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Introduction

This research is driven by the growing environmental concerns associated with burning fossil fuels and the efforts to develop a sustainable and reliable energy source to ensure both the development of society and a greener planet.¹ Lignocellulosic biomass is an abundant, natural, and renewable resource that has enormous applications in producing higher-value chemicals^{2,3} and biofuels.^{4–6} Lignocellulosic biomass is comprised of three primary components – cellulose, hemicellulose, and lignin – where each component has distinct characteristics and properties that allows it to be tailored to a unique purpose.⁷

Furfural is a versatile chemical derived from pentosane-rich agricultural and forestry residues such as corn cobs, corn stover, saw dust, and straw. Despite the reported concerns in regards to the production of potential biofuels and fuel additives, such as 2-methylfuran,^{8,9} γ-valerolactone¹⁰⁻¹² and long chain hydrocarbons,¹³ using furfural as a feedstock, conversion of furfural into valuable chemicals, such as dicarboxylic acid,^{14–16} furfuryl alcohol¹⁷ and tetrahydrofurfuryl alcohol¹⁸ – which has broad

Production of furfural from xylose and corn stover catalyzed by a novel porous carbon solid acid in γ -valerolactone[†]

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A resorcinol-formaldehyde resin carbon (RFC) catalyst with a well-developed, ordered, mesoporous framework was prepared using a soft template method at room temperature. The carbon was sulfonated in water using sulfanilic acid under mild atmospheric conditions. The sulfonated RFC (S-RFC) was characterized by N₂ adsorption–desorption, elemental analysis, TEM, XPS, and FT-IR. It was determined that S-RFC is an efficient solid acid catalyst for furfural production from xylose and corn stover in γ -valerolactone (GVL). The effects of reaction time, reaction temperature, catalyst loading, substrate dosage and water concentration were investigated. 80% furfural yield and 100% xylose conversion were obtained from xylose at 170 °C in 15 min with 0.5 g catalyst. Comparatively, 68.6% furfural yield was achieved from corn stover at 200 °C in 100 min when using 0.6 g catalyst. Since there was no discernable decrease in furfural yield after multiple conversions utilizing the same catalyst, the recyclability of the catalyst is considered good.

uses in polymer, rubber, and pharmaceutical applications – attracted the interest of many researchers. Ultimately, it is agreed that the production and utilization of furfural would be beneficial for mitigating the energy and environment crisis and increasing profitability of a biorefinery economical profits.

For the first time in 1921, Quaker Oats Company commercially produced furfural from xylose and xylan using H₂SO₄ as catalyst.¹⁹ Since then improvements in furfural production have been made using homogenous catalysts such as mineral acids,²⁰ organic acids,²¹ and Lewis acids²²⁻²⁴ as well as ionic liquid.²⁵ Despite the improvements, the poor recyclability of homogenous catalysts and equipment corrosion they cause hinder their use. To overcome these obstacles, an increasing number of greener, heterogeneous catalysts have been developed.

Under the circumstance, multifarious zeolites were explored and gained more and more popularity in biomass conversion including SBA-15,²⁶ functionalized MCM-41 (ref. 27) and Sn-MMT²⁸ as well as SAPO-34.²⁹ But hydrothermal stability of zeolites still needs to be improved. Besides, commercial ion exchange resins (Amberlyst-70, Amberlyst-15 and Nafion) were also investigated in detail.³⁰⁻³² Nevertheless, the large-scale industrial applications of ion exchange resin are hindered by low porosity, high price and the poor endurance against high temperature. Moreover, recent years has witnessed a fast development of sugar catalyst, which was typically prepared through a two-step process.³³⁻³⁶ These catalysts were expected to be promising in biomass conversion because they are inexpensive, a source of ample and renewable carbon source as well as good acid density. However, the further development is still

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faced with some challenges, such as high sulfonation temperature and low porosity.

Sulfonated ordered mesoporous carbons (S-OMCs) was a good alternative by virtue of well-developed porosity with high specific surface area and symmetrical pore distribution, which provides the appropriate support for catalytic conversion of sugars into chemicals. Many investigations suggested that S-OMCs performed well in biodiesel production37,38 which was usually prepared via a nanocasting method^{39,40} followed by sulfonation with H₂SO₄. It's worth noting that the environmental and safety issues associated with the use of HF to remove the hard templates cannot be ignored. Meanwhile, sulfonation with concentrated H₂SO₄ was inefficient and could cause damage to the mesoporous framework. Recently, an easier, safer and milder sulfonation technique was proposed with sulfanilic acid,⁴¹ which can sulfonate single wall carbon nanotubes under moderate atmospheric conditions effectively. Inspired by their work, we prepared a resorcinol-formaldehyde resin carbon (RFC) using a scaled-up experiment based on previous work42 with some minor modifications, followed by mild sulfonation using sulfanilic acid as sulfonation reagent in water to obtain a novel porous carbon solid acid catalyst (S-RFC). During the whole process of catalyst preparation, HF and H₂SO₄ were avoided, which is more efficient and environmental friendly over other similar catalyst. To the best of our knowledge, the novel catalyst (S-RFC) has not been reported for use in biomass conversion.

In this study, a novel porous carbon solid acid was prepared and characterized by various instruments for its physical and chemical properties. The catalyst was utilized to produce furfural from xylose and corn stover. The influences of reaction temperature, reaction time, and catalyst loading were investigated. Bio-based GVL was used as solvent due to its superior properties in biomass utilization.^{43,44} More importantly, GVL can be derived from biomass by a integrated process.^{45,46}

Experimental section

Materials

D-(+)-xylose (98%), furfural (99%), 5-HMF (99%), sulfanilic acid (AR, 99.5%) and isoamyl nitrite (95%) were all purchased from Aladdin. Pluronic F127 ($M_{av} = 12\,600, EO_{106}PO_{70}EO_{106}$) was supplied by Sigma-Aldrich. Hydrochloric acid (HCl, 36–38%), ethanol (AR), acetone (AR), *N*,*N*-dimethylformamide (DMF, AR), resorcinol (AR, 99%), formaldehyde solution (AR, 37 wt%) and anhydrous NaCO₃ (AR) were obtained from Sinopharm Chemical Reagent Co., Ltd. γ -Valerolactone (95%) was provided by LangFang Hawk Technology and Development Co., Ltd. Corn stover was gathered from a cropland located in AnHui Province and cut into pieces, then flushed with running water to remove any impurities. After drying to constant-weight at 80 °C, the corn stover was ground into uniform particles and sieved by a 40 mesh screen.

Synthesis of RFC

RFC was prepared per the reported method⁴² with slight modifications. In this procedure, 0.056 g Na_2CO_3 and 11.3 g

formaldehyde solution (37 wt%) was added into a 50 ml roundbottle flask under vigorous agitation at room temperature. After the anhydrous Na₂CO₃ dissolved completely, 11.0 g resorcinol was put into the alkaline solution for pre-polymerization. After 70 min, the solution was poured into a mixture containing 8.0 g F127, 50.0 g ethanol and 40.0 g distilled water under stirring. After 10 min, 5.0 ml HCl (2 M) was added into the hybrid to accelerate the polymerization process. After agitation for about 2.2-2.5 min, a turbid mixture appeared which suggested the occurrence of phase separation. The hybrid was further agitated for 60 min and kept standing overnight to form the sedimentary polymer gel. Finally, the gel was natural withering for 12 h then aged at 80 °C for one day. The resulting soft, sticky, orange polymer was calcined under a N2 atmosphere at 350 °C for 2.5 h to remove the template (F127) and then at 500 °C for 4 h to accomplish the carbonization at a heating rate of 1 °C min⁻¹ to obtain the ordered mesoporous carbon (RFC).

Sulfonation of RFC

Sulfonation of RFC was conducted following the reported procedures⁴¹ with slight modifications. 3 g RFC and 12 g sulfanilic acid were put into a 500 ml round-bottom flask containing 300 ml distilled water. The mixture was heated to 80 °C then 6 g isoamyl nitrite was added once the sulfanilic acid was completely dissolved. The mixture was agitated vigorously overnight at 80 °C and then cooled to room temperature for filtration. The filter cake was washed with distilled water, ethanol and acetone repeatedly till the filtrate was clear. The catalyst was collected and sonicated in DMF (50 ml) for 20 min to eliminate any residual substrates. The black solid powder was isolated by filtration and swilled with acetone several times and then dried in vacuum oven. The obtained samples were donated as S-RFC.

Catalyst characterization

Both RFC and S-RFC were characterized by FT-IR (Nicolet 8700 (KBr disks)), BET (Tristar II 3020), XPS (Thermo Scientific ESCALAB 250Xi), TEM (JEM 2010 electron microscope) and elemental analysis (EA, Elementar model Vario EL III). Since sulfur existed in the single form of $-SO_3H$, per XPS, the amount of $-SO_3H$ was determined by the mole of sulfur present within the carbon support and calculated by elemental analysis.

Typical procedure for furfural production from xylose and corn stover

Experiments for furfural production from xylose and corn stover were implemented in a 100 ml mechanical stirring zirconium autoclave equipped with a PID temperature controller. Different proportions of catalyst, substrate, and solvent were charged into the reactor. The sealed reactor was heated to a given temperature and maintained for different time duration with a rotation of 500 rpm. The reaction ended by immersing the autoclave in a water bath to cool the reaction mixture to room temperature rapidly. Afterwards, the reaction mixture was filtered and the filtrate was preserved in a refrigerator for subsequent analysis by means of HPLC.

HPLC analysis of furfural, HMF and xylose

The concentration of products (furfural and HMF) in the filtrate was determined using a high-performance liquid chromatograph (Waters 515 pump) equipped with a Waters Symmetry®-C18 column and an Ultraviolet Detector (Waters 2489) at a wavelength of 280 nm. A mixture of methanol/water with a volume ratio of 2/3 was used as eluent flowing at 0.4 ml min⁻¹ and the temperature of column oven was set as 30 $^\circ$ C. The concentration of xylose was determined separately using highperformance liquid chromatograph (Waters 515 pump) that was equipped with a Waters XBridgeTM Amide column and a refractive index detector (Waters 2414). Both the column oven and the detector were kept at 45 °C. Acetonitrile/distilled water (3/2, v/v) served as mobile phase and was run at 0.4 ml min⁻¹. Pre-constructed calibration curves were used for quantitative analysis and xylose conversion, furfural yield, furfural selectivity and HMF yield were calculated as shown below:

Xylose conversion = $(1 - \text{moles of xylose remained}/ \text{moles of starting xylose}) \times 100\%$

Furfural yield (from xylose) = (moles of furfural produced/ moles of starting xylose) \times 100%

Furfural selectivity = (furfural yield/xylose conversion) \times 100%

Furfural yield (from corn stover) = (moles of furfural produced/ moles of starting xylan in corn stover) $\times 100\%$

HMF yield (from corn stover) = (moles of HMF produced/ moles of starting glucan in corn stover) $\times 100\%$

Results and discussion

Characterization of the carbon solid acid catalyst

Physical properties of RFC and S-RFC are listed in Table 1. RFC presented a well-developed porous structure with specific surface area, pore volume, and average pore diameter of $604 \text{ m}^2 \text{ g}^{-1}$, 0.72 cm³ g⁻¹, and 4.78 nm respectively. After sulfonation, different levels of decline occured to various parameters but S-RFC still maintained an excellent porous framework and its BET parameters were 530 m² g⁻¹, 0.56 cm³ g⁻¹, and 4.2 nm respectively. The grafted SO₃H, occupying some pore space, might be the reason for this decrease. It was concluded because of the modest decline in these parameters that sulfonation does not cause a serious collapse or deconstruction of the pore structure.

Mesopores were clearly visible in the TEM images (Fig. S1 in ESI[†]). The ordered mesoporous structure was confirmed by the

Table 1	able 1 Textural parameters of RFC and S-RFC			
Entry	$S_{BET}\left(m^2 \; g^{-1}\right)$	$V^{a}\left(m^{3}\text{ g}^{-1}\right)$	$D^{b}(nm)$	
RFC	604	0.72	4.78	
S-RFC	530	0.56	4.2	
RFC	604	0.72	4.78	
S-RFC	530	0.56	4.2	

^{*a*} Pore volume. ^{*b*} Average pore diameter.

uniform distribution of honeycomb-shaped hexagonal pores and stripe-like channels. In addition, Fig. S1[†] also illustrates the mesoporous structure was well preserved after sulfonation because no serious collapse and deconstruction of pores and channels was discovered between image A and image B, proving that the sulfonation technique was mild and efficient, which was consistent with the BET results. Besides, these wellpreserved pore channels could provide abundant reaction places during reactions, which promotes the diffusion and adsorption of xylose molecules.

Table 2 shows the elemental composition of RFC and S-RFC. A trace amount of nitrogen was incorporated into RFC, most likely during calcination since it was calcined in a N_2 atmosphere. This trace amount of nitrogen was enriched to some extent in the sulfonated RFC. It has been demonstrated that sulfonation of carbon with sulfanilic acid and isoamyl nitrite result in the direct incorporation of aromatic ring to the Sp² carbon of amorphous carbon, and the presence of the trace amount of nitrogen must be due to the surface contamination.⁴¹ Sulfonation also resulted in an incorporation of sulfur, as expected, and the concomitant increase in oxygen and hydrogen contents as can be seen in Table 2.

In FT-IR spectrum of RFC and S-RFC (Fig. S2†), the characteristic peaks at 1124, 1185, and 1220 cm⁻¹ can be ascribed to SO₃H groups. The bands at 1035 and 1011 cm⁻¹ represented S=O asymmetric and symmetric stretching vibrations respectively.⁴⁷ This confirms that $-SO_3H$ groups had been successfully grafted into the carbonaceous material,⁴⁸ which was in good agreement with results of elemental analysis and XPS. In addition, the small band at 3470 cm⁻¹ in RFC is most likely attributed to incomplete carbonization. The stronger absorption at 3430 cm⁻¹ is due to the OH stretching of the sulfonic acid.

Fig. S3[†] shows S 2p XPS spectrum of S-RFC, which was carried out to establish the valence state of sulfur. The single peak at 168.7 eV illustrates the existence of SO_3H species in S-RFC,⁴⁹ and all the sulfur atoms were confined to $-SO_3H$ groups. Therefore, the density of SO_3H was estimated based on sulfur content in elemental analysis.

Effect of reaction temperature and residence time on xylose conversion, furfural yield and furfural selectivity

Xylose dehydration was conducted in a well-sealed autoclave equipped with a stirrer and a PID temperature controller capable of achieving various temperatures (150 °C, 160 °C, 170 °C, and 180 °C) within a time duration from 5 to 30 min with 0.5 g catalyst, 0.8 g xylose, and 32 ml GVL. Fig. 1 illustrated that reaction temperature and residence time play a vital role on xylose conversion, furfural yield and furfural selectivity. The effect of temperature was also significant. As you can see from Fig. 1B, xylose conversion reached 95% at a reaction temperature of 150 °C within 15 minutes. The time required for complete conversion of xylose at 150 °C, 160 °C, 170 °C and 180 °C was 20 min, 15 min, 10 min and 5 min, respectively. The furfural yield and furfural selectivity follow identical trends to the conversion of xylose as seen in Fig. 1A and C. Both furfural

Table 2 Empirical formula of RFC and S-RFC based on elemental analysis data

	Elemental c	Elemental composition (%)				
	С	Н	0	Ν	S	SO_3H acidity ^{<i>a</i>} (mmol H ⁺ per g)
RFC	84.47	3.53	13.788	0.035	_	_
S-RFC	73.02	3.91	20.168	0.20	2.754	0.86

yield and furfural selectivity increase with residence time and reach a maximum at a given temperature at 15 min. After 15 min, both yield and selectivity declines at higher temperatures (170 and 180 °C) but stabilize at lower temperatures (150 and 160 °C). Noteworthy, the maximum furfural yield of 80% was obtained at 170 °C for 15 min. In addition, the lower furfural yields at 150, 160 and 180 $^\circ\mathrm{C}$ compared to that of 170 $^\circ\mathrm{C}$ suggested that side and yield loss reactions compete more favourably at these conditions. Previous studies have proposed three main yield loss reactions limiting the final furfal yield as illustrated in Scheme 1,50-52 including fragmentation, resinification and condensation. Specifically, lower temperatures (150 °C, 160 °C) decelerate the conversion of reactants, which possibly benefits the condensation between xylose (or intermediates) and formed furfural molecules, resulting in decreased furfural yield. However, although higher temperature (180 °C) promoted xylose conversion, fragmentation and resinification of furfural into resinous products were enhanced as well possibly because of the stronger molecular thermal motion,48 which also explained the observation that the reaction mixture produced a deeper color at 180 °C compared with the lower temperatures as seen in Fig. 1A.

Controlled experiments using no catalyst, RFC were also carried out using the optimal condition for xylose conversion to furfural (170 °C, 15 min). The results are illustrated in Table 3. Without the presence of the catalyst, only a trace amount of furfural was formed. Similar result was also obtained using RFC as a catalyst, demonstrating the importance of the $-SO_3H$ bearing catalyst for furfural production. Also, shown in Table 3 is the significance of keeping the reaction system under anhydrate conditions because an addition of 4 ml of water in the system significantly decreased the yield of furfural.

In order to make clear the effects of water on furfural formation, experiments with different water concentrations were conducted at 170 °C for 15 min. The results are shown in Table 4. The furfural selectivity was found to decrease from 80.8% to 39.4% as the water concentration increased from 1 ml to 4 ml, which verified that water has a negative impact on furfural selectivity. On the other hand, prolonging reaction time to 30 min in 32 ml GVL containing 6 ml H₂O resulted in the highest furfural yield and selectivity of 63% and 65%, respectively, which are still lower than those in pure GVL (80% and 80.8%). Thus, it can be concluded that the lower furfural yield was caused by lower furfural selectivity instead of reaction rates.

Effect of various acid catalysts on furfural production

The S-RFC was also experimentally compared with three homogenous acid (HCl, H₂SO₄, PTSA·H₂O) and three solid acid catalyst (PTSA-POM, Amberlyst-15, H-Beta) at 170 °C for 15 min in GVL and the result was depicted in Table 5. Compared with homogeneous acid (HCl, H₂SO₄, PTSA), S-RFC showed superior catalytic performance and easier recyclability, affording a furfural yield of 80% from xylose. The high propensity of furfural towards to polymerization in strong acid system might be the cause for the inferior performance of mineral strong acids.⁵⁰ Among the tested heterogeneous acid, S-RFC also performed better in view of its superior porous structures and good acidity. Overall, S-RFC is an efficient heterogeneous catalyst for furfural formation in a green solvent GVL.

Compared with the conventional sulfonation method (*i.e.*, boiling in concentrated H_2SO_4), the sulfonation with benzenesulfonic acid radical generated by the diazo-reaction between sulfanilic acid and isoamyl nitrite can be carried out under relatively moderate reaction conditions, which effectively avoids the collapse of pore channels of RFC. In this study, the SO_3H was grafted into S-RFC in water at 80 °C under atmospheric environment. After sulfonation, the pore channels were found to be well preserved as shown in TEM images (Fig S1†) and the well-preserved pore channels could provide abundant reaction places during reactions, which promotes the diffusion and adsorption of xylose molecules. Therefore, S-RFC exhibited better furfural yield and selectivity for the conversion of xylose among the test acid catalysts.

In addition, this work also demonstrates some advantages compared with similar works. Firstly, nontoxic GVL is used as green solvent and GVL itself can be produced from furfural.⁶ It is clear that S-RFC exhibits a comparable, even superior, performance to homogenous catalysis with better recyclability properties.²⁰⁻²⁵ In addition, 80% furfural yield is achieved from xylose in 15 min, which is comparable with other heterogeneous catalyst.^{27-32,47,50} Although 93% furfural is obtained from xylose catalyzed by modified MCM-41,27 the furfural yield sharply declined to less than 50% after first run with catalyst recycling. Besides, 80% furfural can be obtained using Nafion NR 50 in a biphase system,³² which is a comparable result with S-RFC, but the reaction time is longer (1 h) requiring microwave irradiation and an extra addition of cocatalyst (NaCl). Moreover, SC-CCA47 shows a good furfural yield from xylose and corn stalk while the catalyst preparation need isolated 4-BDS as sulfonation reagent.



Fig. 1 Effect of temperature and time on furfural production from xylose. Reaction conditions: 0.8 g xylose, 0.5 g S-RFC, 32 ml GVL, 25 min heating-up time.

Effect of catalyst loading

The effect of catalyst loading on furfural yield was also investigated with a catalyst loading (mass ratio of catalyst/xylose) between 37.5–87.5% (Fig. 2). The catalyst dosage was of great importance for the conversion of xylose into furfural since only



Scheme 1 Conversion of xylose to furfural and plausible reactions in the process.

Table 3 Controlled experiments^a

Substrate	Catalyst	Solvent	Furfural yield (%)
0.8 g xylose	No catalyst	32 ml GVL	Trace
0.8 g xylose	0.5 g RFC	32 ml GVL	Trace
0.8 g xylose	0.5 g S-RFC	32 ml GVL	80.0 ± 2.1
0.8 g xylose	0.5 g S-RFC	32 ml GVL + 4 ml H_2O	69.0 ± 1.9
a 170 °C 15			

⁴ 170 °C, 15 min for all experiments, 25 min heating-up time.

trace amount of furfural was obtained in the controlled experiments using no catalyst (Table 3). Increasing catalyst dosage had a positive impact on furfural production when the loading was less than 62.5% (0.5 g). Furfural yield decreased once the catalyst loading increased beyond 62.5%, which is probably due to superfluous and accessible acid sites allowed for more furfural degradation reactions (fragmentation, resinification and condensation),^{50–52} resulting in the generation of humins or other unknown products as illustrated in Scheme 1.

Reusability of catalyst

To understand the recyclability of the solid acid, three kinds of catalyst were synthesized by changing the formula among RFC, sulfanilic acid and isoamyl nitrite with a mass ratio of 1:2:2 (S-RFC-1), 1:4:2 (S-RFC-2) and 1:4:4 (S-RFC-3) in the process of sulfonation. Then, a four-cycle experiment was conducted consecutively for each catalyst. After each experiment, the catalyst was separated by filtration, followed by wash with water and acetone and drying in oven for next run.

The recycling experiments were carried out at 170 °C in 10 min rather than 15 min since the difference in furfural yield between these time periods was small (78% vs. 80%) as shown in Fig. 1. Also, 0.6 g S-RFC was used instead of 0.5 g to minimize the effect caused by catalyst loss after each run. The results are shown in Fig. 3. The yield of furfural declined slightly in each recycling run, which might be attributed to the leaching of acid sites, but the yield did not change significantly between the four runs. Specifically, S-RFC-2 (1 : 4 : 2) gave the best yield during all

Table 4 Effect of water addition on furfural produ	ction'
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Time (min)	Solvent	Xylose conversion (%)	Furfural yield (%)	Furfural selectivity (%)
15	32 ml GVL	99.0 ± 0.5	80.0 ± 2.1	80.8 ± 1.7
15	$32 \text{ ml GVL} + 2 \text{ ml H}_2\text{O}$	99.0 ± 0.5	78.5 ± 2.0	79.3 ± 1.6
15	$32 \text{ ml GVL} + 4 \text{ ml H}_2\text{O}$	98.0 ± 0.5	69.0 ± 1.9	70.4 ± 1.5
15	32 ml GVL + 6 ml H_2O	90.5 ± 1.0	54.0 ± 1.2	59.3 ± 1.0
15	32 ml GVL + 8 ml H_2O	68.9 ± 1.5	32.0 ± 1.4	46.4 ± 1.0
15	32 ml GVL + 10 ml H_2O	61.2 ± 2.0	24.1 ± 1.1	39.4 ± 0.5
20	32 ml GVL + 6 ml H_2O	94.0 ± 1.0	59.0 ± 1.5	62.76 ± 0.9
25	32 ml GVL + 6 ml H_2O	96.0 ± 0.7	62.4 ± 1.7	65.0 ± 1.3
30	32 ml GVL + 6 ml H ₂ O	97.0 ± 0.5	63.0 ± 1.4	65.0 ± 1.1
40	32 ml GVL + 6 ml H_2O	99.0 ± 0.5	60.0 ± 1.6	60.6 ± 1.3

^{*a*} Reaction conditions: 170 °C, 0.5 g xylose, 0.8 g xylose, 25 min heating-up time.

 Table 5
 Furfural production from xylose using various catalysts^a

Entry	Catalyst	Furfural yield (%)	Xylose conversion (%)
1	PTSA-POM	72.5 ± 1.5	$99\%\pm0.5$
2	Amberlyst-15	64.8 ± 1.5	$99\%\pm0.5$
3	H-Beta	78.0 ± 1.2	$99\%\pm0.5$
1	$PTSA \cdot H_2O^b$	74.0 ± 1.6	$99\%\pm0.5$
5	$H_2SO_4^c$	73.0 ± 2.2	$99\%\pm0.5$
5	HCl^{b}	68.0 ± 1.9	$98\%\pm0.5$
7	S-RFC	80.0 ± 2.1	$99\%\pm0.5$

^{*a*} Reaction conditions: 0.5 g different acid catalyst, 0.8 g xylose, 32 ml GVL, 170 °C, 15 min reaction time, 25 min heating-up time. ^{*b*} 0.215 mmol HCl and PTSA·H₂O (corresponding to 0.25 g S-RFC). ^{*c*} 0.1075 mmol H₂SO₄ (corresponding to 0.25 g S-RFC).



Fig. 2 Effect of catalyst loading (mass ratio of catalyst/xylose) on furfural production from xylose. Reaction conditions: 0.8 g xylose, 32 ml GVL, 170 $^{\circ}$ C, 15 min, 500 rpm, 25 min heating-up time.

runs, which was chose as optical formula and applied in all other experiments. However, the differences among the three catalysts in terms of furfural yield and recyclability are relatively small.

To further understand the deactivation of S-RFC, a five-cycle consecutive recycling was conducted with 0.8 g xylose and



Fig. 3 Reusability of S-RFC-x (x = 1, 2, 3). Reaction conditions: 0.6 g catalyst, 0.8 g xylose, 32 ml GVL, 170 °C, 10 min.

0.6 g S-RFC in 32 ml GVL at 170 °C for a shorter reaction time of 5 min. The result was shown in ESI (Table S1⁺). The furfural yield decreased slightly in former four runs and reduced remarkably at 5th run, indicating that the S-RFC deactivated seriously after 4th reusability. No obvious mass addition was observed for reused catalyst after recycling experiments, suggesting that the deposits is not the main cause for the deactivation of S-RFC. In addition, the sulfur content of reused catalyst was measured by an Elementar (EA, Elementar model Vario EL III), which was shown in ESI (Table S2[†]). It is observed that the S content decreases gradually in former four runs and remarkably decreases at run 5, suggesting the partial leaching of SO₃H after reaction, which also explains the deactivation of S-RFC. Similarly, some other acid catalysts^{50,53} also suffered from the deactivation and the regeneration was attempted. Regeneration of reused S-RFC was attempted by removal of deposits or replenishing the S lost with a new sulfonation cycle. However, the activity of deactivated S-RFC cannot be recovered by these two ways (Table S1[†]). Currently, the S-RFC can only be reused for four runs with a furfural yield of above 70%. The stability and regeneration of S-RFC still needs to be studied in a further step.

Influence of substrate concentration on furfural production

Experiments with different substrate concentration were conducted using S-RFC under optimized reaction conditions. The results are shown in Table 6. 67.4% furfural yield was obtained when 4.8% xylose was employed and only 18% furfural yield was achieved when 9.6% corn stover was added. The results demonstrated that the yield loss reactions were more tend to happen with the increase of substrate concentration. As illustrated in Scheme 1, we suppose that the condensation between furfural and substrate or intermediates may be the main cause for the decreasing furfural yield. When higher concentration of substrate was employed, more reactants and intermediates would exist in reaction medium, which enlarged the collision between formed furfural and xylose or intermediates. And as a result, more humins and other by-products were formed, leading to lower furfural yield.

Production of furfural from corn stover

Given the availability and diversity of raw material, corn stover was chosen as a substrate to produce furfural in a one-pot reaction. The reaction was carried out in a well-sealed, mechanically stirred autoclave running at different temperatures (180 °C, 190 °C, 200 °C, 210 °C) with time ranging from 20-140 min with a mixture of 0.6 g catalyst, 0.8 g corn stover and 32 ml GVL. The corn stover used for experiments contained 31.6% glucan and 20.5% xylan in accordance with our previous work.54 This data was used to calculate the yields of HMF and furfural. Furfural yield exhibited an unambiguous response to residence time and reaction temperature (Fig. 4). A comparison of Fig. 4A with Fig. 1A clearly demonstrates the need of prolonging time and increasing temperature for the conversion of corn stover directly to furfural. The highest furfural yield (68.6%) was obtained at 200 °C for 100 min as contrasted to high xylose conversion at 170 °C with 15 min. The prolonged time and increased temperature are expected as xylan in corn stover needs to be hydrolyzed to xylose before it can be converted to furfural. The lower yield of furfural (68.6% from corn stover versus 80% for xylose) is also expected as the higher temperature and prolonged time cause some decomposition of furfural as shown in Fig. 1A and 4A.



Fig. 4 Furfural production from corn stover. Reaction conditions: 0.6 g S-RFC, 0.8 g corn stover, 32 ml GVL, 30 min heating-up time.

Despite, a lower yield of 68.6% for direct conversion of corn stover to furfural, the results indicate that furfural is relative stable even at 200 °C for 100 min, demonstrating the efficacy of GVL as a solvent for furfural production.

	Table 6	concentration on furfural produ	iction ^a
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Catalyst	Reaction conditions	Furfural yield (%)
0.5 g S-RFC	170 °C, 15 min, 32 ml GVL	80.0 ± 2.1
0.5 g S-RFC	170 °C, 15 min, 32 ml GVL	72.0 ± 1.8
0.5 g S-RFC	170 °C, 15 min, 32 ml GVL	67.4 ± 1.5
0.5 g S-RFC	170 °C, 15 min, 32 ml GVL	55.0 ± 1.1
0.5 g S-RFC	170 °C, 15 min, 32 ml GVL	40.0 ± 1.2
0.5 g S-RFC	170 °C, 15 min, 32 ml GVL	20.0 ± 1.0
0.6 g S-RFC	200 °C, 100 min, 32 ml GVL	68.6 ± 1.6
0.6 g S-RFC	200 °C, 100 min, 32 ml GVL	40.0 ± 1.3
0.6 g S-RFC	200 °C, 100 min, 32 ml GVL	26.2 ± 1.4
0.6 g S-RFC	200 °C, 100 min, 32 ml GVL	18.0 ± 1.2
0.6 g S-RFC	200 $^{\circ}\mathrm{C},$ 100 min, 32 ml GVL	13.3 ± 0.8
	Catalyst 0.5 g S-RFC 0.5 g S-RFC 0.5 g S-RFC 0.5 g S-RFC 0.5 g S-RFC 0.5 g S-RFC 0.6 g S-RFC	Catalyst Reaction conditions 0.5 g S-RFC 170 °C, 15 min, 32 ml GVL 0.5 g S-RFC 170 °C, 15 min, 32 ml GVL 0.5 g S-RFC 170 °C, 15 min, 32 ml GVL 0.5 g S-RFC 170 °C, 15 min, 32 ml GVL 0.5 g S-RFC 170 °C, 15 min, 32 ml GVL 0.5 g S-RFC 170 °C, 15 min, 32 ml GVL 0.5 g S-RFC 170 °C, 15 min, 32 ml GVL 0.5 g S-RFC 170 °C, 15 min, 32 ml GVL 0.6 g S-RFC 200 °C, 100 min, 32 ml GVL 0.6 g S-RFC 200 °C, 100 min, 32 ml GVL 0.6 g S-RFC 200 °C, 100 min, 32 ml GVL 0.6 g S-RFC 200 °C, 100 min, 32 ml GVL 0.6 g S-RFC 200 °C, 100 min, 32 ml GVL 0.6 g S-RFC 200 °C, 100 min, 32 ml GVL

^{*a*} 25 min heating-up time.

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 Table 7
 Effect of water on furfural yield^a

Entry	Substrate	Solvent	Furfural yield (%)	
1 2	0.8 g corn stover 0.8 g corn stover	32 ml GVL 32 ml GVL + 4 ml H ₂ O	$68.6 \pm 1.8 \\ 61.5 \pm 1.3$	
^{<i>a</i>} 200 °C, 100 min, 0.6 g S-RFC, 25 min heating-up time.				

Compared to similar catalytic system, an obvious difference is noted regarding different types of biomasses. For example, 60% furfural is gained from corn stalk but only 29% furfural is produced from pinewood.23,47 Interestingly, 83.5% furfural is obtained from corn stalk which is a higher yield than the furfural produced from xylose (80.4%). The differences in yield are ascribed to the conversion of cellulose⁵⁰ need to explain this a bit more. However, the phenomenon did not occur in our previous study.47 In present work, the acid density played an important role on the direct conversion of biomass to furfural because the acid density of S-RFC (SO₃H 0.86 mmol g⁻¹) and SC-CCA⁴⁷ (SO₃H 1.14 mmol g⁻¹) is lower than the density of PTSA- POM^{50} (SO₃H 2.3 mmol g⁻¹). 68.6% furfural yield from corn stover is acceptable, but the critical point is how to separate a catalyst from the biomass residue. Introducing magnetism is a promising technique, and the doping of iron into S-RFC is possible in the fabrication process of resorcinol and formaldehyde.55 Improving acid density and introducing magnetism are good areas for future work to improve S-RFC.

Influences of water on furfural production from corn stover were also studied and the results are illustrated in Table 7. As seen with the dehydration of xylose, the addition of 11% of water (4 ml water in 32 ml of GVL) reduced furfural yield from corn stover as well. The presence of water accelerates furfural degradation and promotes side reactions, resulting in lower furfural selectivity. Compared to experiments without water, a much darker reaction mixture is observed in the water/GVL system.

No scaling nor sticky agglomerated residue was observed after any of the reactions, allowing it to be concluded that GVL is a good solvent for corn stover dehydration into furfural.

Furthermore, furfural (boiling point: 162 $^{\circ}$ C) can be isolated from GVL (boiling point: 208 $^{\circ}$ C) by distillation, which is an extra advantage over other efficient solvents, such as DMSO (boiling point: 189 $^{\circ}$ C).

A small amount of HMF was also measured during the dehydration of corn stover, which is less than 5% yield, indicating that a few hexoses was converted (Fig. 4B). The acid strength of the catalytic system was not strong enough to penetrate and hydrolyze crystalline cellulose. In addition, no Lewis acid was present in the system to isomerize the hexoses to fructose, which is an intermediate in the conversion of hexoses to HMF. Ultimately the yield of HMF was too small to be of commercial significance.

Conclusions

In conclusion, we have prepared a novel, effective, and stable solid acid catalyst *via* the mild sulfonation of carbon produced

by calcining resorcinol-formaldehyde resin. The catalyst exhibited good acid density, specific surface area, pore volume, and average pore diameter of 0.86 mmol g^{-1} SO₃H, 530 m² g^{-1} , 0.56 cm³ g^{-1} , and 4.2 nm respectively. The resulting catalyst was used to convert xylose and corn stover into furfural in GVL. High furfural yield was obtained from xylose (80%) with a reaction time of 15 min at 170 °C and corn stover (68.6%) conversion under similar reaction conditions. After analyzing the recyclability of the catalyst across four consecutive runs, it was concluded that the catalyst retained its activity. In addition to the applications investigated in this paper, the catalyst also displays an enormous potential to be used in other acidcatalyzed reactions and industrial applications.

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