Effect of Dilute Acid and Alkali Pretreatments on the Catalytic Performance of Bamboo-Derived Carbonaceous Magnetic Solid Acid

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Abstract: Lignocellulose is a widely used renewable energy source on the Earth that is rich in carbon skeletons. The catalytic hydrolysis of lignocellulose over magnetic solid acid is an efficient pathway for the conversion of biomass into fuels and chemicals. In this study, a bamboo-derived carbonaceous magnetic solid acid catalyst was synthesized by FeCl₃ impregnation, followed by carbonization and –SO₃H group functionalization. The prepared catalyst was further subjected as the solid acid catalyst for the catalytic conversion of corncob polysaccharides into reducing sugars. The results showed that the as-prepared magnetic solid acid contained –SO₃H, –COOH, and polycyclic aromatic, and presented good catalytic performance for the hydrolysis of corncob in the aqueous phase. The concentration of H⁺ was in the range of 0.6487 to 2.3204 mmol/g. Dilute acid and alkali pretreatments of raw material can greatly improve the catalytic activity of bamboo-derived carbonaceous magnetic solid acid. Using the catalyst prepared by 0.25% H₂SO₄-pretreated bamboo, 6417.5 mg/L of reducing sugars corresponding to 37.17% carbohydrates conversion could be obtained under the reaction conditions of 120 °C for 30 min.

Keywords: bamboo; pretreatment; magnetic solid acid; corncob; reducing sugar

1. Introduction

The depletion of fossil fuel reserves and climate change issues have raised concerns about renewable petroleum alternatives with the increment of global energy demand [1,2]. Biomass has received increasing attention in recent decades due to it being widespread, abundant, diverse, and inexpensive. Moreover, it has been intensively investigated as a highly sustainable carbon-containing source for the production of bioplatform molecules and biochemicals. The unique property of lignocellulosic biomass as the only renewable carbon carrier makes it an attractive source for bioenergy production. The conversion of lignocellulosic biomass to useful chemicals and biofuels via green and efficient approaches is one of the most popular topics in recent years [3]. However, problems such as its high pretreatment cost and difficulty in catalyst recovery hinder their utilization. Therefore, the development of new reaction techniques, including novel catalysts, novel pretreatment methods, or reaction media, is crucial for biomass-to-bioenergy industries [4].

The cell wall of lignocellulose mainly consists of lignin, cellulose, and hemicellulose [5]. The amount of each constituent is related to the type of plant species and their age [6]. Although...
lignocellulose is rich in cellulose and hemicellulose, its high lignin content, and tough and strong physical structure make it difficult to convert into chemicals and biofuels. Chemical methods such as acid pretreatment are commonly used to prepare reducing sugars. Compared to concentrated acid pretreatment, dilute acid pretreatment needs a higher reaction temperature and longer reaction time. Although the required reaction time and temperature of concentrated acid pretreatment are milder than that of dilute acid pretreatment, disadvantages such as a high equipment loss rate and environmental pollution impede its competitiveness [7]. In order to achieve low-cost and green sustainable production, solid acid catalysts had been proposed and applied to the production of reducing sugars [8].

The most common used solid acid catalysts include silica solid acids [9], biopolymer-based solid acids [10], ion-exchange resin solid acids [11], zirconia solid acids [12], and hydroxyapatite solid acids [13]. Nowadays, green catalysts, which are based on the use of renewable raw materials, are getting more and more attention [14]. Hence, more environmentally and economically-friendly solid acids were proposed. Biomass-based magnetic solid acid is prepared by using lignocellulose as a carbon carrier. It was regarded as a porous solid with a large surface area. Biomass-based magnetic solid acid was widely used in a large amount of reactions, such as the separation and purification of gases, and the removal of organic pollutants from water, refrigeration, and electrochemical devices [15]. Compared to traditional heterogeneous acid catalysts, the biomass-based magnetic solid acid has the characteristics of simple preparation, better recovery, convenient material selection, and low cost. Li et al. used a corn straw biomass-based solid acid to catalyze the hydrolysis of corn straw. The results showed that the prepared catalyst exhibited high catalytic activity for the conversion of corn straw into levulinic acid, and the most favorable values of catalyst dosage, hydrolysis temperature, hydrolyzation duration, and the maximum yield of LA were 3 g, 249.66 °C, 67.3 min, and 23.17%, respectively [15].

Chen et al. prepared a series of carbonaceous solid acids from biorenewable feedstock and used them as catalysts for the direct conversion of carbohydrates into 5-ethoxymethylfurfural (EMF) [16]. The results showed that the prepared catalysts presented a porous structure, high acid density, and easy separation. An EMF yield of 63.2% could be obtained from fructose at 120 °C. Lignocellulose contains a large amount of hemicellulose. It has been reported that the yield of xylan-based activated carbon (mainly based on hemicellulose) was much lower than that of cellulose and lignin due to the instability of hemicellulose [17]. Moreover, the presence of hemicellulose decreases the specific surface area of the solid acid when the carbonized temperature was up to 400 °C, which may reduce the catalytic performance of the solid acid. Simultaneously, hemicelluloses decompose at low temperatures and produce waste gas, which lead to environmental pollution. Therefore, in order to achieve a better carbon precursor, the biomass needs to be treated with suitable pretreatment methods [18]. Dilute acid and dilute alkaline pretreatments are usually employed to destroy the complex structure of biomass. Dilute acid pretreatment can not only effectively remove hemicellulose, but can also minimize the damage of lignin and cellulose [19]. Meanwhile, dilute alkali pretreatment can effectively expand the biomass, leaving carbohydrates (cellulose and hemicelluloses) behind, thus increasing the contact area of the solid acid [20].

Bamboo is a fast-growing perennial herbaceous plant with a large phytomass, which is widely distributed in China [21]. Bamboo has many excellent properties that make it a suitable carbonized material for catalyst preparation, such as its porous structure and high thermal stability. Corncob is one of the abundant lignocellulose sources in China, and the annual global corncob production exceeds 1.03 billion metric tons, which can be used as a substrate for the production of platform products [8]. In this study, a bamboo-derived carbonaceous magnetic solid acid with a unique magnetic core–shell and high acid content was prepared by the impregnation-incomplete carbonization–sulfonation method and used as a magnetic solid acid to catalyze the hydrolysis of corncob to produce reducing sugar. The effects of dilute acid and dilute alkaline pretreatments on the catalytic performance of the as-prepared catalysts were investigated. The pretreated bamboo-derived carbonaceous support is expected with a porous structure for the introducing of –SO$_3$H, forming layers of adsorbate molecules that can interact with reactants. This process mainly comprises two steps: the preparation
of bamboo-based magnetic solid acid and the catalytic hydrolysis of corncob by solid acid to prepare reducing sugars.

2. Results and Discussion

2.1. Characterization of the Catalyst

The Fourier transform infrared (FT-IR) spectrum of bamboo-derived carbonaceous magnetic solid acid prepared by different pretreatment methods is shown in Figure 1. The peak of 1560 cm\(^{-1}\) that appeared in all the samples corresponds to the C=C stretching vibration in aromatic carbons [22]. The typical band that appeared at 585 cm\(^{-1}\) represents the Fe–O vibration in Fe\(_3\)O\(_4\), indicating that the solid acid was successfully magnetized during magnetization [23]. Moreover, strong bands such as 1041 cm\(^{-1}\) and 1380 cm\(^{-1}\) (O=S=O asymmetric) indicate that the –SO\(_3\)H group was successfully introduced into the bamboo-derived magnetic solid materials [24]. However, the strength of 1137 cm\(^{-1}\) (O=S=O symmetric stretching vibrations) was varied between solid acids prepared by different pretreatment methods. The order of the strength of the O=S=O peak at 1137 cm\(^{-1}\) was: dilute acid pretreated > dilute alkali pretreated > deionized (DI) water pretreated. The activated carbon prepared by dilute acid pretreatment was better combined with sulfuric acid, which was consistent with the subsequent catalytic hydrolysis results. In addition, a band at 3423 cm\(^{-1}\) corresponds to the O–H stretching vibration in –COOH, suggesting that phenolic –OH groups were also successfully generated to the prepared solid acid during the carbonization and sulfonation processes [25].

![Figure 1. Fourier transform infrared (FT-IR) spectrum of bamboo-derived carbonaceous magnetic solid acid.](image)

In order to understand the H\(^+\) concentration on the surface of the prepared materials, an acid/base titration test was performed, and the results are shown in Figure 2. H\(^+\) concentration on the surface of bamboo-derived carbonaceous magnetic solid acid prepared by different pretreatment methods was in the range of 0.6487 mmol/g to 2.3204 mmol/g. The acidity of the catalyst increased with the increment of acid/alkaline concentration, which may be related to the better interaction between the substrate and chemicals [18]. Compared with dilute alkali pretreatment, the acid density of the solid acids prepared by dilute acid pretreatment is higher, except at high concentration (2%). This phenomenon
was consistent with the above FT-IR results. However, the acid density of the sample prepared by 2% KOH was much higher than that of the sample prepared by 2% H$_2$SO$_4$. Furthermore, 2.3204 mmol/g of H$^+$ concentration could be obtained from the DI-pretreated samples. These results indicated that the surface of a bamboo-derived carbonaceous magnetic solid had been successfully acidified.

![Figure 1.](image1)

**Figure 1.** Fourier transform infrared (FT-IR) spectrum of bamboo-derived carbonaceous magnetic solid acid.

![Figure 2.](image2)

**Figure 2.** H$^+$ concentration of the bamboo-derived magnetic solid acid prepared by different pretreatment conditions.

During the carbonization and sulfonation processes, changes occurred in the crystallinity of the material. The XRD spectras of bamboo-derived magnetic solid acid prepared at different pretreatment conditions are shown in Figure 3. The observed sharp peaks at $2\theta$ values of 35.61°, 57°, and 62° were assigned to the (220), (311), and (440) lattice planes of Fe$_3$O$_4$ (JCPDS19-629) [22,24], which indicated that the carbon coated by Fe$_3$O$_4$ existed in the form of polycyclic aromatic hydrocarbons, and their structures were kept stable during the sulfonation process. Moreover, material prepared by 0.5% H$_2$SO$_4$ pretreated bamboo showed the strongest intensity at 35.61°, which may lead to the better catalytic performance for the reducing production of sugars. This speculation was also verified by the following catalysis experiments. Compared with the solid acid prepared by dilute alkali pretreated under the same concentration, the peak intensity of the dilute acid pretreated sample was higher, which was consistent with the results of the subsequent catalytic output. In addition, both patterns exhibited a broad and weak diffraction peak at $2\theta = 20-30^\circ$, which was due to the presence of amorphous carbon, which was composed of aromatic carbon sheets oriented in a random fashion [26].
The thermal decomposition of the prepared catalyst can be divided into three stages. The weight loss which occurred before 150 °C was mainly because of the evaporation of water adsorbed on the surface of the material [27]. The weight loss stage from 180 °C to 420 °C corresponded to the decomposition of –SO$_3$H groups [3]. The last stage that occurred above 400 °C was attributed to the further condensation of amorphous carbons [25]. About an 11% weight loss of the Fe precursor may be occurred between 180–500 °C, which may be ascribed to the decomposition and conversion reaction of the Fe species of the catalyst at high temperatures [24].

The thermal behavior of the bamboo-derived magnetic solid acid (pretreated by 0.25% H$_2$SO$_4$) was shown in Figure 4. The thermal decomposition of the prepared catalyst can be divided into three stages. The weight loss which occurred before 150 °C was mainly because of the evaporation of water adsorbed on the surface of the material [27]. The weight loss stage from 180 °C to 420 °C corresponded to the decomposition of –SO$_3$H groups [3]. The last stage that occurred above 400 °C was attributed to the further condensation of amorphous carbons [25].

The detection of chemical composition of lignocelluloses can visually verify their structure in different conditions. In order to evaluate the effects of dilute acid and alkali pretreatments on the major sugar compositions of bamboo, dewaxed bamboo was treated by dilute H$_2$SO$_4$ and KOH in various concentrations (0.25%, 0.5%, 0.75%, 1%, and 2%) in a solid ratio of 1:10 (g/mL) at 120 °C for 30 min, respectively. The major sugar components of hydrolysates and solid residues are shown in Tables 1 and 2.
Table 1. Concentrations of major sugars in bamboo hydrolysates (mg/L).

| Entry | Sample  | Xylose   | Arabinose | Glucose  |
|-------|---------|----------|-----------|----------|
| 1     | 0.25% H₂SO₄ | 1995.35  | 510.50    | 166.85   |
| 2     | 0.5% H₂SO₄  | 2157.45  | 582.70    | 243.45   |
| 3     | 0.75% H₂SO₄ | 2805.00  | 605.05    | 266.75   |
| 4     | 1% H₂SO₄    | 6278.50  | 665.25    | 417.15   |
| 5     | 2% H₂SO₄    | 8258.90  | 711.00    | 613.30   |
| 6     | 0.25% KOH   | ND       | ND        | ND       |
| 7     | 0.5% KOH    | ND       | ND        | ND       |
| 8     | 0.75% KOH   | ND       | ND        | ND       |
| 9     | 1% KOH      | ND       | ND        | ND       |
| 10    | 2% KOH      | ND       | ND        | ND       |
| 11    | DI Water    | ND       | ND        | ND       |

a ND: Undetectable.

Table 2. Major sugar composition of bamboo residues (g/g).

| Entry | Sample  | Xylose | Arabinose | Glucose |
|-------|---------|--------|-----------|---------|
| 1     | 0.25% H₂SO₄ | 9.61   | 0.058     | 38.02   |
| 2     | 0.5% H₂SO₄  | 6.08   | 0.051     | 39.93   |
| 3     | 0.75% H₂SO₄ | 5.71   | ND        | 42.05   |
| 4     | 1% H₂SO₄    | 4.17   | ND        | 44.81   |
| 5     | 2% H₂SO₄    | 4.83   | ND        | 48.31   |
| 6     | 0.25% KOH   | 9.69   | 0.69      | 40.61   |
| 7     | 0.5% KOH    | 12.14  | 0.84      | 40.55   |
| 8     | 0.75% KOH   | 11.79  | 0.88      | 43.14   |
| 9     | 1% KOH      | 14.74  | 1.15      | 50.23   |
| 10    | 2% KOH      | 12.05  | 0.74      | 51.82   |
| 11    | DI Water    | 10.93  | 0.74      | 33.94   |

a ND: Undetectable.

In the absence of a catalyst (H₂SO₄ and KOH), the dissolution of reducing sugars (xylose, arabinose, and glucose) was not observed under the investigated conditions (Table 1, entry 11). However, after dilute H₂SO₄ was added as the catalyst, the contents of reducing sugars in the hydrolysates enhanced sharply (Table 1, entries 1–5). The productions of xylose, arabinose, and glucose increased from 1995.35 mg/L to 8258.9 mg/L, 510.5 mg/L to 711.0 mg/L, and 166.85 mg/L to 613.3 mg/L with the acid concentration increased from 0.25% to 2.0%, respectively. This result indicated that about 74.74% of hemicellulose and 1.56% of cellulose could be extracted by 2.0% H₂SO₄ at 120 °C for 30 min. Therefore, the major compounds in the acid-treated bamboo residues may be cellulose and lignin. This phenomenon illustrated that a higher acid concentration benefited the dissolution of bamboo hemicellulose, especially for xylose during the pretreatment process. In addition, the hemicellulose structure of bamboo was elucidated as arabinoxylan oligosaccharides with xylose as the backbone and arabinose as the side chain [27]. Compared with xylose (16.61–68.83%), about 25.52–35.55% of arabinose was removed during dilute H₂SO₄ pretreatment, which suggested that the main chain of bamboo hemicellulose breaks faster than the side chain. However, glucose, xylose, and arabinose could not be detected in the KOH-pretreated hydrolysates (Table 1, entries 6–10), which suggested that dilute alkali pretreatment showed less power for the dissolution of hemicellulose and cellulose from bamboo than dilute acid pretreatment, which was consistent with the previous reports [2]. As shown in Table 1, xylose was the dominating sugar in the liquid fractions, and its content increased gradually as the pretreatment acid concentration increased. Moreover, it was found that arabinose was the secondary sugar constituent in the liquid fractions, and the yield of glucose was much lower than that of the former two. These results indicated that the dilute acid pretreatment mainly promotes the dissolution of hemicellulose rather than cellulose.
The hydrolyzed residues were simultaneously subjected to sugar analysis to verify the effect of pretreatments on the change of bamboo composition (Table 2). The contents of xylose and arabinose decreased gradually as the concentration of dilute acid increased (Table 2, entries 1–5), which was consistent with the results in Table 1. Moreover, a sugar composition analysis of dilute alkali-pretreated bamboo showed that the contents of major monosaccharides were kept stable in different KOH concentrations. This phenomenon suggested that cellulose and hemicellulose did not change much after the dilute alkali pretreatment. No monosaccharides could be detected in the hydrolysates after the dilute alkali and DI water pretreatments, which may be due to their further conversion into formic acid, acetic acid, furfural, etc. [17].

An FT-IR spectra of the bamboo residues obtained from dilute acid and dilute alkali pretreatments was performed to complete the study of all the samples from the experimental design (Figure 5). A band near 1733 cm$^{-1}$ was ascribed to the stretching of C=O in hemicelluloses [28]. However, the absorption of this band decreased with the increment of sulfuric acid concentration, which suggested that the hemicellulose partly dissolved during the pretreatment process. Additionally, strong bonds at 1205 cm$^{-1}$ (OH in-plane bending in cellulose I and cellulose II), 1160 cm$^{-1}$ (C–O–C stretching asymmetric), 1100 cm$^{-1}$ (glucose ring-stretching asymmetric), 898 cm$^{-1}$ (β-glycosidic linkages between glucose units in cellulose) could be observed both in dilute acid and alkali pretreated samples [27]. The strong bands at 1596 cm$^{-1}$ and 1267 cm$^{-1}$ corresponded to the aromatic skeletal vibration breathing with C=O stretching and vibration of the guaiacyl ring of lignin, respectively [16], which suggested that hemicelluloses could be removed effectively during the pretreatment process, resulting in the increment of the relative content of lignin in the bamboo residues. Therefore, the FT-IR results showed that the relative amount of the lignin and cellulose increased during the dilute acid/alkaline pretreatment process, and the change of the chemical composition of bamboo may affect the catalytic ability of the following prepared bamboo-derived carbonaceous magnetic solid acid.
2.3. Hydrolysis of Corncob with Bamboo-Derived Carbonaceous Magnetic Solid Acid

It should be noted that the pretreatment conditions had a great influence on the catalytic performance of the prepared bamboo-derived carbonaceous magnetic solid acid. In this study, experiments were executed for the catalytic hydrolysis of corncob at 120 °C for 30 min via the prepared magnetic solid acids. The main components of the hydrolysates and corncob solid residues were shown in Tables 3 and 4. The basic trend of xylose, arabinose, and glucose yields decreased when the pretreatment concentration of H$_2$SO$_4$ rose from 0.25% to 2%, which may be due to the reduction of the carbohydrates contents in the H$_2$SO$_4$-pretreated bamboo residues [29]. A higher carbohydrate content can achieve higher surface areas of specific materials during carbonization, which may be because an incomplete carbonization process is primarily the process of carbohydrates dehydrating and becoming volatile [18]. Moreover, the acidity of solid acids enhanced when prepared by a higher H$_2$SO$_4$ concentration. During the hydrolysis process, the obtained reducing sugar will be further catalyzed to form other products, such as furfural, 5-hydroxymethylfurfural, and so on [30]. However, the opposite phenomenon was observed for bamboo-derived magnetic solid acid prepared by dilute alkali pretreatment. When the KOH concentration was raised from 0.25% to 2%, the yields of xylose, arabinose, and glucose increased from 1856.2 mg/L to 2601.0 mg/L, 27.4 mg/L to 402.7 mg/L, and 672.5 mg/L to 1226.2 mg/L, respectively. This phenomenon may be because lignin was partly removed during the dilute alkali pretreatment, leaving most of the carbohydrates behind [31]. Therefore, higher reducing sugars yields could be obtained from the solid acid prepared by high concentration alkali-pretreated bamboo. In addition, solid acid prepared by authohydrolysis presented the lowest reducing sugars productivity, which may be ascribed to the weak damage strength of the bamboo structure under mild conditions. The highest reducing sugars yield of 37.17% could be obtained from bamboo-derived carbonaceous magnetic solid acid prepared by 0.25% H$_2$SO$_4$-pretreated bamboo. The prepared catalyst possessed a good catalytic performance for the conversion of hemicellulose into xylose and arabinose without further dehydration to form other products, which may be due to its moderate acidity and crystallinity.
Table 3. Effect of the pretreatment conditions on the catalytic performance of bamboo-derived magnetic solid acid (mg/L).

| Entry | Sample       | Xylose  | Arabinose | Glucose  |
|-------|--------------|---------|-----------|----------|
| 1     | 0.25% H\textsubscript{2}SO\textsubscript{4} | 4643.40 | 662.80    | 1111.30  |
| 2     | 0.5% H\textsubscript{2}SO\textsubscript{4} | 3100.05 | 492.15    | 1100.90  |
| 3     | 0.75% H\textsubscript{2}SO\textsubscript{4} | 2284.05 | 360.20    | 683.6    |
| 4     | 1% H\textsubscript{2}SO\textsubscript{4} | 3356.75 | 497.80    | 991.40   |
| 5     | 2% H\textsubscript{2}SO\textsubscript{4} | 2259.40 | 318.40    | 219.50   |
| 6     | 0.25% KOH | 1856.20 | 278.40    | 672.50   |
| 7     | 0.5% KOH | 2642.85 | 366.55    | 686.50   |
| 8     | 0.75% KOH | 2358.30 | 320.90    | 562.90   |
| 9     | 1% KOH   | 2034.75 | 302.4     | 850.80   |
| 10    | 2% KOH   | 2601.00 | 402.70    | 1226.20  |
| 11    | DI Water | 286.90  | 25.55     | 386.45   |

Reaction conditions: 1 g of corn cob, 0.2 g of bamboo-derived magnetic solid acid, 20.0 mL of DI water, 300 rpm, 120 °C and 30 min.

Table 4. Analysis of corn cob solid residue after catalysis (mg/L).

| Entry | Sample       | Xylose  | Arabinose | Glucose  |
|-------|--------------|---------|-----------|----------|
| 1     | 0.25% H\textsubscript{2}SO\textsubscript{4} | 22.35   | 0.00      | 1172.05  |
| 2     | 0.5% H\textsubscript{2}SO\textsubscript{4} | 46.30   | 0.00      | 1288.85  |
| 3     | 0.75% H\textsubscript{2}SO\textsubscript{4} | 205.85  | 0.10      | 874.35   |
| 4     | 1% H\textsubscript{2}SO\textsubscript{4}  | 39.20   | 0.00      | 1150.00  |
| 5     | 2% H\textsubscript{2}SO\textsubscript{4}  | 63.55   | 0.00      | 1193.85  |
| 6     | 0.25% KOH | 42.00   | 0.00      | 1038.50  |
| 7     | 0.5% KOH  | 44.30   | 0.00      | 1073.10  |
| 8     | 0.75% KOH | 105.30  | 0.65      | 959.90   |
| 9     | 1% KOH    | 197.15  | 0.50      | 817.05   |
| 10    | 2% KOH    | 0.00    | 0.00      | 1004.10  |
| 11    | DI Water  | 0.00    | 0.00      | 999.05   |

Determining the recyclability of a catalyst is important to evaluate its efficiency based on economic and environmental factors. The solid acids prepared in this study had the characteristic of being easily separated due to their magnetic properties. In this study, the recyclability of the prepared bamboo-derived magnetic solid acid (pretreated by 0.25% H\textsubscript{2}SO\textsubscript{4}) was performed, and the results are shown in Figure 6. After three recycle runs, the prepared catalyst remained active for the conversion of corn cob into reducing sugar. In comparison to the fresh catalyst, the yields of xylose, arabinose, and glucose decreased slightly from 4643.4 mg/L to 3902.5 mg/L, 662.8 mg/L to 455.5 mg/L, and 1111.3 mg/L to 805.4 mg/L after three recycles, respectively, which suggested that the prepared catalyst had good reusability. Compared with conventional solid acids, the biomass-based magnetic solid acid used in this study has the advantages of easy recycling, moderate acidity, and widely resourced. Moreover, it possessed good catalytic performance for the conversion of lignocellulosic raw materials into reducing sugars.
was used as the indicator. Experiments were done in triplicate, and the average value was obtained.

The X-ray diffraction (XRD) patterns of the prepared catalysts were detected in the 2θ range of 10° to 90°.

3. Materials and Methods

3.1. Materials

The bamboo used in the experiment was collected from Hunan Province, China. Prior to the experiments, the bamboo was decorticated, ground, and sieved to about 40-mesh size. The obtained particles were oven-dried at 55 °C to a constant weight. The compositional analysis (glucose, xylose, arabinose, and lignin) of the bamboo was performed according to an established National Renewable Energy Laboratory procedure [32] with a resulting composition of 49.1 wt.% glucose, 12.0 wt.% xylose, 2.0 wt.% arabinose, and 37.1 wt.% lignin.

The corncob used in this study was obtained from Shandong Province, China. Before the experiments, corncob was ground to pass through a 40-mesh screen, and then dewaxed with a 2:1 (v/v) acetone/ethanol mixture in a Soxhlet extractor (1000 mL, Synthware Glass Co. Ltd., Beijing, China) for 6 h. The dewaxed corncob was oven-dried at 60 °C to constant weight and milled for 6 h (300 rpm) with a ball-milling machine (DECO-PBM-V, Deco Co. Ltd., Hunan, China). The composition of the dewaxed corncob was 38.1 wt.% glucose, 31.9 wt.% xylose, 4.2 wt.% arabinose, and 25.8 wt.% lignin.

Chemicals FeCl₃•6H₂O (AR, ≥99.0%), H₂SO₄ (AR, ≥98.0%), ethanol (AR, ≥99.0%), phenolphthalein (AR, ≥99.0%), and NaOH (AR, ≥99.0%) were purchased from Kermel Co. Ltd. (Tianjin, China). Standard reagents, including glucose (HPLC, ≥99.0%), xylose (HPLC, ≥99.0%), arabinose (HPLC, ≥98.0%) were purchased from Shanghai Sigma-Aldrich Trading Co. Ltd. (Shanghai, China). Deionized (DI) water was used to prepare all of the solutions. All of the chemicals were used as received.

3.2. Methods

3.2.1. Catalyst Characterization

The Fourier transform infrared (FT-IR) spectrum of the prepared bamboo-derived magnetic solid acid was recorded on a spectrophotometer (Tensor 27, Bruker Optics, Karlsruhe, Germany). An acid-base titration test was performed to verify the free hydrogen ion (H⁺) concentration in the bamboo-derived magnetic solid acid. In briefly, 0.1 g of catalyst was added into 20 mL of NaCl solution (20 mmol/L), and then stirred for 24 h (100 rpm) at room temperature. Subsequently, the mixture was filtered, and a liquid fraction (5 mL) was titrated with 50 mmol/L of NaOH solution. Phenolphthalein was used as the indicator. Experiments were done in triplicate, and the average value was obtained.

The X-ray diffraction (XRD) patterns of the prepared catalysts were detected in the 2θ range of 10° to 90° on a Bruker D8 ADVANCE X-ray diffractometer (Karlsruhe, Germany) with Cu Kα radiation. The
thermostability of the samples was tested with thermogravimetric analysis (TA Q200, New Castle, DE, USA).

3.2.2. Two-Step Preparation of Bamboo-Derived Magnetic Carbonaceous Solid Acid

The hydrothermal pretreatment of bamboo was carried out in a high-pressure reactor (SLM-100, Shenlang Co. Ltd., Beijing, China). In this study, a mixture of 10 g of feedstock and 100 mL of liquid (KOH/H$_2$SO$_4$/water) was added into the reactor. The concentrations of the KOH and H$_2$SO$_4$ solution were 0.25%, 0.5%, 0.75%, 1%, and 2% respectively. A control group was performed using DI water to compare with dilute acid and alkali pretreatments. The pretreatment time, temperature, and the agitation rate were 120 °C, 30 min, and 300 rpm, respectively. Once the reaction finished, flowing water was used to cool the reactor quickly. After that, the mixture was separated by filtration. Solid residue was washed with DI water several times and dried at 60 °C overnight for the following preparation of bamboo-derived magnetic solid acid. The liquid products were determined by high-performance liquid chromatography (HPLC, Waters 2414, America) coupled with a refractive index detector (RID) and a Bio-rad Aminex HPX-87H (300 × 7.8 mm) column. Five mM of H$_2$SO$_4$ was employed as the eluent with a flow rate of 0.5 mL/min at 60 °C.

Five g of pretreated residue was dispersed in 500 mL of the FeCl$_3$ •6H$_2$O solution (10 mmol/L), and then stirred at room temperature (150 rpm) for 5 h. After impregnation, bamboo was carbonized at 500 °C for 1 h under nitrogen atmosphere to produce the bamboo carbon. The bamboo-derived carbon was mixed with a concentrated sulfuric acid at a ratio of 1:10 (g/mL) and sonicated for 15 min. Subsequently, the mixture was heated under vigorous at 90 °C for 10 h to introduce the sulfo-group (–SO$_3$H) to the surface of the bamboo-derived magnetic solid precursor. After the reaction, the mixture was diluted with DI water and dried in a vacuum oven at 80 °C for 12 h.

3.2.3. Hydrolysis of Corncob by Bamboo-Derived Magnetic Solid Acid

One g of ball-milled corncob, 0.2 g of bamboo-derived magnetic solid acid, and 20 mL of DI water were mixed first and ultrasonicated for 30 min, and then added into the reactor. The reaction time, temperature, and the agitation was 120 °C, 30 min, and 300 rpm, respectively. At the same time, a catalyst-free reaction including 1 g of ball-milled corncob and 20 mL of DI water was also conducted at the same reaction conditions. After the reaction, the product was filtered with a 0.22-µm syringe. Liquid fractions were stored in the fridge prior to HPLC analysis, as mentioned above. Solid residues were washed with DI water several times and oven-dried at 60 °C to a constant weight.

3.2.4. Recyclability of Catalyst

After reaction, the bamboo-derived magnetic solid acid catalyst was separated by a magnet. The obtained catalyst was washed with DI water and oven-dried at 70 °C for 6 h for the next catalytic run.

4. Conclusions

The conversion of corncob into reducing sugars was achieved using bamboo-derived carbonaceous magnetic solid acid as the catalyst. The prepared catalysts contained –SO$_3$H, –COOH, and polycyclic aromatic, and the number of H$^+$ sites was from 0.6487 mmol/g to 2.3204 mmol/g. Comparing with the catalysts prepared by dilute alkali and DI water pretreatments, bamboo-derived carbonaceous magnetic solid acid prepared by dilute acid-pretreated bamboo showed better catalytic activity for the production of reducing sugars. The highest reducing sugars yield of 37.17% could be obtained using 0.25% of H$_2$SO$_4$-pretreated bamboo-derived carbonaceous solid acid as catalyst at 120 °C for 30 min.

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