

Hydrolysis of Corncob Using a Modified Carbon-based Solid Acid Catalyst

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Lignocellulosic biomass is a very important renewable resource that can be used to produce biofuels and various platform chemicals. The conversion of biomass to reducing sugars is an important intermediate step that can impact the economic benefits of the process. Modified carbon-based solid acid is a novel catalyst used in the hydrolysis process of lignocellulosic materials. The catalyst material was prepared through the incomplete carbonization and subsequent sulfonation of a mixture of glucose and *p*-toluenesulfonic acid, followed by oxidation using 30% H₂O₂ to promote the acidity. The hydrolysis efficiency of the solid acid catalyst thus prepared was considerably increased. The effects of the carbonization temperature, time, and the glucose/*p*-toluene-sulfonic acid ratio on catalytic efficiency were investigated in this study. Under the appropriate preparation conditions, the catalyst could hydrolyze corncob to produce 78% xylose. The activity of the catalyst slightly declined after five cycles of application.

Keywords: Carbon-based solid acid catalyst; Modification; Corncob hydrolysis

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INTRODUCTION

The conversion of lignocellulosic biomass into biofuels and platform chemicals may provide a renewable way to meet the growing shortage of fuels and help to reduce the increasing severe climate change issues (Jin *et al.* 2008; Kunkes *et al.* 2008; Tuck *et al.* 2012; Lam and Luong 2014). Biomass is the most abundant renewable resource available, with an estimated global production of 1.0×10^{11} tons per year (Zhang and Zhao 2010). Lignocellulosic biomass, such as bagasse (Zhuang *et al.* 2015), corncob (Li *et al.* 2014; Xu *et al.* 2015), and eucalyptus (Wu *et al.* 2013), which are primarily composed of cellulose, hemicellulose, and lignin (Zhang *et al.* 2015), can be degraded to recover sugars and other platform chemical products.

Lignocellulosic material can be depolymerized by biological, chemical, physical, and physicochemical methods. Acid-catalyzed hydrolysis, one of the chemical methods for depolymerization, has been viewed as the most efficient approach for lignocellulosic degradation. Acid hydrolysis can be carried out with mineral and organic acids in the form of free or solid state (Hara *et al.* 2015; Loow *et al.* 2016). The application of a carbon-based solid acid (CSA) catalyst to hydrolyze the substrate has received wide attention because of its low cost, limited equipment corrosion, high reactivity, and stability (Qi *et al.*

2015). A carbon material bearing $-\text{SO}_3\text{H}$ groups can hydrolyze cellulose to yield 4% glucose and 64% β -1,4-glucan under hydrothermal conditions, while the yields of glucose and β -1,4-glucan from cellulose catalyzed by sulfuric acid were 10% and 38%, respectively (Suganuma *et al.* 2008). In addition, when compared with the traditional mineral acid catalysts, the use of CSA can avoid residue control and high energy input (Namchot *et al.* 2014). Thus, CSA has the potential to replace mineral acids. However, further research on the use of CSA is needed to increase the hydrolysis efficiency and yield of desired products.

Generally, sulfonated carbonaceous materials are synthesized in two steps: incomplete carbonization of carbon-based materials and subsequent sulfonation by H_2SO_4 or oleum (Toda *et al.* 2005; Shen *et al.* 2013; Bai *et al.* 2015; Hu *et al.* 2015). Recently, a one-step method utilizing carbonization and sulfonation synchronously in an autoclave was used to prepare a strong Brønsted acid catalyst made from glucose and *p*-toluenesulfonic acid (Zhang *et al.* 2010; Guo *et al.* 2012). This method not only can simplify the preparation process, but also it can yield a stable active catalyst. Wang *et al.* (2011) adopted the one-step method to prepare a catalyst that catalyzed fructose into 5-hydroxymethylfurfural in aqueous dimethyl sulfoxide and yielded 91.2% 5-hydroxymethylfurfural. However, the sulfonated CSA had low catalytic ability to catalyze the biomass degradation into monosaccharides (Kitano *et al.* 2009). To *et al.* (2015) reported that the catalytic activity of the nanoporous carbon material MSC-30 could be improved by oxidizing it in NaClO and HNO_3 solutions, respectively, at various temperatures and pH values. Thus, the weak acid sites on the surface of MSC-30 increased, and 96% glucose yield was obtained from β -1,4-glucan under the catalysis of the modified MSC-30. The above studies indicate that the catalytic activity of sulfonated CSA should be enhanced *via* the oxidation process. Until now, the utilization of H_2O_2 -modified sulfonated CSA for catalyzing biomass conversion into monosaccharides has rarely been reported. This work investigated the characteristics of H_2O_2 -modified sulfonated CSA and evaluated its stability and catalytic performance for biomass degradation.

EXPERIMENTAL

Materials

Corncob powder was obtained from a farm in Shandong province (China). It was oven-dried (to a constant weight) at 80 °C for 12 h. The compositional analysis revealed that it contains 44.81% cellulose, 39.31% hemicellulose, and 5.77% acid-insoluble lignin according to the NREL standard analytical method (Sluiter *et al.* 2008). Glucose (AR), *p*-toluenesulfonic acid (AR), and aqueous H_2O_2 solution (AR) were purchased from Tianjin Damao Chemical Reagent Factory (China), Tianjin Fu Chen Chemical Reagents Factory (China), and Guangzhou Chemical Reagent Factory (China), respectively. Xylose, glucose, and furfural standards were purchased from Aladdin (China).

Preparation of the $\text{Gp-SO}_3\text{H}$

A mixture of glucose/*p*-toluenesulfonic acid was ball-milled for 2 h and then transferred into a 100-mL Teflon®-lined stainless steel autoclave reactor. The autoclave reactor was placed in a heating mantle to obtain a black solid, which was then subsequently collected and placed in a muffle furnace at 180 °C for one day to remove the small organic compounds adsorbed on the surface of the material. Then, the dark solid was ground and

washed with hot water (above 80 °C) until a neutral pH was achieved and then dried at 105 °C oven for 4 h. This sample was denoted Gp-SO₃H.

Modification of Gp-SO₃H

A mixture of 1 g of Gp-SO₃H and 50 mL of 30% H₂O₂ was added to a thick-walled pressure bottle and oxidized at 50 °C for 1 h in an oil bath with magnetic stirring. The solid residue was collected after filtration followed by washing with water. It was then dried in an oven at 105 °C overnight and denoted Gp-SO₃H-H₂O₂.

Selective Catalytic Hydrolysis of Corncob

A mixture of corncob, deionized water, and Gp-SO₃H-H₂O₂ was stirred in a thick-walled pressure bottle with a magnetic stirrer. The time (*t*) required for the reaction temperature to reach the target temperature was considered to be zero. The reactor was removed from oil bath and cooled to room temperature after the reaction. Then, the products were filtered to separate the liquid and solid residues. The liquid was analyzed by high-performance liquid chromatography (HPLC), and the solid was washed several times with water to separate the catalyst from the corncob residue.

Analytical Methods

Analysis of liquid products

Xylose, glucose, and furfural were identified by HPLC (Waters 2695, Milford, USA) analysis with a Shodex SH-1011 column. The mobile phase used was 5 mM H₂SO₄ with a flow rate of 0.5 mL/min at 50 °C. Calibration curves were established for quantitative estimations of the products. Xylose, glucose, and furfural yields were calculated from the following equation,

$$\text{Yield} = n_{\text{prod}}/n_{\text{corn}} \times 100\% \quad (1)$$

where n_{prod} is the experimentally obtained moles of the products and n_{corn} is the theoretical moles of xylose, glucose, or furfural calculated from the corncob.

Characterization of Gp-SO₃H and Gp-SO₃H-H₂O₂

The functional groups present in the prepared catalysts Gp-SO₃H and Gp-SO₃H-H₂O₂ were analyzed by Fourier transform infrared spectroscopy (FTIR) using a TENSOR 27 spectrometer (Bruker, Karlsruhe, Germany) in the range of 400 to 4000 cm⁻¹. The crystalline structure of the catalysts was analyzed by X-ray diffraction (XRD) using a X'PertPro MPD (PANalytical, Almelo, Netherlands) operating at 40 kV and 40 mA (Cu K α 1 radiation). The selected 2θ range was 5° to 80° with a scanning step of 0.0167°. The surface morphologies of the catalysts were observed using scanning electron microscopy (SEM, S-4800, Hitachi, Tokyo, Japan), and their specific surface areas were measured by the Brunauer, Emmett, and Teller (BET) method using the ASI QMO002-2, (Quantachrome, Boynton Beach, USA). The acidic functional groups of the catalyst surface were studied by following the neutralization titration: 0.25 g of catalyst was added to 40 mL of 0.05 M sodium hydroxide and 40 mL of 0.05 M sodium chloride solutions, respectively, at room temperature for 1 h. After centrifugation, the supernatants were separately titrated (three times in parallel) with 0.05 M hydrochloric acid and 0.05 M sodium hydroxide standard solutions to determine the amounts of total acidic sites and the -SO₃H groups. During the titration process, phenolphthalein was used as the indicator. A Vario EL cube analyzer (Elementar, Frankfurt, Germany) was used for the elemental

analysis of C, H, N, and S in $Gp\text{-SO}_3\text{H}$ and $Gp\text{-SO}_3\text{H-H}_2\text{O}_2$. Thermogravimetric (TG) and differential thermogravimetric (DTG) analyses of the samples were performed using a TGAQ50 (TA Instruments, New Castle, USA) with a heating rate of 20 °C/min from 30 to 1000 °C in a N_2 flow. X-ray photoelectron spectroscopy (XPS) was performed using an ESCALAB 250Xi (Thermo, Waltham, USA).

RESULTS AND DISCUSSION

Catalyst Characteristics

Structural properties of carbonaceous material

During the sulfonated CSA ($Gp\text{-SO}_3\text{H}$) preparation, glucose was used as the carbon donor and *p*-toluenesulfonic acid provided the required $\text{-SO}_3\text{H}$ groups. Its elemental composition was calculated to be $\text{C}_{0.613}\text{H}_{0.043}\text{O}_{0.322}\text{S}_{0.022}$, which showed an increase in the C relative content and a decrease in the relative contents of H and O elements compared with the glucose composition of $\text{C}_{0.400}\text{H}_{0.067}\text{O}_{0.533}$. This revealed that the glucose was incompletely carbonized and sulfonated during the catalyst preparation process. The surface morphologies of the catalysts were analyzed and are shown in Fig. 1. Compared with glucose (Fig. 1a), many spheres were formed on the surface of the $Gp\text{-SO}_3\text{H}$ (Fig. 1b). It had been reported that mono-dispersed carbon spheres could be synthesized by the hydrothermal carbonization of glucose (Liang *et al.* 2010). The oxidation of the sulfonated CSA by H_2O_2 ($Gp\text{-SO}_3\text{H-H}_2\text{O}_2$) only slightly changed its surface (Fig. 1c). The BET surface areas of $Gp\text{-SO}_3\text{H}$ and $Gp\text{-SO}_3\text{H-H}_2\text{O}_2$ were analyzed by N_2 adsorption-desorption and were found to be 0.30 and 0.25 m^2/g , respectively. This hinted that the microporous or mesoporous structures of the catalyst might be scarcely formed; nevertheless, it had a high catalytic performance in many acid-catalyzed reactions (Toda *et al.* 2005).

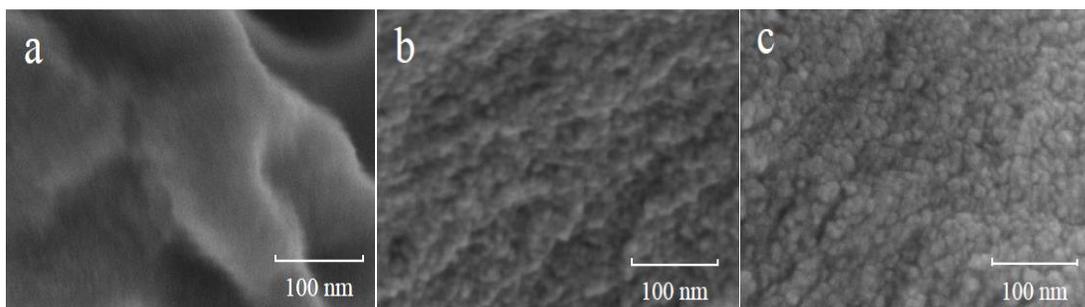


Fig. 1. Scanning electron microscopic images of the catalysts, (a) glucose, (b) $Gp\text{-SO}_3\text{H}$, and (c) $Gp\text{-SO}_3\text{H-H}_2\text{O}_2$

The XRD patterns of $Gp\text{-SO}_3\text{H}$ and $Gp\text{-SO}_3\text{H-H}_2\text{O}_2$ were also measured. There were two diffraction peaks in the XRD patterns: a broad diffraction peak between 10° to 30° was ascribed to the (002) planes of the amorphous carbon framework (Okamura *et al.* 2006), and the weak diffraction peaks between 35° and 50° were attributed to the (101) plane of amorphous carbon corresponding to the *a*-axis direction of the graphite structure (Tsubouchi *et al.* 2003; Suganuma *et al.* 2008). It can be observed in Fig. 2 that H_2O_2 oxidation had no impact on the XRD pattern of $Gp\text{-SO}_3\text{H}$.

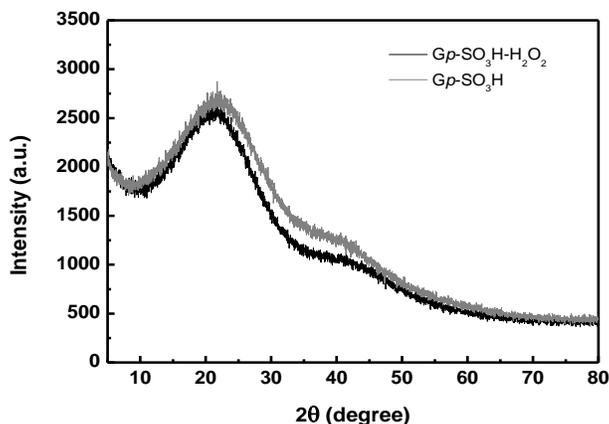


Fig. 2. X-ray diffraction spectra of the catalysts

The TG/DTG analyses were performed to compare the thermal stability of the catalysts $Gp-SO_3H$ and $Gp-SO_3H-H_2O_2$ (Fig. 3). For $Gp-SO_3H$, three stages of degradation were observed in the DTG curves. A weight loss of 3.6% occurring below 150 °C was attributed to the removal of water absorbed on the catalyst; 17.4% weight loss appearing between 150 and 400 °C was due to the additional carbonization of the incompletely carbonized glucose; and 19.7% weight loss above 400 °C may have been caused by the aromatization of the structural network (Bai *et al.* 2015). These results show that the weights of these two catalysts decreased with an increase in temperature. However, $Gp-SO_3H$ was slightly more stable than $Gp-SO_3H-H_2O_2$ at 150 to 250 °C, and the weight loss rate of $Gp-SO_3H$ was slower than that of $Gp-SO_3H-H_2O_2$. Based on the above findings, the H_2O_2 modification only slightly changed the structural features of $Gp-SO_3H$, and also had little impact on its thermal stability.

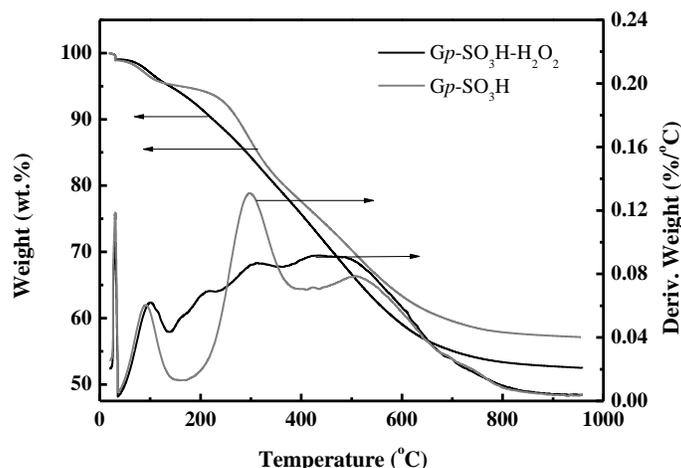


Fig. 3. The thermogravimetric/differential thermogravimetric spectra of the catalysts

Group changes in $Gp-SO_3H$ after H_2O_2 modification

The acidity of the catalysts was examined using a neutralization titration method, and the results are shown in Table 1. The amount of $-SO_3H$ groups in the $Gp-SO_3H$ and $Gp-SO_3H-H_2O_2$ remained almost the same, which revealed that the H_2O_2 modification did not cause the loss of the $-SO_3H$ group in the catalyst. However, the elemental analysis showed that the amount of elemental S in $Gp-SO_3H$ was 0.69 mmol/g, which was higher than the results from the acid-base titration. This indicated that a portion of the elemental

S might exist as another molecular form. The XPS-peak-differentiation-imitating analysis was used to determine the existence of elemental S in Gp -SO₃H and Gp -SO₃H-H₂O₂ (Fig. 4). The black line in Fig. 4 is the practical spectrum of catalysts, and the gray lines are the split peaks of the practical spectrum determined by the peak separation method. The S2p line shows two distinct signals for Gp -SO₃H (Fig. 4a): one with the S2p_{3/2} main component centered at 167.9 eV, and the minor S2p_{1/2} component centered at 169.0 eV, was assigned to -SO₃H; the S2p_{3/2} and S2p_{1/2} signals centered at 164.0 eV and 165.1 eV, respectively, were ascribed to -SH groups (Karaki *et al.* 2013). The peak signal for Gp -SO₃H-H₂O₂ was the same as that for Gp -SO₃H. This indicated that the catalysts not only contained -SO₃H groups, but they also had -SH groups. The formation of the -SH group might be a result of the strong reducibility of glucose under hydrothermal carbonization, which restored -SO₃H to -SH. However, the -SH group accounted for 34.8% of the total S element in Gp -SO₃H, while it decreased to 20.2% in Gp -SO₃H-H₂O₂, which might be ascribed to the oxidation of a part of -SH during H₂O₂ modification (Karimi *et al.* 2005). Table 1 showed that the amount of -SO₃H had little change after H₂O₂ modification, which meant that -SH was not oxidized into -SO₃H. A simple treatment of Gp -SO₃H with 30% H₂O₂ aqueous solution under mild conditions increased the total amount of acidity groups by nearly a factor of 1.5. The oxidization process may oxidize the aliphatic CH₃/CH₂ groups to carboxylic acid groups (Mo *et al.* 2008).

Table 1. Solid-Base Titration Results for the Catalysts

Catalyst	The total amount of acidic groups (mmol/g)	-SO ₃ H (mmol/g)
Gp -SO ₃ H-H ₂ O ₂	2.55	0.49
Gp -SO ₃ H	1.80	0.51

Preparation conditions: 3:1 mixture of glucose/*p*-toluenesulfonic acid and carbonization at 180 °C for 24 h

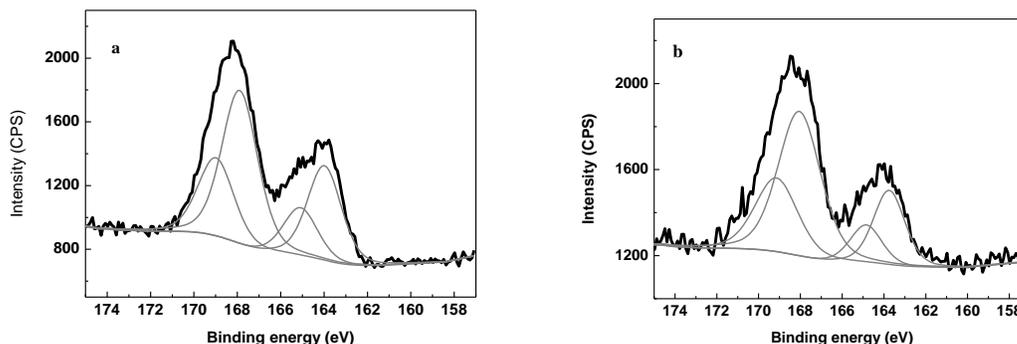


Fig. 4. X-ray photoelectron spectroscopy (XPS) of the catalysts: (a) Gp -SO₃H and (b) Gp -SO₃H-H₂O₂

Optimization of Catalytic Activity of Gp -SO₃H-H₂O₂

The introduction of sulfonic acid groups into the carbonaceous matrix occurs by an electrophilic substitution mechanism during the reaction between the *p*-toluenesulfonic acid and glucose (Fraga *et al.* 2015). The preparation process might influence the catalytic

activity of $Gp-SO_3H-H_2O_2$. Further studies would be needed to optimize the preparation condition to obtain higher activity of $Gp-SO_3H-H_2O_2$. The corncob was selected as the feedstock, and the carbonization temperature, carbonization time, and glucose/*p*-toluenesulfonic acid ratio were selected as the parameters to be optimized.

Effects of carbonization temperature on the catalytic activity

The carbonization temperature is an important parameter for catalyst preparation. The catalysts were prepared at temperatures varying from 150 to 210 °C for 24 h with a glucose/*p*-toluenesulfonic acid ratio of 2:3. The hydrolysis of corncob by catalysts was used to evaluate the catalytic activity. The glucose released from the corncob was trivial (data not shown here), so the release of xylose from corncob was used to determine the catalytic activities of catalysts. As the preparation temperature for the catalyst increased from 150 to 180 °C, the xylose yield increased from 43.5% to 55.2% (Fig. 5). This was attributed to the formation of incompletely carbonized amorphous structures, and the -OH, -COOH, and -SO₃H acidic functional groups were successfully grafted onto the carbon skeleton (Wang *et al.* 2011). When the preparation temperature for catalysts was further increased from 180 to 210 °C, the xylose yield decreased to 24.7%. This might be attributed to the high temperature, which would affect the structure of *p*-toluenesulfonic acid and decrease the loading amounts of -SO₃H groups. The optimum carbonization temperature was found to be 180 °C, which was used for subsequent experiments.

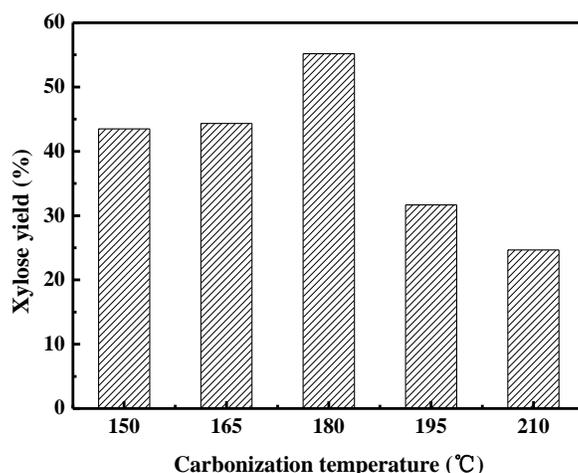


Fig. 5. Catalysts prepared at various carbonization temperatures and their catalysis of corncob into xylose. Catalytic conditions: 140 °C for 14 h, 1.0 g of catalyst, and 0.5 g of corncob in 75 mL of deionized water

Effects of carbonization time on the catalytic activity

The catalysts were prepared at 180 °C at various carbonization times from 18 to 36 h with a glucose/*p*-toluenesulfonic acid ratio of 2:3. From Fig. 6, it is clear that with the increase of carbonization time from 18 to 24 h, the yield of xylose increased from 62.9% to 67.4% under the catalysis of the catalysts (Fig. 6). This may be because the increased amount of carbonization time made the conjunction between functional groups and the carbon skeleton become tighter. However, when the carbonization time surpassed 24 h, the xylose yield decreased (Fig. 6). This may be attributed to the loss of acidic functional groups, such as carboxylic and phenolic groups.

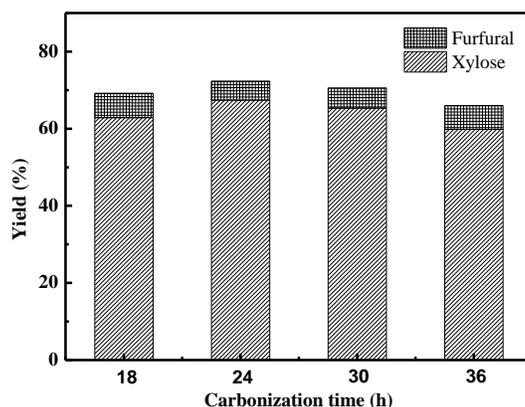


Fig. 6. Catalysts prepared at 180 °C for different hours and their catalysis of corncob into xylose. Catalytic conditions: 140 °C for 14 h, 1.0 g of catalyst, and 0.5 g of corncob in 75 mL of deionized water

*Effects of glucose/*p*-toluenesulfonic acid ratio on the catalytic activity*

Various glucose/*p*-toluenesulfonic acid ratios were used for preparing catalysts, and their effects were investigated. As the glucose/*p*-toluenesulfonic acid ratio decreased from 5:1 to 2:1, the xylose yield increased from 70.1% to 78.4% under the action of catalysts (Fig. 7). This could be because of the larger proportion of *p*-toluenesulfonic acid present in the reaction mixture, which resulted in more -SO₃H groups grafted onto the carbon skeleton. This process could selectively break the C-O bonds of the adjacent units in the hemicellulose structure (Dutta *et al.* 2012), yielding more xylose. A decreased yield of xylose was found when the glucose/*p*-toluenesulfonic acid ratio was decreased further (Fig. 7), which might have occurred because of the superabundant *p*-toluenesulfonic acid units capable of covering the functional groups on the surface of the catalyst.

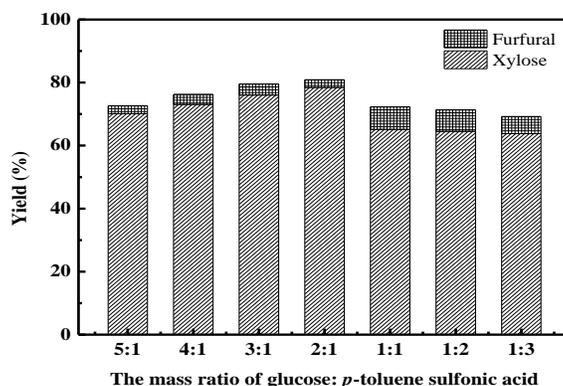


Fig. 7. Catalysts prepared at 180 °C for 24 h with various glucose/*p*-toluenesulfonic acid ratios and their catalysis of corncob into xylose. Catalytic conditions: 140 °C for 14 h, 1.0 g of catalyst, and 0.5 g of corncob in 75 mL of deionized water

Catalytic activity comparison between Gp-SO₃H and Gp-SO₃H-H₂O₂

As per the above studies, the optimum carbonization conditions of 180 °C, 24 h, and a glucose/*p*-toluenesulfonic acid ratio of 2:1 were used to prepare Gp-SO₃H and Gp-SO₃H-H₂O₂ catalysts. The catalytic activities of Gp-SO₃H and Gp-SO₃H-H₂O₂ were

compared with their reaction on corncob and soluble starch used as the substrates. The hydrolysis of substrates was conducted at 140 °C for 12 h. The xylose and glucose generated from corncob were 54.7% and 9.3%, respectively, under the catalysis of $Gp-SO_3H$, while 79.7% xylose and 11.5% glucose were obtained from corncob during the action of $Gp-SO_3H-H_2O_2$ (Fig. 8). The yield of glucose from soluble starch that was catalyzed by $Gp-SO_3H$ was 28.8%, whereas 90.4% was provided by $Gp-SO_3H-H_2O_2$ (Fig. 8). This data reveals that the catalytic efficiency of the catalyst was observably improved by the H_2O_2 modification treatment. This may be a result of the increase in the total amount of acidic groups after oxidation reaction (Table 1). The H_2O_2 modification process played an important role in obtaining a catalyst with a higher acidity and better catalytic effect. The modification method described here could be further extended to various functionalized carbon materials by increasing the amount of acidic groups.

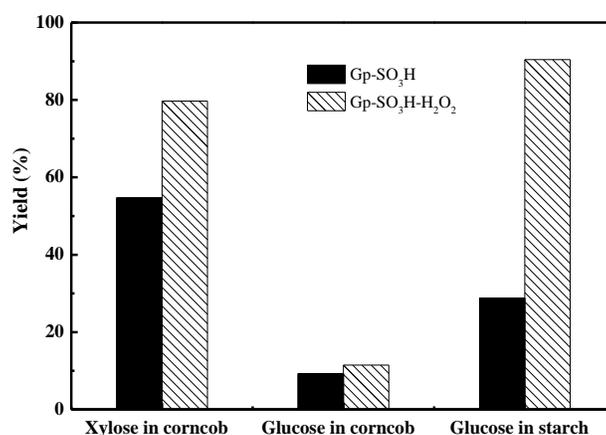


Fig. 8. The catalytic hydrolysis of $Gp-SO_3H$ and $Gp-SO_3H-H_2O_2$. Reaction conditions: 140 °C for 12 h, 0.5 g of catalyst, and 0.25 g of feedstock in 25 mL of deionized water

Comparison of Catalytic Activities of Various Acid Catalysts

The catalytic activities of $Gp-SO_3H-H_2O_2$ and other commercial catalysts were compared. The corncob was used as the feedstock, and it was hydrolyzed at 140 °C for 14 h. The hydrolysates yield from corncob under the catalysis of various catalysts are shown in Table 2. A control experiment was conducted in the absence of catalyst, which confirmed that only trace amounts of xylose and glucose were obtained. It indicated that the autocatalysis of corncob was negligible. The xylose yields obtained from corncob in the presence of HZSM-5, Amberlyst-15, SBA-15, Al_2O_3 , and zeolite were 11.4%, 60.2%, 9.3%, 0.6%, and 0%, respectively. Zeolite is a type of mineral acid, and the low amount of acidic sites, large particle sizes, and small surface area may have led to the poor catalytic effect. Alumina (Al_2O_3) could not provide enough surface area, which led to the similar poor catalysis efficiency (Onda *et al.* 2008). Molecular sieves (SBA-15 and HZSM-15) can catalyze the corncob degradation to hydrolysates partly because of their larger surface area and better surface acidity (Nandiwale *et al.* 2014). Amberlyst-15 is an ion exchange resin with a large surface area, and it contains a large amount of $-SO_3H$ groups (Suganuma *et al.* 2008). It acquired a higher catalysis efficiency, which demonstrated that the $-SO_3H$ moiety was an active group on the catalyst surface. However, from the FTIR spectra in Fig. 9, other surface functional groups, including the carboxylic acid (1708 cm^{-1}) and phenolic groups (3438 cm^{-1}), also existed in $Gp-SO_3H-H_2O_2$ in addition to the $-SO_3H$ (1031 and

1165 cm^{-1}) group. They certainly played an important role in the hydrolysis process because $Gp\text{-SO}_3\text{H-H}_2\text{O}_2$ exhibited a higher catalytic performance even though it had fewer sulfonic groups and much lower surface area than Amberlyst-15 (Hara 2010). The commercial catalysts were not as good as the modified carbon solid acid; $Gp\text{-SO}_3\text{H-H}_2\text{O}_2$ displayed the highest activity of the tested catalysts (providing a yield as high as 78.4%). Thus, the carbon-based solid acid (CSA) has good application prospects in biomass conversion.

Table 2. Effects of Various Catalysts on the Product Yield

Entry	Xylose yield (%)	Glucose yield (%)	Furfural yield (%)	Formic acid (g/100g corncob)	Acetic acid (g/100g corncob)
$Gp\text{-SO}_3\text{H-H}_2\text{O}_2$	78.4	6.1	2.2	1.1	1.4
HZSM-5	11.4	5.7	/	0.5	/
Amberlyst-15	60.2	5.8	5.8	1.4	0.4
SBA-15	9.3	6.1	0.4	0.7	/
Al_2O_3	0.6	1.4	0.3	0.9	/
Zeolite	/	2.3	/	1.2	/
None	2.3	1.9	/	/	/

Reaction conditions: 140 °C for 12 h, 0.5 g of catalyst, and 0.25 g of feedstock in 25 mL of deionized water

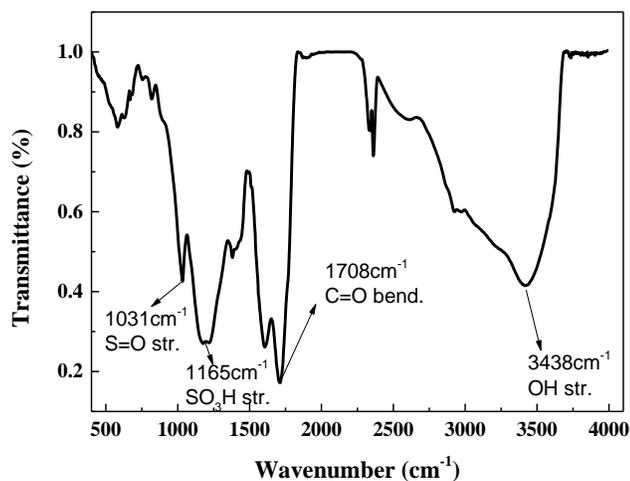


Fig. 9. Fourier transform infrared spectroscopy (FTIR) of $Gp\text{-SO}_3\text{H-H}_2\text{O}_2$

Reusability of the Catalyst

The reusability of the catalyst is of great importance for the practical hydrolysis of corncob. The reusability of $Gp\text{-SO}_3\text{H-H}_2\text{O}_2$ was investigated at optimized carbonization conditions: 180 °C, 24 h, and glucose/*p*-toluenesulfonic acid ratio of 2:1. When the reaction was complete, the catalyst was separated from the corncob, collected, washed several times with deionized water, and then dried in the oven at 105 °C until a constant weight was

achieved. The same catalyst was reused for the subsequent four cycles. As depicted by Fig. 10, a xylose yield of 77.5% was obtained in the first run, while the yield decreased to 65.0% after five cycles. Thus, the catalyst could be reused, although there was a decreasing yield trend that may be attributed to the loss of $Gp\text{-SO}_3\text{H-H}_2\text{O}_2$ in the reusing process or leaching of the $\text{-SO}_3\text{H}$ groups during the reaction (Bai *et al.* 2015).

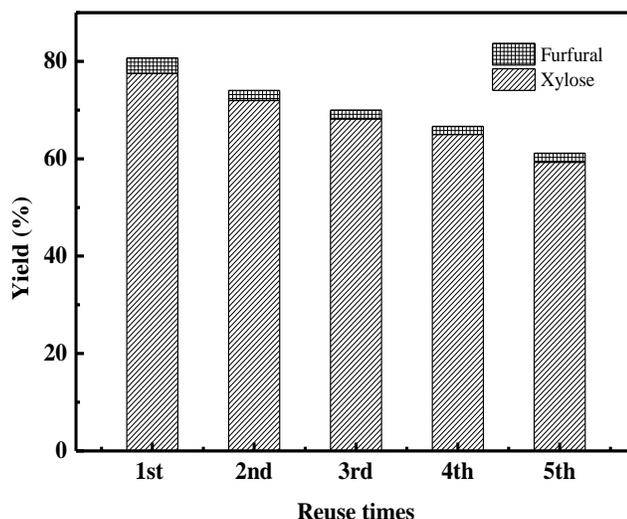


Fig. 10. Reusability of $Gp\text{-SO}_3\text{H-H}_2\text{O}_2$. Reaction conditions: 140 °C for 14 h, 1.0 g of catalyst, and 0.5 g of feedstock in 75 mL of deionized water

CONCLUSIONS

1. A highly efficient carbon-based solid acid catalyst, denoted $Gp\text{-SO}_3\text{H-H}_2\text{O}_2$, was functionalized with sulfonic acid groups and modified by H_2O_2 . It exhibited a much higher activity in the lignocellulosic biomass hydrolysis reaction than $Gp\text{-SO}_3\text{H}$, as it had notably increased acidity.
2. The highest xylose yield (78%) was obtained when the catalyst was prepared at carbonization conditions of 180 °C for 24 h with a glucose/*p*-toluenesulfonic acid ratio of 2:1.
3. The catalyst was superior to various common commercial catalysts in the corncob hydrolysis process; moreover, it was relatively stable and can be reused many times.

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REFERENCES CITED

- Bai, Y. Y., Xiao, L. P., and Sun, R. C. (2015). "Microwave-assisted conversion of biomass derived hemicelluloses into xylo-oligosaccharides by novel sulfonated bamboo-based catalysts," *Biomass Bioenerg.* 75, 245-253. DOI: 10.1016/j.biombioe.2015.02.023
- Dutta, S., De, S., Saha, B., and Alam, M. I. (2012). "Advances in conversion of hemicellulosic biomass to furfural and upgrading to biofuels," *Catal. Sci. Technol.* 2(10), 2025-2036. DOI: 10.1039/C2CY20235B
- Fraga, A. C., Quitete, C. P. B., Ximenes, V. L., Sousa-Aguiar, E. F., Fonseca, I. M., and Rego, A. M. B. (2015). "Biomass derived solid acids as effective hydrolysis catalysts," *J. Mol. Catal. A-Chem.* 83, 408-413. DOI: 10.1016/j.molcata.2015.12.005
- Guo, H. X., Qi, X. H., Li, L. Y., and Smith, R. L. (2012). "Hydrolysis of cellulose over functionalized glucose-derived carbon catalyst in ionic liquid," *Bioresour. Technol.* 116, 355-359. DOI: 10.1016/j.biortech.2012.03.098
- Hara, M. (2010). "Biodiesel production by amorphous carbon bearing SO₃H, COOH and phenolic OH groups, a solid Brønsted acid catalyst," *Top. Catal.* 53(11-12), 805-810. DOI: 10.1007/s11244-010-9458-z
- Hara, M., Nakajima, K., and Kamata, K. (2015). "Recent progress in the development of solid catalysts for biomass conversion into high value-added chemicals," *Sci. Technol. Adv. Mater.* 16(3), 1-22. DOI: 10.1088/1468-6996/16/3/034903
- Hu, S., Jiang, F., and Hsieh, Y. (2015). "1D lignin-based solid acid catalysts for cellulose hydrolysis to glucose and nanocellulose," *ACS Sustain. Chem. Eng.* 3(10), 2566-2574. DOI: 10.1021/acssuschemeng.5b00780
- Jin, F. M., Yun, J., Li, G. M., Kishita, A., Tohji, K., and Enomoto, H. (2008). "Hydrothermal conversion of carbohydrate biomass into formic acid at mild temperature," *Green Chem.* 10(6), 612-615. DOI: 10.1039/B802076K
- Karaki, M., Karout, A., Toufaily, J., Rataboul, F., Essayem, N., and Lebeau, B. (2013). "Synthesis and characterization of acidic ordered mesoporous organosilica SBA-15: Application to the hydrolysis of cellobiose and insight into the stability of the acidic functions," *J. Catal.* 305, 204-216. DOI: 10.1016/j.jcat.2013.04.024
- Karimi, B., Ghoreishi-Nezhad, M., and Clark, J. H. (2005). "Selective oxidation of sulfides to sulfoxides using 30% hydrogen peroxide catalyzed with a recoverable silica-based tungstate interphase catalyst," *Org. Lett.* 7(4), 625-628. DOI: 10.1021/o1047635d
- Kitano, M., Yamaguchi, D., Suganuma, S., Nakajima, K., Kato, H., Hayashi, S., and Hara, M. (2009). "Adsorption-enhanced hydrolysis of beta-1,4-glucan on graphene-based amorphous carbon bearing SO₃H, COOH, and OH groups," *Langmuir* 25(9), 5068-5075. DOI: 10.1021/la8040506
- Kunkes, E. L., Simonetti, D. A., West, R. M., Serrano-Ruiz, J. C., Gärtner, C. A., and Dumesic, J. A. (2008). "Catalytic conversion of biomass to monofunctional hydrocarbons and targeted liquid-fuel classes," *Science* 322(5900), 417-421. DOI: 10.1126/science.1159210
- Lam, E., and Luong, J. H. T. (2014). "Carbon materials as catalyst supports and catalysts in the transformation of biomass to fuels and chemicals," *ACS Catal.* 4(10), 3393-3410. DOI: 10.1021/cs5008393
- Li, H. L., Deng, A. J., Ren, J. L., Liu, C. Y., Lu, Q., Zhong, L. J., Peng, F., and Sun, R. C. (2014). "Catalytic hydrothermal pretreatment of corncob into xylose and furfural via

- solid acid catalyst,” *Bioresour. Technol.* 158, 313-320. DOI: 10.1016/j.biortech.2014.02.059
- Liang, X. Z., Xiao, H. Q., Shen, Y. M., and Qi, C. Z. (2010). “One-step synthesis of novel sulfuric acid groups' functionalized carbon via hydrothermal carbonization,” *Mater. Lett.* 64(8), 953-955. DOI: 10.1016/j.matlet.2010.01.070
- Loow, Y. L., Wu, T. Y., Jahim, J. M., Mohammad, A. W., and Teoh, W. H. (2016). “Typical conversion of lignocellulosic biomass into reducing sugars using dilute acid hydrolysis and alkaline pretreatment,” *Cellulose* 23(3), 1491-1520. DOI: 10.1007/s10570-016-0936-8
- Mo, X., López, D. E., Suwannakarn, K., Liu, Y. J., Lotero, E., Goodwin, J. G., and Lu, C. Q. (2008). “Activation and deactivation characteristics of sulfonated carbon catalysts,” *J. Catal.* 254(2), 332-338. DOI: 10.1016/j.jcat.2008.01.011
- Namchot, W., Panyacharay, N., Jonglertjanya, W., and Sakdaronnarong, C. (2014). “Hydrolysis of delignified sugarcane bagasse using hydrothermal technique catalyzed by carbonaceous acid catalysts,” *Fuel* 116, 608-616. DOI: 10.1016/j.fuel.2013.08.062
- Nandiwale, K. Y., Galande, N. D., Thakur, P., Sawant, S. D., Zambre, V. P., and Bokade, V. V. (2014). “One-pot synthesis of 5-hydroxymethylfurfural by cellulose hydrolysis over highly active bimodal micro/mesoporous H-ZSM-5 catalyst,” *ACS Sustain. Chem. Eng.* 2(7), 1928-1932. DOI: 10.1021/sc500270z
- 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,” *Chem. Mat.* 18(13), 3039-3045. DOI: 10.1021/cm0605623
- Onda, A., Ochi, T., and Yanagisawa, K. (2008). “Selective hydrolysis of cellulose into glucose over solid acid catalysts,” *Green Chem.* 10(10), 1033-1037. DOI: 10.1039/B808471H
- Qi, X. H., Liu, N., and Lian, Y. F. (2015). “Carbonaceous microspheres prepared by hydrothermal carbonization of glucose for direct use in catalytic dehydration of fructose,” *RSC Adv.* 5(23), 17526-17531. DOI: 10.1039/C4RA15296D
- Shen, S.G., Wang, C. Y., Cai, B., Li, H. M., Han, Y., Wang, T., Qin, H. F. (2013). “Heterogeneous hydrolysis of cellulose into glucose over phenolic residue-derived solid acid,” *Fuel* 113, 644-649. DOI: 10.1016/j.fuel.2013.06.021
- Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., and Crocker, D. (2008). “Determination of Structural Carbohydrates and Lignin in Biomass,” *NREL Technical Report*, NREL/TP-510-42618
- Suganuma, S., Nakajima, K., Kitano, M., Yamaguchi, D., Kato, H., Hayashi, S., and Hara, M. (2008). “Hydrolysis of cellulose by amorphous carbon bearing SO₃H, COOH, and OH groups,” *J. Am. Chem. Soc.* 130(38), 12787-12793. DOI: 10.1021/ja803983h
- To, A. T., Chung, P. W., and Katz, A. (2015). “Weak-acid sites catalyze the hydrolysis of crystalline cellulose to glucose in water: Importance of post-synthetic functionalization of the carbon surface,” *Angew. Chem.-Int. Edit.* 54(38), 11050-11053. DOI: 10.1002/anie.201504865
- Toda, M., Takagaki, A., Okamura, M., Kondo, J. N., Hayashi, S., Domen, K., and Hara, M. (2005). “Green chemistry - Biodiesel made with sugar catalyst,” *Nature* 438(7065), 178-178. DOI: 10.1038/438178a

- Tsubouchi, N., Xu, C. B., and Ohtsuka, Y. (2003). "Carbon crystallization during high-temperature pyrolysis of coals and the enhancement by calcium," *Energy Fuels* 17(5), 1119-1125. DOI: 10.1021/ef020265u
- Tuck, C. O., Pérez, E., Horváth, I. T., Sheldon, R. A., and Poliakoff, M. (2012). "Valorization of biomass: Deriving more value from waste," *Science* 337(6095), 695-699. DOI: 10.1126/science.1218930
- Wang, J. J., Xu, W. J., Ren, J. W., Liu, X. H., Lu, G. Z., and Wang, Y. Q. (2011). "Efficient catalytic conversion of fructose into hydroxymethylfurfural by a novel carbon-based solid acid," *Green Chem.* 13(10), 2678-2681. DOI: 10.1039/C1GC15306D
- Wu, L., Lee, S. H., and Endo, T. (2013). "Effect of dimethyl sulfoxide on ionic liquid 1-ethyl-3-methylimidazolium acetate pretreatment of eucalyptus wood for enzymatic hydrolysis," *Bioresour. Technol.* 140, 90-96. DOI: 10.1016/j.biortech.2013.04.072
- Xu, Z. P., Li, W. Z., Du, Z. J., Wu, H., Jameel, H., Chang, H. M., and Ma, L. L. (2015). "Conversion of corn stalk into furfural using a novel heterogeneous strong acid catalyst in γ -valerolactone," *Bioresour. Technol.* 198, 764-771. DOI: 10.1016/j.biortech.2015.09.104
- Zhang, Z. H., and Zhao, Z. B. K. (2010). "Microwave-assisted conversion of lignocellulosic biomass into furans in ionic liquid," *Bioresour. Technol.* 101(3), 1111-1114. DOI: 10.1016/j.biortech.2009.09.010
- Zhang, B. H., Ren, J. W., Liu, X. H., Guo, Y., Guo, Y. L., Lu, G. Z., and Wang, Y. Q. (2010). "Novel sulfonated carbonaceous materials from p-toluenesulfonic acid/glucose as a high-performance solid-acid catalyst," *Catal. Commun.* 11(7), 629-632. DOI: 10.1016/j.catcom.2010.01.010
- Zhang, J., Choi, Y. S., Yoo, C. G., Kim, T. H., Brown, R. C., and Shanks, B. H. (2015). "Cellulose-hemicellulose and cellulose-lignin interactions during fast pyrolysis," *ACS Sustain. Chem. Eng.* 3(2), 293-301. DOI: 10.1021/sc500664h
- Zhuang, X. S., Yu, Q., Yuan, Z. H., Kong, X. Y., and Qi, W. (2015). "Effect of hydrothermal pretreatment of sugarcane bagasse on enzymatic digestibility," *J. Chem. Technol. Biotechnol.* 90(8), 1515-1520. DOI: 10.1002/jctb.4467

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