) were synthesized from 1,2-bis-2-naphthol

and 1-pyrenemethanol, respectively. Besides, the solid acids from benzyl alcohol (PPSA2) and 3-phenylphenol (PPSA4) also had impressive performance (better than the cellulases) in hydrolyzing cellulose (Fig. 2), but the solid acids from benzyl chloride (Yang & Pan, 2016a) and phenylboronic acid (Yang & Pan, 2016b) both had worse performance than the cellulases. These observations suggested that the functional groups (chloride, boronic acid, and hydroxyl) have had a significant effect on the Friedel-Crafts polymerization of the aromatic monomers and thereby affect the porous structure of the resultant polymeric solid acids and their performance in cellulose hydrolysis.

4. Conclusions

The present study successfully demonstrated the synthesis of bifunctional porous polymeric solid acids bearing hydroxyl and sulfonic groups for the hydrolysis of cellulose in water from aromatic monomers via the Friedel-Crafts “knitting” polymerization. The results confirmed that the presence of the hydroxyl group in the solid acids as a cellulose-binding site was an important contributor to the outstanding performance of the solid acids in hydrolyzing microcrystalline cellulose, in addition to their porous structure and large surface area. Like other sulfonated solid acids, the leaching of the sulfonic group occurred to the polymeric solid acids synthesized in this study. However, the overall catalytic activity of the investigated solid acids (PPSA7 and PPSA8) was retained at about 94 % and 70 %, respectively, after used 4 times.

CRediT authorship contribution statement

Qiang Yang: Conceptualization, Methodology, Investigation, Formal analysis, Writing - original draft, Writing - review & editing.
Xuejun Pan: Conceptualization, Supervision, Project administration, Writing - original draft, Writing - review & editing, Funding acquisition.

Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.carbpol.2021.117895>.

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