Catalytic Conversion of Corn Stover into Furfural over Carbon-based Solid Acids

Wenzhi Li, Tingwei Zhang,* and Gang Pei

To ascertain the applicability of the isoamyl nitrite-assisted sulfanilic acid sulfonation method, a series of carbon precursors (sucrose-derived disordered mesoporous carbon, ordered mesoporous carbon CMK-3, glucose-based hydrothermal carbon, and activated carbon) were utilized in attempts to synthesize carbon-based solid acids. Scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, elemental analysis (EA), and temperature-programmed desorption of ammonia (NH_3-TPD) were applied to characterize the catalysts. The carbon-based solid acids were applied in the dehydration of xylose and corn stover to evaluate their catalytic performance. Sucrose-derived disordered mesoporous carbon (C-CCA) and ordered mesoporous carbon CMK-3 were successfully sulfonated by isoamyl nitrite-assisted sulfonation, while glucose-based hydrothermal carbon (HGC) and activated carbon (AC) were unsuccessful. Compared with ordered mesoporous carbon CMK-3 solid acid (S-CMK-3), sucrose-derived disordered mesoporous carbon solid acid (ISC-CCA) showed better performance for the production of furfural. The reusability of ISC-CCA for furfural production from xylose during 5 runs was favorable. Using pure water and ISC-CCA as a solvent and catalyst, from corn stover, achieved a furfural yield of 43.1% at 190 °C in 4 h.

Keywords: Sucrose-derived disordered mesoporous carbon solid acid; Ordered mesoporous carbon CMK-3 solid acid; Furfural; Corn stover

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INTRODUCTION

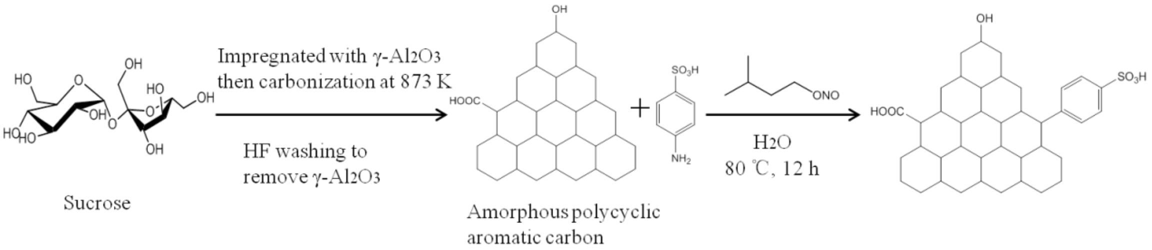
In regards to the environment issues caused by the consumption of fossil fuels, the green production of fuels and value-added chemicals from lignocellulosic biomass has been widely studied in recent years (Yan *et al*. 2014). Lignocellulosic biomass mainly consists of hemicelluloses (20% to 35%), cellulose (35% to 50%), and lignin (10% to 25%). Its characteristics of abundant supply and renewability make it an ideal feedstock for chemicals and fuel synthesis (You and Park 2014; Bruce *et al*. 2016; Zhang *et al*. 2017d,e). Furfural, one of the chemicals derived from lignocelluloses, is regarded as a versatile platform molecule for lignocellulosic biorefineries (Agirrezabal-Telleria *et al*. 2013). Furfural has two functional groups (the aromatic ring and aldehyde group), which allows furfural to be involved in a variety of reactions including acylation, acetalisation, Grignard reactions, aldol and Knoevenagel condensations, oxidation to carboxylic acids, reduction to alcohols, reductive amination to amines, decarbonylation, substitution reactions, halogenation, oxidation, hydrogenation, and nitration reactions (Yan *et al*. 2014; Mariscal *et al.* 2016). Due to its high chemical reactivity, furfural is utilized in many industries such as manufacture of fuel additives, plastics, oil refining, pharmaceuticals, and agrochemicals.

Generally, furfural is obtained from the hemicelluloses fraction of lignocelluloses. Utilizing dilute mineral acid as a catalyst has been widely studied (Marcotullio and de Jong 2010; Choudhary *et al*. 2012; Li *et al*. 2016a; Mittal *et al*. 2017). A continuous thermal process with the use of sulfuric acid as a catalyst is applied for the industrial production of furfural. However, this kind of method has several drawbacks, including the corrosion of the reactor by dilute mineral acid and the difficulty of post-reaction separation between the homogeneous catalyst and other components in the reaction system. Although other homogeneous catalysts (metal chlorides and ionic liquids) can obtain high furfural yields, the post-reaction separation process is still challenging (Zhang and Yu 2013; Wang *et al.* 2014; Zhang *et al.* 2014; Lin *et al.* 2017). Therefore, developing a high-efficiency heterogeneous catalytic system for furfural production is necessary.

Furfural can be readily produced by the heterogeneous acid-catalyzed dehydration of xylose, which is obtained by the acid hydrolysis of hemicelluloses. The reaction pathway of xylose dehydration is relatively clear. One molecule of xylose can be converted to furfural in the presence of acid catalysts with the loss of three molecules of water. Many kinds of solid acids including carbon-based solid acids (Lam *et al.* 2012; Zhang *et al.* 2016; Zhu *et al.* 2017), zeolites (Zhang *et al.* 2012; Gallo *et al.* 2013; Agirrezabal-Telleria *et al.* 2014), ion-exchange resins (Xu *et al.* 2015), functionalized silica (Sadaba *et al.* 2014), metal oxide (García-Sancho *et al.* 2013; García-Sancho *et al.* 2014; Gupta *et al.* 2017), metal phosphate (Pholjaroen *et al.* 2013; Bernal *et al.* 2014), and solid super acids (Yan *et al*. 2014) have been investigated for the dehydration of xylose to furfural in water and/or organic phase solvents. Previous works have obtained relatively high furfural yields using such catalysts. In addition to the catalyst, the solvent also plays an important role in furfural production. Xylose dehydration in an organic solvent-containing system results in a much higher furfural yield than in water alone. Among different organic solvents, γ-valerolactone (GVL), a green and renewable solvent, is widely used for the conversion of xylose to furfural, and high furfural yields have been obtained in its utilization (Xu *et al.* 2015; Zhang *et al.* 2016, 2017a). The solvent GVL has excellent dissolving capacity, allowing intermediates, secondary products, and polymeric compounds that are involved in the dehydration of xylose to be solubilized in the GVL. Additionally, the degradation reactions of furfural are hindered, thus preventing the deactivation of the catalyst from the deposition of carbonaceous byproducts on the surface of the catalyst.

In addition to the utilization of xylose as feedstock for furfural production, several kinds of raw lignocellulosic biomass (corn stover, corn cob, corn fiber, switchgrass, sugarcane bagasse, *etc.*) have been studied for furfural production over different heterogeneous catalysts containing an ion-exchange resin (p-toluenesulfonic acid-paraformaldehyde resin solid acid; PTSA-POM) (Xu *et al.* 2015), carbon solid acids (sulfonated sucrose-derived disordered mesoporous carbon; SC-CCA, sulfonated resorcinol-formaldehyde resin carbon; S-RFC) (Zhang *et al.* 2016, 2017), zeolites (H-beta, H-Mordenite, Al-beta) (Gallo *et al.* 2013; Zhang *et al.* 2017b), porous polytriphenylamine-SO_3H (Zhang *et al.* 2017c), and solid superacid ($SO_4^{2-}/TiO_2–ZrO_2/La^{3+}$) (Li *et al.* 2014). Many favorable results have been obtained using such additives. Furfural production from raw lignocellulosic biomass requires the hydrolysis of the hemicelluloses fraction of biomass to xylose and then the conversion of xylose into furfural. Achieving a high furfural yield from raw lignocelluloses by a one-pot multi-step process is difficult, but it has practical significance for the commercial production of furfural.

Carbon solid acids with high surface activity, high -SO_3H density, and good thermal stability show promising catalytic performance for the conversion of pentose to furfural, and precursors for carbonaceous material preparation commonly are available in nature. In a precursor study to the present work, carbon solid acid (SC-CCA) was synthesized (Zhang *et al.* 2016). Under the aid of sodium nitrite, sucrose-derived disordered mesoporous carbon (C-CCA) was sulfonated with sulfanilic acid. The SC-CCA showed good performance for the production of furfural from xylose and corn stover (Zhang *et al.* 2016). In the current study, an isoamyl nitrite-assisted sulfanilic acid sulfonation method was applied to synthesize carbon solid acid (as shown in scheme 1, functionalization of sucrose-derived mesoporous carbon). Sodium nitrite, a carcinogen, was substituted by isoamyl nitrite, and it was also used for the diazotization of sulfanilic acid. The process of preparing the catalyst was further simplified. To detect the applicability of the isoamyl nitrite-assisted sulfonation method, a series of carbon-based carbon precursors (C-CCA, glucose-based hydrothermal carbon, ordered mesoporous carbon CMK-3, and activated carbon) were used to synthesize carbon solid acids, and the above catalysts were named as ISC-CCA, S-HGC, S-CMK-3 and S-AC, respectively. Scanning electron microscopy (SEM), NH_3 adsorption-desorption, elemental analysis (EA), and Fourier transform infrared spectroscopy (FT-IR) were applied to characterize the catalysts. The catalytic activity of the four carbon solid acids was measured by the production of furfural from xylose and corn stover in GVL. The reusability of ISC-CCA was then investigated for furfural production from xylose.



Scheme 1. Functionalization of sucrose-derived mesoporous carbon

EXPERIMENTAL

Materials

The GVL (95%) was obtained from LangFang Hawk Technology and Development Co., Ltd. (Hebei, China). Ordered mesoporous carbon (CMK-3) was purchased from XFNANO Materials Tech Co., Ltd. (Nanjing, China). D-(+)-xylose (98%), furfural (99%), 5-hydroxymethylfurfural (5-HMF) (99%), N,N-dimethylformamide (DMF, AR), and acetone were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Sucrose (AR), D-(+)-glucose (≥ 99.5%), sulfanilic acid (AR), isoamyl nitrite, γ-alumina (γ-Al_2O_3, 99.99%), activated carbon (AC), and hydrofluoric acid (HF, 40%) were supplied by Aladdin Industrial Inc. (Shanghai, China). All chemicals were directly used for experiments without further treatment. The corn stover was obtained from Bozhou, China. The raw biomass was first washed with distilled water (DIW) to remove impurities, and oven-dried at 80 °C for two days. The clean biomass was later ground using an electronic pulverizer, sieved to pass an 80-mesh screen, and then oven-dried at 80 °C to constant weight. According to the previous study, Table 1 shows the composition of the raw corn stover (Zu *et al.* 2014).

Table 1. Composition of Raw Corn Stover (Dry weight) (Zu *et al.* 2014)

	Glucan	Xylan	Arabinan	Galactan	Lignin	Ash	Others
Raw corn stover	39.6	19.5	2.0	1.2	19.1	3.1	15.5

Methods

Catalyst synthesis and characterization

The C-CCA and glucose-based hydrothermal carbon (HGC) were synthesized according to previously reported literature (Maciá-Agulló *et al.* 2010; Zhang *et al.* 2016). In a typical synthetic process for ISC-CCA, 1 g of C-CCA was added to 150 mL of DIW in a three-necked round flask. The suspension was heated in a preheated oil bath at 80 °C with constant stirring under reflux. Then, 2 g of sulfanilic acid was added to the mixture, with constant stirring for another 30 min, followed by the addition of 2 g of isoamyl nitrite. The mixture was kept at 80 °C for 12 h. The catalyst was then collected by filtration, washed with DIW, DMF, and acetone, in that order, and then oven-dried at 100 °C to a constant weight before being used for furfural production. The synthetic procedure of S-HGC, S-CMK-3, and S-AC were similar to that of ISC-CCA except for using 0.5 g of CMK-3, 1 g of sulfanilic acid, and 1 g of isoamyl nitrite for S-CMK-3 preparation.

Total acidic sites of the four catalysts were determined from temperature-programmed desorption of ammonia NH_3 (NH_3-TPD) by using a ChemStar TPx chemisorption analyzer (Quantachrome Instruments, Boynton Beach, FL, USA). The SEM images of the catalysts were collected on a ZEISS scanning electron microscope (ZEISS, Oberkochen, Germany). The FT-IR spectra were recorded with the use of a Thermo Scientific Nicolet (Thermo Scientific, Waltham, USA) iS-50 instrument (KBr disks). The sulfur content of the catalysts was analyzed by element analysis using a Elementar model Vario EL III (Elementar, Germany).

Experiment procedure

The catalytic tests of furfural formation from xylose and corn stover over the carbon solid acids were performed in a thick-walled glass vessel (15 mL). In a typical procedure, 0.05 g of carbon solid acid, 0.1 g of xylose or corn stover, and 4.5 mL of GVL were added to the glass reactor. The reactor was sealed and fixed in a preheated oil bath with magnetic stirring. After keeping the reaction at a desired temperature for a specific residence time, the reactor was quickly cooled to ambient temperature by placing it in cooling water. The mixture was separated by filtration using a 0.45-μm syringe filter, and the filtrate was collected for furfural determination in high performance liquid chromatography (HPLC).

Product analysis

The furfural and HMF contents in the filtrate were quantified by HPLC (Shimadzu Corporation, Kyoto, Japan; Shimadzu LC-10ADvp pump equipped with a Shimadzu SPD-10Avp ultraviolet detector). The filtrate was diluted with DIW, and separated in an Agilent C18 column (Agilent Technologies, Santa Clara, CA, USA) at 0.4 mL/min and 30 °C using DIW/methanol (3/2, v/v) as the mobile phase. Standard calibration curves were applied for the calculation of furfural and HMF concentrations in the diluted filtrate.

The furfural yield from xylose and corn stover, and the HMF yield from corn stover were calculated as follows:

$$\text{Furfural yield (from xylose; \%)} = (\text{moles of furfural produced} / \text{moles of starting xylose}) \times 100 \quad (1)$$

$$\text{Furfural yield (from corn stover; \%)} = (\text{moles of furfural produced} / \text{moles of starting xylan in corn stover}) \times 100 \quad (2)$$

$$\text{HMF yield (from corn stover; \%)} = (\text{moles of HMF produced} / \text{moles of starting glucan in corn stover}) \times 100 \quad (3)$$

RESULTS AND DISCUSSION

Characterization of Carbon Solid Acid Catalyst

Price and Tour (2006) synthesized a series of functionalized single-walled carbon nanotubes “on water” in the presence of a substituted aniline and an oxidizing agent. They attempted different oxidizing agents (including isoamyl nitrite and sodium nitrite) for the diazotization of aniline. And they found using isoamyl nitrite as oxidizing agent gave the highest degree of functionalization. Therefore, isoamyl nitrite was chosen in this study for the diazotization of sulfanilic acid. Using isoamyl nitrite as oxidizing agents, the reaction was conducted in aqueous neutral condition. While using sodium nitrite, an aqueous acidic pH condition was needed.

The SEM analysis revealed that the morphologies of the four catalysts were very different (Fig. 1). First, ISC-CCA exhibited an irregular and disordered porous structure. The disordered porous structure of ISC-CCA corresponds to using γ-Al_2O_3 as a hard-template (Geng *et al.* 2011; Zhang *et al.* 2016). Second, S-CMK-3 showed an ordered porous structure and S-AC showed an irregular structure without any other characteristic morphology. Lastly, S-HGC was composed of quasi-spherical particles, but with serious particle agglomeration.

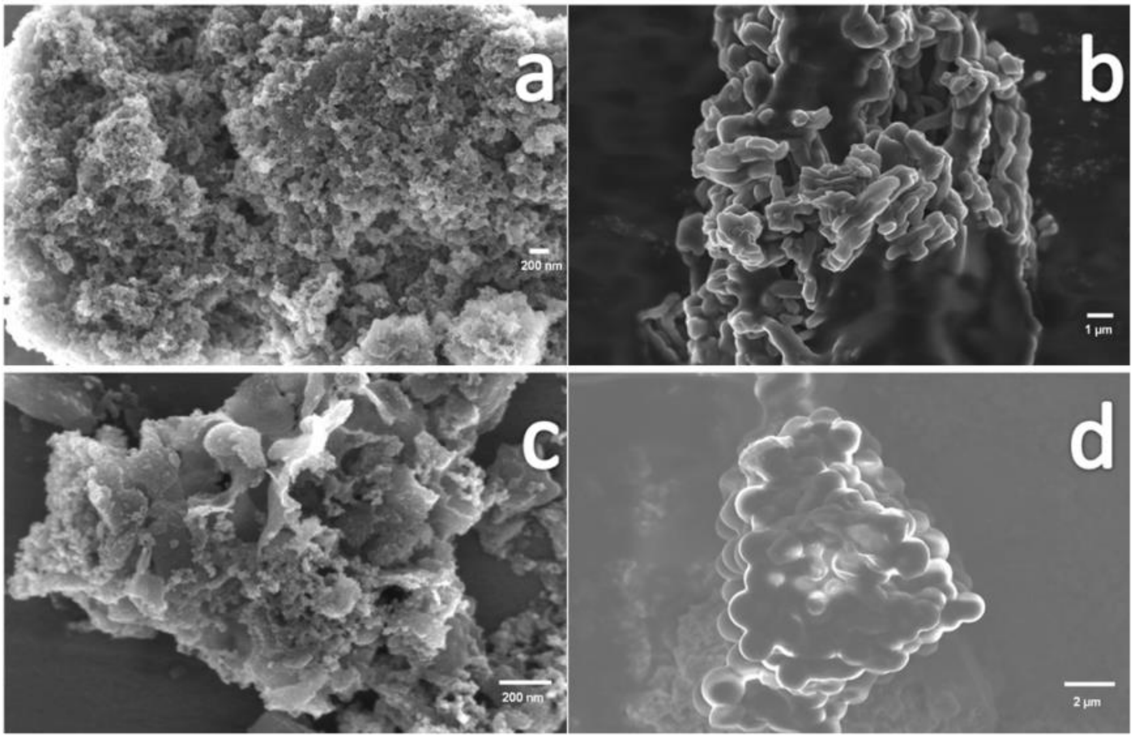


Fig. 1. SEM images of (a) ISC-CCA, (b) S-CMK-3, (c) S-AC, and (d) S-HGC

According to previous studies, the characteristic peaks of sulfonic acid groups should appear at around 1180 cm^{-1} (SO_3-H stretching vibration) and 1040 cm^{-1} (O=S=O stretching vibration) (Ji *et al.* 2011; Zhang *et al.* 2016). Comparing the FT-IR spectra of the four samples (Fig. 2), C-CCA and CMK-3 were sulfonated successfully by sulfanilic acid with the assistance of isoamyl nitrite. In addition, ISC-CCA exhibited stronger signals of -SO_3H than S-CMK-3. However, no apparent characteristic peaks of sulfonic acid groups were observed in S-HGC and S-AC. The broad bands at around 3440 cm^{-1} for ISC-CCA and S-HGC revealed the presence of -COOH and/or phenolic OH, while S-OMC and S-AC did not exhibit these characteristics. Sulfur content of the ISC-CCA (6.1 wt%), S-CMK-3 (4.8 wt%), S-HGC (0.4 wt%) and S-AC (0.3 wt%) were detected by elemental analysis. The results also confirmed sucrose-derived mesoporous carbon and ordered mesoporous carbon was successfully sulfonated, which is in good agreement with the results obtained from FT-IR.

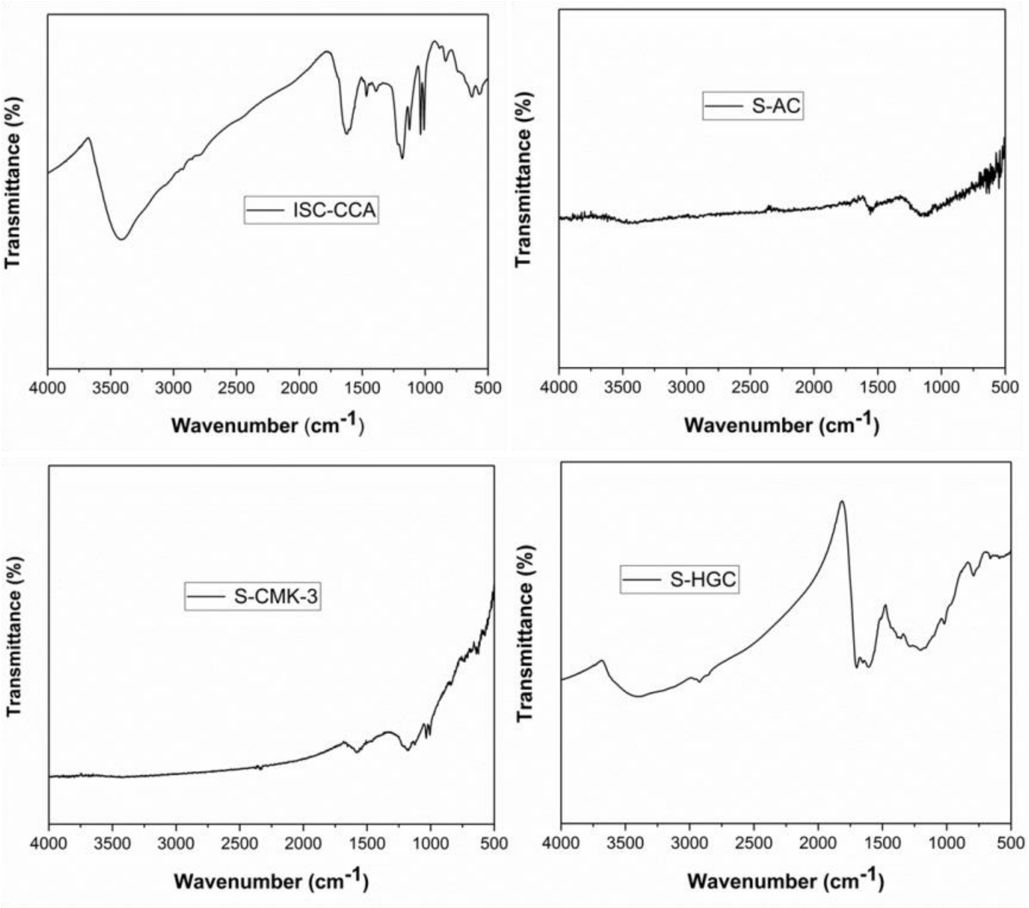


Fig. 2. FT-IR spectra of ISC-CCA, S-CMK-3, S-AC, and S-HGC

The total amount of acid sites of the samples was measured by NH_3-TPD experiments, and the NH_3-TPD patterns are shown in Fig. 3. In the synthesis of carbon acids, only Brønsted acid sites of -SO_3H were introduced to the carbon materials, where it is understood that the carbon acids mainly have Brønsted acid sites. Generally, different kinds of acidic sites exhibit their desorption peaks in NH_3-TPD patterns at different temperatures; the higher the temperature of the peak, the stronger the corresponding acid (You and Park 2014).

The desorption peaks of ISC-CCA and S-CMK-3 were presented at as high temperature as 400 to 600 °C, revealing that the ISC-CCA and S-CMK-3 had high acid strength, and the results are in agreement with published literature (Liang *et al.* 2010; Testa *et al.* 2013). Both S-HGC and S-AC showed only one peak. As listed in Table 2, the total amount of acid sites decreased in the following order: S-HGC > ISC-CCA > S-CMK-3 > S-AC. Interestingly, S-HGC had the highest total acid sites, even if -SO_3H was not grafted on its surface. The high amount of acid sites found in S-HGC should have been formed during carbonization, which have little effect on xylose dehydration.

In the light of previously reported literature, the carbonaceous materials that could be successfully sulfonated through covalent attachment of benzenesulfonic acid have several common traits: high BET area, large pores, and certain amount of large polycyclic aromatic carbon structure (Price and Tour 2006; Peng *et al.* 2010; Geng *et al.* 2011). The glucose-based hydrothermal carbon (low BET surface and porosity) and activated carbon (lacking of mesoporous porosity, mainly micropore) did not meet the traits (Maciá-Agulló *et al.* 2010), and these should be the reason for the failure of the sulfonation of the two materials.

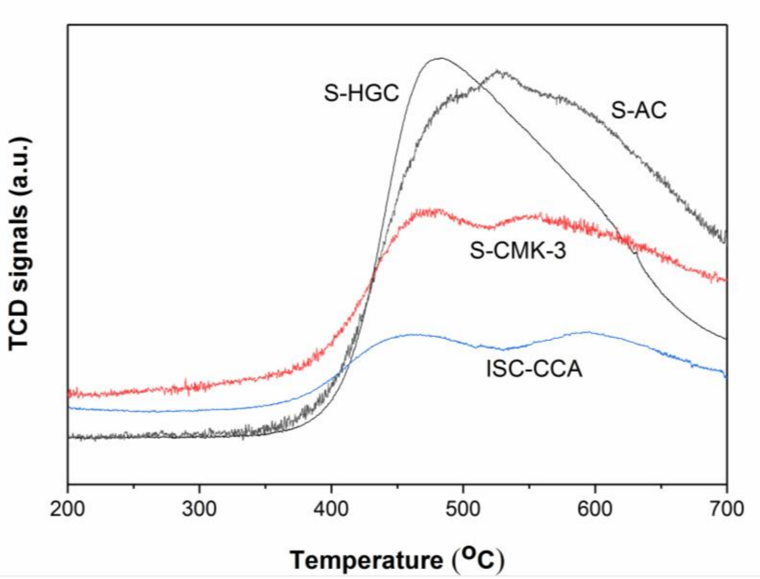


Fig. 3. NH_3-TPD patterns for the four carbon catalysts

Table 2. Total Acid Amounts of the Catalysts [a]

	ISC-CCA	S-CMK-3	S-HGC	S-AC
Total amount of acid sites ($mmol\ NH_3/g$)	8.3	4.1	14.0	1.7

[a] Amounts of samples used in NH_3-TPD experiments: ISC-CCA (0.034 g), S-CMK-3 (0.036 g), S-HGC (0.080 g), S-AC (0.154 g).

Production of Furfural from Xylose

The conversion of xylose into furfural catalyzed by ISC-CCA was investigated by performing the reaction at 160 °C to 170 °C for 5 min to 50 min in GVL. As shown in Fig. 4, the reaction temperature had an effect on furfural production. A higher furfural yield was obtained at 170 °C as compared to 160 °C. At a temperature of 170 °C, the furfural yield underwent an initial increase (5 min to 30 min), followed by a decrease (30 min to 50 min). In contrast, at 160 °C the furfural yield increased throughout the whole reaction time. The highest furfural yield of 74.4% was achieved at 170 °C after 30 min. The ISC-CCA exerted high catalytic activity for the dehydration of xylose to furfural. However, the reaction solution became dark brown as the reaction progressed, indicating that more side reaction of the formation of humins had occurred. Experiments for a blank condition and using sucrose-derived disordered mesoporous carbon (C-CCA) as catalyst were performed, and the results are summarized in Table 3. The results revealed that the sulfonic acid group grafted on the carbon material are of crucial importance for achieving high furfural yield.

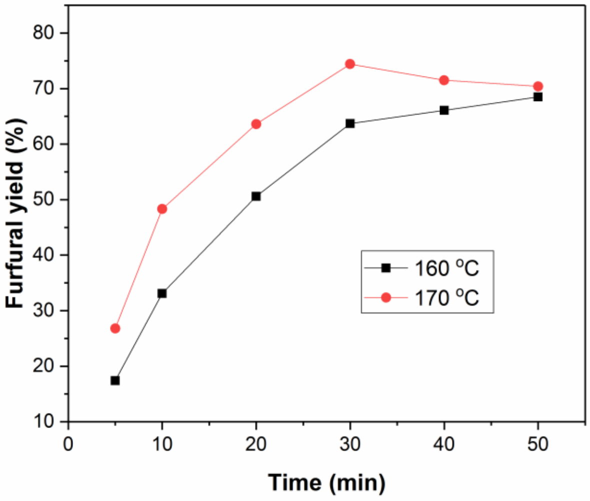


Fig. 4. Effect of temperature and reaction time on furfural yield from xylose (0.10 g) in GVL (4.5 mL) catalyzed by ISC-CCA (0.05 g)

Table 3. Furfural Yield from Xylose Over the Other Three Catalysts [a]

Entry	Catalyst	Reaction Condition	Furfural Yield (%)
1	S-CMK-3	170 °C, 20 min	51.1
2	S-CMK-3	170 °C, 30 min	59.2
3	S-AC	170 °C, 20 min	0
4	S-AC	170 °C, 30 min	0.1
5	S-HGC	170 °C, 20 min	0.2
6	S-HGC	170 °C, 30 min	0.7
7[b]	No catalyst	170 °C, 30 min	0
8	C-CCA	170 °C, 30 min	1.1

[a] 0.05 g of catalyst, 0.1 g of xylose, and 4.5 mL of GVL were loaded into reactor.
[b] blank experiment, no catalyst was loaded into reactor.

Table 3 summarizes the furfural yield from xylose for S-CMK-3, S-AC, and S-HGC catalysts. The S-CMK-3 showed a certain catalytic activity for yielding furfural from xylose, but it was not as high as that of ISC-CCA. The result was reasonable, as xylose can dissolve in GVL, and diffuse into the catalyst. Additionally, ISC-CCA has a higher sulfonic acid density than S-CMK-3, leading to more sulfonic acid sites for xylose. Therefore, the furfural formation rate over ISC-CCA is better than that for S-CMK-3. Both S-AC and S-HGC had almost no catalytic activity against xylose dehydration, which was in accordance with the characteristic results of FT-IR.

Catalyst Recycles

A successful industrial solid catalyst must have a fairly high reusability. Considering the fact that ISC-CCA had better catalytic performance for xylose dehydration than the other three catalysts, a five-run experiment was conducted at 170 °C for 30 min to evaluate the reusability of the ISC-CCA. To avoid operation errors, a larger reaction scale of xylose dehydration was adopted (0.2 g of ISC-CCA, 0.4 g of xylose, and 18 mL of GVL). After each run, the mixture was separated by filtration. The collected catalyst was washed with DIW, then with acetone, then dried at 80 °C, and then directly used for the next run. As shown in Fig. 5, the reusability of ISC-CCA was fairly good. The yield of furfural first increased and then decreased during the rest of the recycle experiment, still 68.1% of furfural yield was obtained after the fifth cycle.

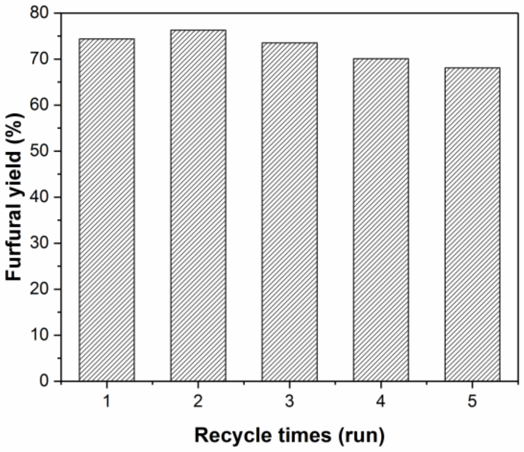


Fig. 5. Reusability study for the ISC-CCA catalyst. Reaction conditions: 0.40 g of xylose, 0.2 g of ISC-CCA, 18.0 mL of GVL, 170 °C, and 30 min reaction time

In relation to previously reported studies, leaching of the H^+ from ISC-CCA during the process of furfural formation should be responsible for the decrease in furfural yield. An experiment was designed to further clarify the leaching. Firstly, just 0.05 g ISC-CCA in 4.5 mL GVL was heated in preheated oil at 170 °C for 30 min with magnetic stirring. Then, the catalyst was filtered out, and a reaction using collected GVL plus 0.1 g xylose was conducted at 170 °C for 30 min. Furfural yield of 15.0% was obtained, and revealed that some H^+ indeed leached from the carbon acids. In addition, the S content of fresh ISC-CCA and five-cycle reused ISC-CCA were detected by elemental analysis, and the S content decreased from 6.1 wt% to 4.2 wt%. The first run reaction solution was also analyzed by elemental analysis, and S content of 0.53 wt% was detected. The leaching of sulfur species also occurred during reaction. Although GVL is a good solvent for furfural production, and considering that the color of the reaction solution was quite dark, there may have still been a small amount of carbonaceous compounds deposited on the surface of ISC-CCA, which would also cause the reduction of furfural yield.

Production of Furfural and 5-HMF from Corn Stalk

Despite furfural preparation from xylose being efficient with high yield, xylose is not suitable as a feedstock for the industrial production of furfural because of its relatively high cost. To date, a relevant chemical synthesis procedure for furfural production has not been developed. Only using raw lignocellulosic biomass for furfural production is practicable. Hence, utilizing corn stover as the starting material for the production of furfural was studied.

Corn stover was decomposed to furfural in GVL over ISC-CCA at a reaction temperature of 180 °C to 190 °C and reaction time in the range of 30 min to 180 min. The results are presented in Fig. 6. Both the reaction temperature and time had large effects on the furfural yield. Firstly, the growth trend of furfural yield gradually slowed with prolonged reaction time. Thereafter, an optimal reaction time was achieved and the furfural yield began to decrease. The highest furfural yield of 70.2% was obtained at 190 °C after 120 min. The catalytic activity of ISC-CCA for corn stover was inferior to that of xylose, but still very good. There are several reasons for the difficulty of the conversion of corn stover to furfural. The composition of raw biomass is complex, so some compounds that formed during the deconstruction of raw biomass may hinder the mass-transport that occurred during furfural production, and react with furfural production-related compounds. Another difficulty for the conversion was due to the fact that the solubility and dispersibility of raw biomass in solvents is poor, as the particles of the biomass are too large to diffuse to the inside of the mesoporous acid catalyst. In addition, the contacts between the active acid sites and the target molecule on the biomass are limited. Lastly, the hydrolysis of raw biomass is difficult by virtue of its network of lignin-cellulose-xylan. Among these factors, in this work it was inferred that the inability of corn stover particles to diffuse to the inside of ISC-CCA had a significant negative influence on furfural production, resulting in the reduction of the acid catalysis ability of ISC-CCA.

According to the previous studies in the authors' group, the S content of the sucrose-derived mesoporous carbon solid acid prepared by sodium nitrite-assisted sulfanilic acid sulfonation method is 3.6 wt%, and for the conversion of corn stover, the catalyst gave the highest furfural yield of 60.6% in 100 min at 200 °C (Zhang *et al.* 2016). In this study, the S content of the ISC-CCA is 6.1 wt%，and the highest furfural yield of 70.2% was achieved by ISC-CCA in 120 min at 190 °C. The ISC-CCA carbon solid acid showed higher efficiency for furfural production from corn stover.

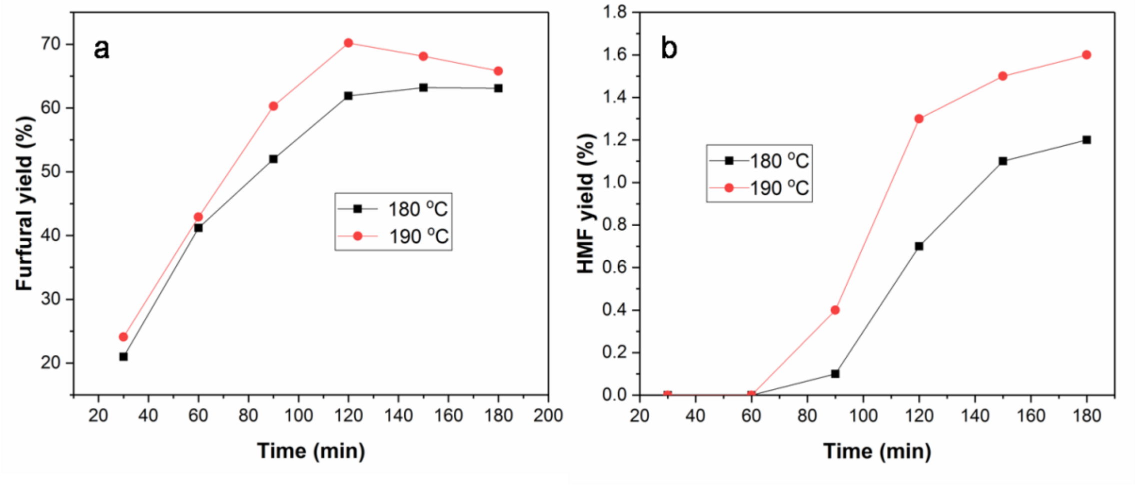


Fig. 6. Effect of temperature and reaction time on furfural (a) and HMF (b) yield from corn stover (0.10 g) in GVL (4.5 mL) catalyzed by ISC-CCA (0.05 g)

Because corn stover contains a certain amount of cellulose, HMF was detected in the reaction solution. The HMF yield increased slightly with a longer reaction time or higher temperature. It is difficult to simultaneously obtain a high furfural and HMF yield. Both the hydrolysis of cellulose and the conversion of glucose to HMF are quite difficult in the presence of a solid Brønsted acid alone (Van Putten *et al.* 2013; Li *et al.* 2017; Zhang *et al.* 2017e). Moreover, because furfural production requires a higher temperature than HMF, the dehydration of hexoses from corn stover at the high temperature may generate other compounds, such as furfural, not HMF (Gürbüz *et al.* 2013; Li *et al.* 2016b; Zhang *et al.* 2017c). Even if HMF was obtained, it cannot remain stable at such a high temperature and complicated system and thus would be involved in a further reaction.

The recyclability of ISC-CCA for furfural production from corn stover was studied. There is no efficient method to separate the reacted corn stover residue and catalyst. Therefore, after each run, the solid mixture was washed with water and acetone, oven-dried, and directly used for the next cycle by adding a new batch of fresh corn stover. Upon setting the mass ratio of catalyst to feedstock at 0.5, it was found that the recyclability of ISC-CCA for corn stover dehydration was much inferior to that of xylose dehydration. In the previously reported literature, the recyclability of catalysts using lignocellulosic feedstock were also worse than using xylose, and to obtain a acceptable results, high mass ratio of catalyst to feedstock (3 or 4) had been adopted (Li *et al.* 2017; Zhang *et al.* 2017b). Hence, 0.3 g ISC-CCA and 0.1 g corn stover were used in this study, and the reaction was conducted at 190 °C for 60 min. As shown in Fig.7, furfural yield declined considerably at the 2nd cycle, and it remained stable during the third to fifth recycles. A furfural yield of 62.3% was still achieved in the fifth recycle. The recyclability of ISC-CCA for furfural preparation from corn stover was reasonable.

Table 4 summarizes the furfural yield from corn stover over S-CMK-3, S-AC, and S-HGC catalysts. Similar to the results obtained from xylose dehydration, S-CMK-3 exhibited good activity for furfural production, but it was not better than ISC-CCA. Both S-AC and S-HGC had almost no activity.

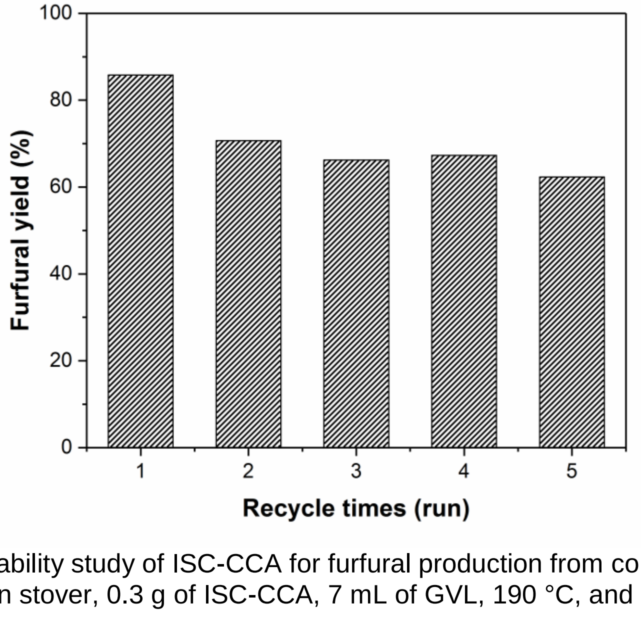


Fig. 7. Reusability study of ISC-CCA for furfural production from corn stover. Reaction conditions: 0.10 g of corn stover, 0.3 g of ISC-CCA, 7 mL of GVL, 190 °C, and 60 min reaction time

Table 4. Furfural Yield from Corn Stover Over the Other Three Catalysts [a]

Entry	Catalyst	Reaction Condition	Furfural Yield (%)	HMF Yield (%) [b]
1	S-CMK-3	180 °C, 60 min	39.8	ND
2	S-CMK-3	180 °C, 120 min	58.6	0.4
3	S-CMK-3	190 °C, 60 min	59.5	0.5
4	S-CMK-3	190 °C, 120 min	66.4	2.0
5	S-AC	180 °C, 60 min	0.3	ND
6	S-AC	180 °C, 120 min	1.0	ND
7	S-AC	190 °C, 60 min	1.5	ND
8	S-AC	190 °C, 120 min	3.2	ND
9	S-HGC	180 °C, 60 min	0.2	ND
10	S-HGC	180 °C, 120 min	0.5	ND
11	S-HGC	190 °C, 60 min	0.4	ND
12	S-HGC	190 °C, 120 min	1.5	ND

[a] 0.05 g of catalyst, 0.1 g of corn stover, and 4.5 mL of GVL loaded into reactor
[b] ND: No HMF was detected

Table 5. Furfural Yield from Corn Stover with the Use of Water as Solvent [a]

Entry	Reaction Condition	Furfural Yield (%)	HMF Yield (%)
1	190 °C, 2 h	17.8	ND
2	190 °C, 3 h	22.4	0.1
3	190 °C, 4 h	43.1	0.8
4	190 °C, 5 h	42.7	1.3

[a] 0.05 g of ISC-CCA, 0.1 g of corn stover, and 4.5 mL of DIW loaded into reactor
[b] ND: No HMF was detected

High target product yield can usually be achieved in an organic solvent-containing system, but for industrial application, the cost of organic solvent, the difficulty of post-reaction separation process, and relevant environment issues of using organic solvent have to be seriously considered. Thus, the utilization of pure water as the solvent for furfural production from corn stover over ISC-CCA was studied, and the results are shown in Table 5. A furfural yield of 43.1% was achieved at 190 °C in 4 h. The reaction in water is slower than in organic solvents, and it is difficult to obtain the same high furfural yield as in organic solvent (Lam *et al*. 2012; Li *et al*. 2014). Although the efficiency of using water as the solvent was relatively low, the undesired reaction should have been suppressed, which was confirmed by the reaction solution using water as the solvent that was lighter in color than the organic solvent.

CONCLUSIONS

1. ISC-CCA and S-CMK-3 were successfully synthesized using an isoamyl nitrite-assisted sulfonation method. Both S-HGC and S-AC were not successfully synthesized. More -SO_3H was grafted on C-CCA than CMK-3.
2. Both ISC-CCA and S-CMK-3 had certain catalytic activity for the conversion of xylose and corn stover. The ISC-CCA, with a higher -SO_3H density than that of S-CMK-3, showed better performance for furfural production. For the conversion of xylose and corn stover by ISC-CCA, furfural yields of 74.4% and 70.2% were obtained, respectively.

3. Importantly, the reusability of ISC-CCA for furfural production from xylose was favorable. The difficulty for diffusion of the corn stover particles into the inside of the ISC-CCA may have a substantial negative effect on furfural production from corn stover. The recyclability of ISC-CCA for furfural preparation from corn stover was reasonable.
4. When DIW was used as the solvent, the furfural yield from corn stover was 43.1%, obtained at 190 °C in 4 h.

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