Preparation of Carbon-based Solid Acid from Corncob Residual and its Performance for Acid-Catalyzed Hydrolysis

Rui Li, Guihua Yang,* Qiang Wang, Jiachuan Chen,* Jiran Dong, and Xinhan Zhang

A carbon-based solid acid catalyst (CHACS) derived corncob residual was prepared by incomplete hydrothermal carbonization followed by activation with phosphoric acid impregnation and sulfuric acid sulfonation. The structure of the solid acid catalyst was characterized using Fourier transform infrared spectra (FTIR), thermogravimetric analyzer (TGA), X-ray diffraction (XRD), scanning electron microscope (SEM), specific surface area (SSA), and elemental analysis. The -SO_3H, -COOH, and phenolic -OH functional groups were successfully introduced. Phosphoric acid activation facilitated formation of the porous structure in the solid acid catalyst. The specific surface area and acid density were 1569 m^2/g and 1.030 mmol/g, respectively. The CHACS exhibited better catalytic activity for hydrolysis conversion of corn stalk in ionic liquid with water as solvent. A total reducing sugars (TRS) yield of 68.3% was obtained in water and a TRS yield of 52.5% was obtained in an ionic liquid of [BMIM][Cl] at 140 °C for 120 min. The CHACS expressed good catalytic activity in each of 4 separate instances of reuse.

Keywords: Corn cob residual; Solid acid catalyst; Corn stalk; Total reducing sugar; Hydrolysis

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INTRODUCTION

With the rapid consumption of non-renewable fossil resources and the increasing concern for environmental protection, the conversion of lignocellulosic biomass to various chemicals and biofuels has received more attention (Nanda *et al*. 2014). Corn stalk is a lignocellulosic biomass and agricultural stalk resource that is often burnt or discarded in the field without any economic benefit (Sun *et al.* 2013). Conversion of this abundant crop residual to value-added products would improve its use and value as well as broaden its scope of application.

Many efforts have been devoted to the conversion of corn stalk with the use of mineral acids (Mok *et al.* 1992; Torget *et al.* 2000) and enzymes (Ramakrishnan *et al.* 2010; Das *et al.* 2011; Nemestóthy *et al*. 2017). However, there are many drawbacks as follows: inorganic acid catalysts such as sulfuric acid and hydrochloric acid are cheap and highly effective, but they cause environmental pollution and equipment corrosion, which hinders their widespread application. In addition, inorganic acid is difficult to separate from reaction systems, which results in large amounts of chemical waste. Enzyme treatment is very effective yet has many disadvantages such as high cost, long reaction time, and strict reaction conditions. Increasing interest in environmental protection and green chemistry is a major factor driving the exploration of recyclable solid acids with high efficiency. Various solid acids such as zeolites have been used to treat lignocellulosic biomass (Yang *et al.* 2015). Heteropoly compounds have low acid densities and thus cannot meet the catalytic demand in many catalytic reactions (Nakajima *et al*. 2007).

Carbon-based solid acid catalysts are attractive for their efficiency, non-corrosiveness, reduced reaction time, environmentally friendly qualities, and recyclability. Many studies have investigated the preparation of carbon-based solid acids obtained by incomplete carbonization and sulfonation (Suganuma *et al*. 2010; Guo *et al.* 2012; Bai *et al*. 2014). However, these carbon-based solid acids have lower specific surface area with inferior catalytic activities for biomass conversion. Therefore, the preparation of solid acids with high specific surface areas is necessary to meet the catalytic demand. Kitano *et al.* (2009) prepared a solid acid with a high specific surface area by incomplete carbonization of wood powder activated by $ZnCl_2$ and impregnated by sulfuric acid sulfonation. The $ZnCl_2$ activation method is rarely used due to its high cost and intractable pollution. H_3PO_4 was selected as an activating agent due to its powerful ability to confer catalytic properties to solid acids. Fu *et al*. (2012) and Teng *et al*. (1998) reported a solid acid catalyst prepared by H_3PO_4 impregnation that has lower specific surface area (113 $m^2 \bullet g^{-1}$, 854 $m^2 \bullet g^{-1}$); however, the catalytic performance was not sufficient for the present goals. Therefore, it is necessary to synthesize a solid acid catalyst with both of high specific surface area and catalytic activity.

In this work, a solid acid catalyst was prepared from corncob residual (CCR) as feedstock using the methods of hydrothermal carbonization, H_3PO_4 impregnated activation, and H_2SO_4 sulfonation. The solid acid was analyzed and characterized by Fourier transform infrared spectra (FTIR), X-ray diffraction (XRD), thermogravimetric analyzer (TGA), scanning electron microscope (SEM), specific surface area (SSA), and elemental analysis, and the solid acid was evaluated on its performance for hydrolysis of corn stalk in ionic liquid and water.

EXPERIMENTAL

Materials

Corncob residual (CCR) was supplied by a furfural production mill in Dezhou, China and ground into particles passing through a 100-mesh sieve. CCR was used to synthesize the solid acid in this work. The chemical composition (based on mass) of the CCR was as follows: 72.3% cellulose according to TAPPI T429 cm-84 (1984), 7.2% hemicellulose according to TAPPI T223 cm-84 (1984), 18.9% acid-insoluble lignin according to TAPPI T222 om-88 (1988), and 6.9% ash according to TAPPI T211 om-93 (1993).

Corn stalk was obtained from a farm in Jinan and was hydrolyzed by solid acid. The chemical composition (based on mass) of corn stalk was as follows: 39.1% cellulose according to TAPPI T429 cm-84 (1984), 29.5% hemicellulose according to TAPPI T223 cm-84 (1984), 16.2% acid-insoluble lignin according to TAPPI T222 om-88 (1988), and 4.2% ash according to TAPPI T211 om-93 (1993). The content of sugar components was as follows: 1.15% arabinose, 0.45% galactose, 0.04% rhamnose, 37.56% glucose, 14.89% xylose, and 0.12% mannose.

All organic chemicals were commercial products of the highest purity available (> 98%) and used without further purification. 1-Butyl-3-methylimidazolium chloride

([BMIM][Cl]) (purity of 99%) was purchased from the Lanzhou Institute of Chemical Physics (Lanzhou, China) and used as the ionic liquid. Ethanol (99.7 vol%), phosphoric acid (85 wt.%), and glacial acetic acid (99.5 wt.%) were purchased from Tianjin Fuyu Fine Chemical Co., Ltd. (Tianjin, China).Sulfuric acid (95 to 98 wt.%) and hydrochloric acid (36 to 38 wt.%) were purchased from Laiyang Chemical Co., Ltd. (Laiyang, China). Sodium hydroxide (96 wt.%) was purchased from Tianjin Damao Chemical Co. (Tianjin, China). Silver nitrate (99.8 wt.%) was purchased from Shanghai Reagent Factory (Shanghai, China).

Experimental Procedure

First, 5 g oven dried CCR and 50 mL deionized water were added into a 250 mL PARR stirred pressurized reactor while nitrogen gas was used as a purge (Zhang *et al*. 2015a). The reaction was conducted at 250 °C with a stirring rate of 150 rpm for 4 h, followed by cooling to room temperature (Zhang *et al*. 2015b). The CCR-hydrochar (denoted as CH) was obtained by filtration and washed with ethanol and deionized water until colorless. The washed CH was dried at 105 °C for 24 h prior to use.

A total of 1 g of CH was impregnated with 3 g of 40 wt.% H_3PO_4 aqueous solution. The CH was placed for 1 h at room temperature and dried at 90 °C for 12 h. The sample was transferred to a tube furnace and heated to 400 °C for 1 h under N_2. The heating rate was 4 °C/min. After activation, the porous carbon was cooled to room temperature under nitrogen. The sample was treated with boiling 1 M HCl solution for 1 h. The ratio of HCl to activated carbon was 200 mL:1 g. Finally, the sample was washed with hot deionized water (> 80 °C) until the filtrate was neutral. The CH-active carbon (denoted as CHAC) was dried at 105 °C for 12 h.

Next, 1 g CHAC and 30 mL 98% H_2SO_4 were added into a 100 mL PARR reactor lined with Teflon at 150 °C for 15 h. The mixture was diluted with deionized water, filtered, washed until no SO_4^{2-} ions were detected. When there was SO_4^{2-} ion in the filtrate, the $BaSO_4$ precipitation was produced by adding $BaCl_2$ solution. If there was no SO_4^{2-} ion, no precipitate was produced. The solid acid was completely washed, then vacuum-dried at 80 °C for 12 h to obtain the solid acid catalyst (denoted as CHACS).

The CHACS was used to catalyze the hydrolysis of corn stalk. A reaction mixture was prepared with [BMIM][Cl], corn stalk, water, and CHACS. The dosages of corn stalk, water, and CHACS based 2g [BMIM][Cl] were 5%, 1%, and 5%, respectively (Bai *et al*. 2016). The mixing sequence began with the addition of corn stalk into [BMIM][Cl] followed by the addition of water and the CHACS catalyst. The reaction was conducted in an oil bath bottle with a pressure at 140 °C for 30 min, 60 min, 90 min, 120 min, 150 min, and 180 min.

The solid was separated by filtration, and the liquid sample was diluted with deionized water. In addition, the dosages of corn stalk and CHACS based 5 mL distilled water mass, which were both 2%, were mixed with distilled water in a reaction kettle lined with Teflon (Tian *et al*. 2010). The reaction kettle was kept at 140 °C and a stirring rate of 100 rpm for 30 min, 60 min, 90 min, 120 min, 150 min, and 180 min. After the reaction, the liquid sample was diluted with deionized water and analyzed by using 3, 5-dinitrosalicylic acid (DNS) to determine the produced total reducing sugars (TRS). Total reducing sugars included xylose, glucose, arabinose, galactose and mannose.

Catalysis Analyses

The density of acid on the CHACS catalyst was determined by titration in an aqueous solution. A total of 0.1 g of the CHACS was added into 20 mL of a 2 M NaCl solution. The mixed liquor was ultrasonically treated for 1 h and then filtered, transferred to a 50 mL volumetric flask, and diluted with deionized water to a specified volume. Next, 10 mL of solution was withdrawn and titrated with 5 mmol standard sodium hydroxide solution. The acid density was calculated by the amount of standard sodium hydroxide solution that stoichiometrically reacted with the CHACS catalyst (Zeng *et al.* 2016).

Fourier transform infrared spectra were collected on an FTIR spectrometer (IRPrestige-21, Shimadzu Co., Shimane prefecture, Japan). A dried sample was ground and pelletized with KBr powder. All spectra were recorded from 500 cm^{-1} to 4000 cm^{-1}.

The crystallinities of the CCR, CH, CHAC, and CHACS were determined by X-ray diffraction (XRD, D8-ADVANCE, Bruker, Karlsruhe, Germany) at a scanning angle between 10° and 90° and a scan rate of 2 °/min.

The thermal stability of the CHACS was determined using a thermogravimetric analyzer (TGA Q50, USA). A 10 mg quantity of CHACS was placed in a sample tray and heated from room temperature to 700 °C at a rate of 10 °C min^{-1}. The heating process was carried out under a nitrogen blanket at a flow rate of 30 mL min^{-1}.

An environmental scanning electron microscope (SEM) (QUANTA 200, Holland FEI Co., Ltd., Eindhoven, Holland) was used to observe the morphology of CCR, CH, CHAC, and CHACS. All samples were coated with a thin layer of gold (SCD 005, Switzerland BAL-TEC Corporation (Los Angeles, CA, USA) at an accelerating voltage of 15 kV.

The specific surface area of the CH, CHAC, and CHACS and the N_2 adsorption–desorption isotherm of CHACS were evaluated by particle size analyzer (V-sorb 2800p, Beijing Jinaipu Technology Co., Ltd., Beijing, China).

The element content (wt.%) of carbon (C), hydrogen (H), sulfur (S), oxygen (O), and nitrogen (N) in the samples were determined using a Vario EL III Element Analyzer (Elementar, European Virtual Institute for Speciation Analysis, Fulda, Germany).

RESULTS AND DISCUSSION

Functional Group Analysis

An analysis of the functional groups in CCR, CH, CHAC, and CHACS is shown in Fig. 1. The intensity of the 2920 cm^{-1} band was reduced for the -CH spectrum after activation and sulfonation, which indicated that the CHACS sample became more dehydrated during the treatments. Two bands at 1015 cm^{-1}and 1230 cm^{-1} in the CHACS spectrum were assigned to -SO^{3-} and O=S=O stretching modes in the –SO_3H group, respectively (Suganuma *et al.* 2008). Therefore, the sulfonic acid group was introduced onto the surface of CHACS. The peak at 1540 cm^{-1} was attributed to the C=C stretching mode of the samples.

The presence of carboxylic groups was supported by the C=O characteristic stretching vibration band at 1730 cm^{-1} and the stretching vibration bands of -OH at 3440 cm^{-1} (Liang and Yang 2009; Xiao *et al.* 2010). Therefore, -SO_3H and -COOH were the principal functional groups introduced onto the surface of the CHACS, which was mainly achieved by the activation and sulfonation treatments.

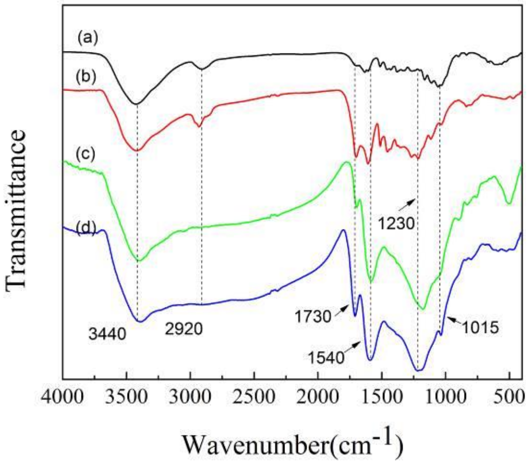

Fig. 1. FTIR spectrum of (a) CCR, (b) CH, (c) CHAC, and (d) CHACS

Crystallinity Analysis

Figure 2 shows the XRD spectra of CCR, CH, CHAC, and CHACS. The diffraction peak arising at 2θ of 23° corresponded to the diffraction of C (002) (Zeng *et al.* 2013). These two diffraction peaks (2θ = 16° and 2θ = 22°) of CCR, assigned to the diffraction peaks of cellulose, disappeared. However, for the CH, CHAC, and CHACS, the two diffraction peaks were not detected. The results indicated that the crystalline structure of CH, CHAC, and CHACS was disrupted primarily due to the degradation of cellulose. The XRD spectrum of CHACS exhibited broad diffraction peaks at 2θ of 10° to 30° centered at 25°, which corresponded to the (002) plane of the micrographites oriented in a random manner (Okamura *et al*. 2006; Lin *et al*. 2010).

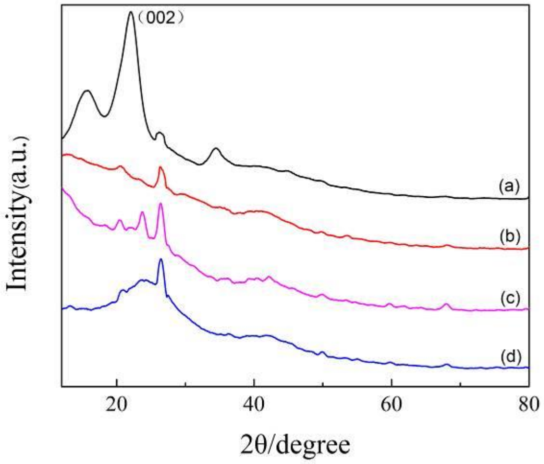

Fig. 2. XRD spectrum of (a) CCR, (b) CH, (c) CHAC, and (d) CHACS

Thermal Stability Analysis

The thermal stability of the CHACS was investigated by TGA, as shown in Fig. 3. With the increase of temperature from 25 °C to 200 °C, a weight loss of 8.15% of CHACS was observed, which was mainly attributed to the evaporation of absorption moisture in an open environment (Okamura *et al*. 2006; Suganuma *et al*. 2008). When the temperature was further increased over 200 °C, a continuous weight decrease was observed, which indicated its gradual decomposition. More weight loss was detected within the range 200 °C to 400 °C, which could be ascribed to oxidization of the non-graphitic and graphitic carbons (Shang *et al*. 2015). Lastly, a rapid weight loss was detected with the continued increase of temperature, which could be attributed to the continuing pyrolysis of incompletely carbonized CCR with high oxygen content (Ibrahim *et al*. 2015). Essentially, the CHACS catalyst was very stable at relatively high temperatures.

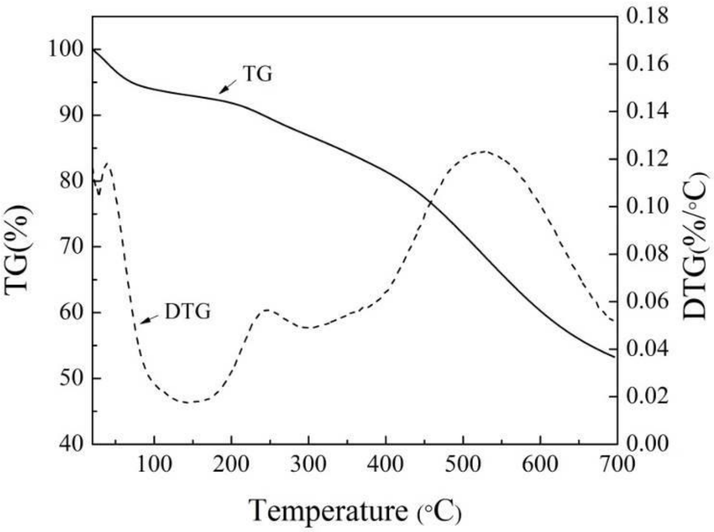

Fig. 3. TG and DTG curves of the CHACS

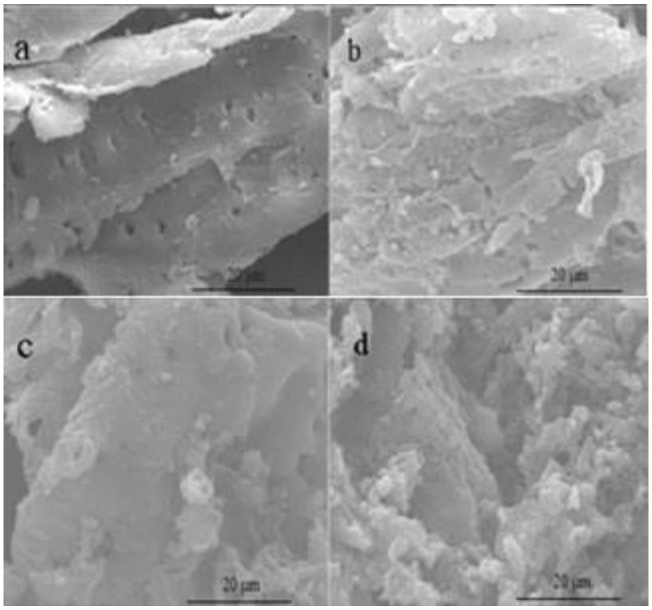

Fig. 4. SEM images of (a) CCR, (b) CH, (c) CHAC, and (d) CHACS

Surface Morphology Analysis

The morphologies of CCR, CH, CHAC, and CHACS analyzed by SEM are shown in Fig. 4. The microstructure of CCR was similar to plant tissues with some holes on the surface. The surface of CH was smooth with a low number of pores, which may have been caused by the release of volatile components from the CH. The CHAC activated by phosphoric acid was transformed into a sponge-like structure with a high specific surface area. The surface of CHACS was structurally amorphous, which was evidenced by the large number of cracks and holes. In addition, the surface of CHACS showed many slit-shaped pores. Typically, increased specific surface area is beneficial to catalytic performance.

Elemental Analysis

Table 1 shows the composition of the samples at different stages. Compared with CCR, the content of hydrogen and oxygen both decreased after hydrothermal treatment and phosphoric acid activation. In contrast, the ratios of C/H, C/O, and O/H were enhanced greatly, which indicated that dehydration occurred during hydrothermal treatment and phosphoric acid activation. After sulfonation, oxygen content increased greatly, yet the hydrogen content decreased in the CHACS, possibly due to the introduction of -SO_3H and -COOH. In addition, dehydration occurred in the residual -OH under sulfonation, which can result in a decrease in the hydrogen content and an increase in the ratios of C/H and O/H in the CHACS. Thus, the presence of -OH, -SO_3H, and -COOH in CHACS was further evidenced.

Table 1. Elemental Analysis, Specific Surface Area, and Acid Density of CCR, CH, CHAC, and CHACS

Sample	C	H	O	N	S	C/H	C/O	O/H	Specific Surface Area (m^2/g)	Acid Density (mmol/g)
CCR	43.1	5.8	44.6	0.23	0.12	7.43	0.96	7.68		
CH	60.4	3.12	29.1	0.62	0.10	19.35	2.07	9.32	5.69	-
CHAC	70.9	2.45	25.4	0.60	0.08	20.85	3.47	10.36	2124	-
CHACS	54.4	2.12	29.8	0.70	0.42	25.66	1.82	14.05	1569	1.0305

Specific Surface Area Analysis

The N_2 adsorption–desorption isotherm of the CHACS is shown in Fig. 5. The isotherm belongs to a mixed-type according to IUPAC classifications. At relatively low pressures, the isotherm exhibited a type I spectrum with a fast increase in N_2 adsorption corresponding to a predominantly microporous structure for the CHACS. Furthermore, at intermediate and high relative pressures, the isotherm was type II with a type H4 hysteresis loop, which indicated many slit-shaped pores existing in the CHACS (Kruk *et al*. 2001; Puziy *et al.* 2007). These results indicated that H_3PO_4 could be used as an effective activating agent for the promotion of the expansion of the CHACS structure corresponding directly to the development of porosity.

The specific surface areas of CH, CHAC, and CHACS were determined as 5.69 $m^2 \cdot g^{-1}$, 2124 $m^2 \cdot g^{-1}$, and 1569 $m^2 \cdot g^{-1}$, respectively (Table 1). Fu *et al*. (2012)

suggested that the larger surface area of CHACS may be attributed to an impregnation activation step. Moreover, compared with CHAC, CHACS had a smaller specific surface area. These reductions were due to partial destruction of the open porous structure during H_2SO_4 sulfonation (Fu *et al*. 2012).

The acid density of CHACS was 1.0305 mmol/g. The solid acid catalyst prepared by H_3PO_4 had the similar acid density of 1.1 mmol/g (Fu *et al*. 2012).

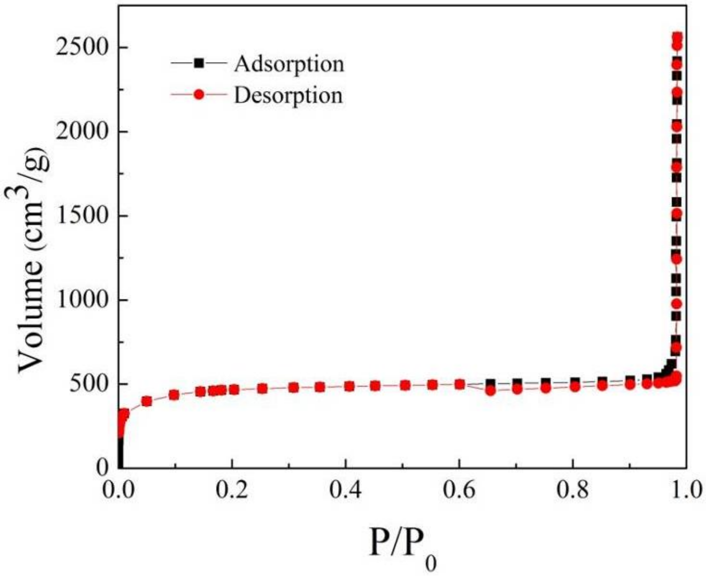

Fig. 5. N_2 adsorption–desorption isotherm of the CHACS

Catalytic Activities

The TRS yield of the hydrolysis of corn stalk treated by CHACS is shown in Fig. 6. The yield of TRS first increased with the extension of time and then decreased after reaching its maximum. When water was used as a solvent and the treatment reaction was carried out for a relatively short time (30 min to 60 min), TRS yield was lower. An optimal TRS yield of 68.32% was achieved at 120 min. However, further extension of time led to a decrease. This result was mainly due to the excessive reaction time promoting the degradation of holocellulose and reducing sugar content. When [BMIM][Cl] was used as solvent, the trend was similar to that of water as solvent, and the maximum TRS yield reached 52.52%, which was lower than the maximum TRS yield with water used as a solvent.

Therefore, the results suggest that the acid-catalyzed hydrolysis of corn stalk with CHACS in water would be the optimal procedure. When water was used as solvent, total reducing sugars included 51.9% xylose, 36.7% glucose, 5.8% arabinose, 2.7% galactose, and 2.9% mannose at 120 min. When [BMIM][Cl] was used as solvent, total reducing sugars included 55.8% xylose, 33.6% glucose, 4.9% arabinose, 3.6% galactose, and 2.1% mannose at 120 min.

In order to measure the amount of leaching of the CHACS, the following experiment was carried out: the CHACS was added to the water and [BMIM][Cl], and the test was run under the optimal reaction conditions with no corn stalk present. Then the solution was filtered, and that solution used to process corn stalk with no catalyst present. The yields of reducing sugar were 3.4% and 2.6% in water and [BMIM][Cl]. This indicated that essentially no solid acid was leached into the water and [BMIM][Cl].

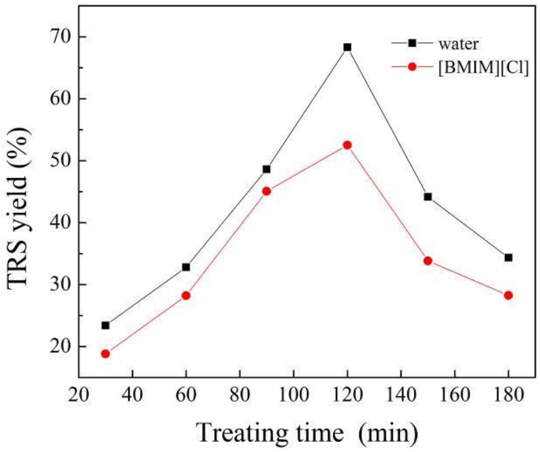

Fig. 6. The effect of CHACS treatment time on TRS of corn stalk hydrolysis in water and [BMIM][Cl]

Table 2. Different Performances of Catalysts for Treatment of Corn Stalk

Catalyst	Solvent	Temperature (°C)	Time (min)	TRS Yield (%)	Reference
HCl	H_2O	100	2880	52	(Li *et al.* 2008)
HCl	$C_4mimCl\text{-}H_2O$	100	30	66	(Li *et al*. 2008)
HCl	$C_4mimCl\text{-}H_2O$	100	330	64	(Li *et al.* 2008)
BLSCM[a]	[BMIM][Cl]	140	120	63.4	(Bai *et al.* 2016)
CHACS	H_2O	140	120	68.32	This work
CHACS	[BMIM][Cl]	140	120	52.52	This work

[a] BLSCM prepared by incomplete carbonization of black liquor lignin without H_3PO_4 impregnation followed by sulfonation and treatment of rice husk

Reuse of the CHACS Catalyst

The effect of the amount of times CHACS was reused on the TRS yield of the hydrolysis of corn stalk is shown in Fig. 7. The reuses of CHACS were carried out under the optimal conditions of [BMIM][Cl] and water. The reclamation process of CHACS was that the used CHACS was separated from the treating system, washed with distilled water, and then vacuum-dried. The dried CHACS was then reused in the next hydrolysis process of corn stalk. The results in Fig. 7 show that the reused CHACS catalysts had good performances. The TRS yield gradually decreased as the number of times CHACS was reused increased. The TRS yield decreased from 68.3% to 45.4% when CHACS was reused for the fourth time in water. In [BMIM][Cl], the TRS yield decreased from 52.5% to 33.0% when CHACS was reused for the fourth time. The TRS yields decreased to the minimums of 40.3% and 30.9% at the fifth instance of reuse in water and [BMIM][Cl], respectively. The reason for these results may be the partially loss of the CHACS catalyst activity in the processes of reclamation and reuse. Bai *et al.* (2014) reported that glucose carbon-based solid acid catalyst recyclability was that the TRS decreased from 63.2% (3rd run) to 39.7% (2nd run) and 23.9% (3rd run). Fu *et al.* (2012) reported that the conversion of methyl acetate decreased notably from 54.0% to 34.6% during the first 4 reaction cycles. The recyclability of CHACS was no worse than that of the two catalysts mentioned above. The CHACS catalyst showed relatively good catalytic performance for the hydrolysis of corn stalk.

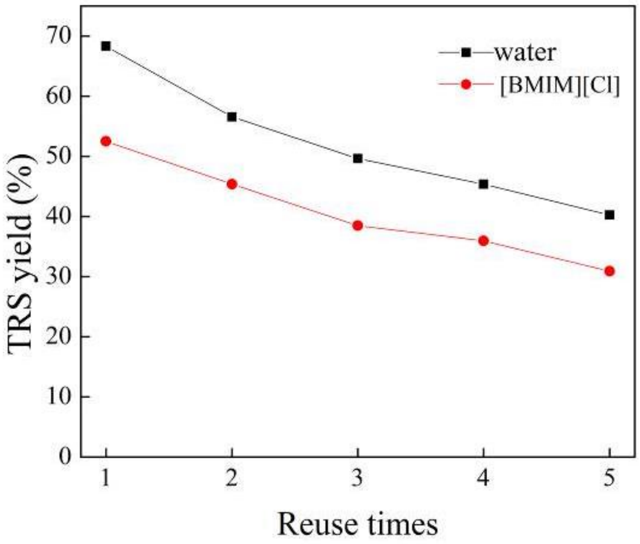

Fig. 7. Effect of reused times of CHACS catalyst on TRS yield of corn stalk

CONCLUSIONS

1. A carbon-based solid acid catalyst (CHACS) derived from corncob residual was successfully prepared by hydrothermal carbonization followed by H_3PO_4 impregnated activation and H_2SO_4 sulfonation. The solid acid was functionalized with -SO_3H, -COOH, and phenolic -OH groups. H_3PO_4-impregnated activation promoted porosity formation in the solid acid catalyst.
2. The CHACS was efficient for the hydrolysis of corn stalk in both [BMIM][Cl] and water reaction systems. A TRS yield of 68.32% was obtained in water at 140 °C for 120 min, and a TRS yield of 52.52% was obtained in [BMIM][Cl] under the same conditions. The effect of CHACS was better in water than in the ionic liquid of [BMIM][Cl].
3. The solid acid catalyst was easily reclaimed and reused in the hydrolysis of corn stalk and expressed good performance and stability in the reclamation and reuse processes.

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REFERENCES CITED

Bai, C., Zhu, L., Shen, F., and Qi, X. (2016). "Black liquor-derived carbonaceous solid acid catalyst for the hydrolysis of pretreated rice straw in ionic liquid," *Bioresource Technology* 220, 656-660. DOI: 10.1016/j.biortech.2016.08.112

Bai, Y. Y., Xiao, L. P., and Sun, R. C. (2014). "Efficient hydrolyzation of cellulose in ionic liquid by novel sulfonated biomass-based catalysts," *Cellulose* 21(4), 2327-2336. DOI: 10.1007/s10570-014-0287-2

Das, S., Berke-Schlessel, D., Ji, H. F., McDonough, J., and Wei, Y. (2011). "Enzymatic hydrolysis of biomass with recyclable use of cellobiase enzyme immobilized in sol–gel routed mesoporous silica," *Journal of Molecular Catalysis B Enzymatic* 70(1–2), 49-54. DOI: 10.1016/j. molcatb. 2011.02.003

Fu, Z., Wan, H., Hu, X., Cui, Q., and Guan, G. (2012). "Preparation and catalytic performance of a carbon-based solid acid catalyst with high specific surface area," *Reaction Kinetics Mechanisms & Catalysis* 107(1), 203-213. DOI: 10.1007/s11144-012-0466-9

Guo, H. X., Qi, X. H., Li, L. Y., and Smith, R. L. J. (2012). "Hydrolysis of cellulose over functionalized glucose-derived carbon catalyst in ionic liquid," *Bioresource Technology* 116, 355-359. DOI: org/10.1016/j.biortech.2012.03.098

Kitano, M., Arai, K., Kodama, A., Kousaka, T., Nakajima, K., Hayashi, S., and Hara, M. (2009). "Preparation of a sulfonated porous carbon catalyst with high specific surface area," *Catalysis Letters* 131(1), 242-249. DOI: 10.1007/s10562-009-0062-4

Liang, X., and Yang, J. (2009). "Synthesis of a novel carbon based strong acid catalyst through hydrothermal carbonization," *Catalysis Letters* 132(3), 460-463. DOI: 10.1007/s10562-009-0109-6

Lin, Q., Tang, H., Guo, D., and Zheng, M. (2010). "Preparation and properties of carbon microbeads by pyrolysis of N -phenyl maleimide modified novolac resin," *Journal of Analytical and Applied Pyrolysis* 87(2), 276-281. DOI: org/10.1016/j.jaap.2010.02.002

Li, C. Z., Qian, W., and Zhao, Z. K. (2008). "Acid in ionic liquid: An efficient system for hydrolysis of lignocellulose," *Green Chemistry* 10(2), 177-182. DOI: 10.1039/b711512a

Mok, W. S. L., Jr, M. J. A., Szabo, P., Varhegyi, G., and Zelei, B. (1992). "Formation of charcoal from biomass in a sealed reactor," *Industrial & Engineering Chemistry Research* 31(4), 1162-1166. DOI**:** 10.1021/ie00004a027

Nakajima, K., Hara, M., and Hayashi, S. (2007). "Environmentally benign production of chemicals and energy using a carbon-based strong solid acid," *Journal of the American Ceramic Society* 90(12), 3725-3734. DOI: 10.1111/j.1551-2916.2007.02082.x

Nanda, S., Mohammad, J., Reddy, S. N., Kozinski, J. A., and Dalai, A. K. (2014). "Pathways of lignocellulosic biomass conversion to renewable fuels," *Biomass Conversion and Biorefinery* 4(2), 157-191. DOI: 10.1007/s13399-013-0097-z

Nemestóthy, N., Megyeri, G., Bakonyi, P., Lakatos, P., Koók, L., Polakovic, M., Gubicza,L., and Bélafi-Bakó, K. (2017). "Enzyme kinetics approach to assess biocatalyst inhibition and deactivation caused by [bmim][cl] ionic liquid during cellulose hydrolysis," *Bioresource Technology* 229, 190-195. DOI: org/10.1016/j.biortech.2017.01.004

Okamura, M., Takagaki, A., Toda, M., Kondo, J.N., Domen, K., Tatsumi, T., Hara, M., and Hayashi, S. (2006). "Acid-catalyzed reactions on flexible polycyclic aromatic carbon in amorphous carbon," *Chemistry of Materials* 18(13), 3039-3045. DOI**:** 10.1021/cm0605623

Puziy, A. M., Poddubnaya, O. I., Martínez-Alonso, A., Castro-Muñiz, A., Suárez-García, F., and Tascón, J. (2007). "Oxygen and phosphorus enriched carbons from lignocellulosic material," *Carbon* 45(10), 1941-1950. DOI:

10.1016/j.carbon.2007.06.014

Ramakrishnan, S., Collier, J., Oyetunji, R., Stutts, B., and Burnett, R. (2010). "Enzymatic hydrolysis of cellulose dissolved in n-methyl morpholine oxide/water solutions," *Bioresource Technology* 101(13), 4965. DOI: 10.1016/j.biortech.2009.09.002

Shang, Y., Jiang, Y., and Gao, J. (2015). "One-step synthesis of peanut shell-derived solid acid for biodiesel production," *Energy Sources Part A Recovery Utilization and Environmental Effects* 7(10), 1039-1045. DOI: 10.1080/15567036.2011.603026

Suganuma, S., Nakajima, K., Kitano, M., Yamaguchi, D., Kato, H., Hayashi, S., and Hara, M. (2010). "Synthesis and acid catalysis of cellulose-derived carbon-based solid acid," *Solid State Sciences* 12(6), 1029-1034. DOI: 10.1016/j.solidstatesciences.2010.02.038

Suganuma, S., Nakajima, K., Kitano, M., Yamaguchi, D., Kato, H., Hayashi, S., and Hara, M. (2008). "Hydrolysis of cellulose by amorphous carbon bearing SO_3H, COOH, and OH groups," *Journal of the American Chemical Society* 130(38), 12787. DOI: 10.1021/ja803983h

Sun, S. L., Wen, J. L., Ma, M. G., and Sun, R. C. (2013). "Successive alkali extraction and structural characterization of hemicelluloses from sweet sorghum stem," *Carbohydrate Polymers* 92(2), 2224. DOI: org/10.1016/j. carbpol. 2012.11.098

TAPPI T211 om-93 (1993). "Ash in wood, pulp, paper, and paperboard: Combustion at 525 °C," TAPPI Press, Atlanta, GA.

TAPPI T222 om-88 (1988). "Acid-insoluble lignin in wood and pulp," TAPPI Press, Atlanta, GA.

TAPPI T223 cm-84 (1984). "Pentosans in wood and pulp," TAPPI Press, Atlanta, GA.

TAPPI T227 (1994). "Freeness of pulp (Canadian standard method)," TAPPI Press, Atlanta, GA.

TAPPI T271 (1991). "Fiber length of pulp and paper by automated optical analyzer," TAPPI Press, Atlanta, GA.

TAPPI T429 cm-84 (1984). "Alpha-cellulose in paper," TAPPI Press, Atlanta, GA.

Teng, H., Yeh, T. S., and Hsu, L. Y. (1998). "Preparation of activated carbon from bituminous coal with phosphoric acid activation," *Carbon* 36(9), 1387-1395. DOI: 10.1016/s0008-6223(98)00127-4

Tian, J., Wang, J., Zhao, S., Jiang, C., Zhang, X., and Wang, X. (2010). "Hydrolysis of cellulose by the heteropoly acid $H_3PW_{12}O_{40}$," *Cellulose* 17(3), 587-594. DOI:10.1007/s10570-009-9391-0

Torget, R. W., Kim, J. S., and Lee, Y. Y. (2000). "Fundamental aspects of dilute acid hydrolysis/fractionation kinetics of hardwood carbohydrates. 1. Cellulose hydrolysis," *Industrial & Engineering Chemistry Research* 39(8), 2817-2825. DOI: 10.1021/ie990915q

Xiao, H., Guo, Y., Liang, X., and Qi, C. (2010). "One-step synthesis of a novel carbon-based strong acid catalyst through hydrothermal carbonization," *Monatshefte für Chemie - Chemical Monthly* 141(8), 929-932. DOI: 10.1007/s00706-010-0332-2

Yang, G., Wang, C., Lyu, G., Lucia, L. A., and Chen, J. (2015). "Catalysis of glucose to 5-hydroxymethylfurfural using Sn-beta zeolites and a Brønsted acid in biphasic systems," *BioResources* 10(3), 5863-5875. DOI:10.15376/biores.10.3.5863-5875

Zhang, L., Wang, Q., Wang, B., Yang, G., Lucia, L. A., and Chen, J. (2015a). "Hydrothermal carbonization of corncob residues for hydrochar production," *Energy and Fuels* 29(2), 150112093612000. DOI: 10.1021/ef502462p

Zhang, L., Liu, S., Wang, B., Wang, Q., Yang, G., and Chen, J. (2015b). "Effect of residence time on hydrothermal carbonization of corn cob residual," *BioResources* 10(3), 3979-3986. DOI: 10.15376/biores.10.3.3979-3986

Zeng, D., Zhang, Q., Chen, S., Liu, S., and Wang, G. (2016). "Synthesis porous carbon-based solid acid from rice husk for esterification of fatty acids," *Microporous & Mesoporous Materials* 219, 54-58. DOI: 10.1016/j.micromeso.2015.07.028

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