



Short Communication

Production of 5-hydroxymethylfurfural from corn stalk catalyzed by corn stalk-derived carbonaceous solid acid catalyst



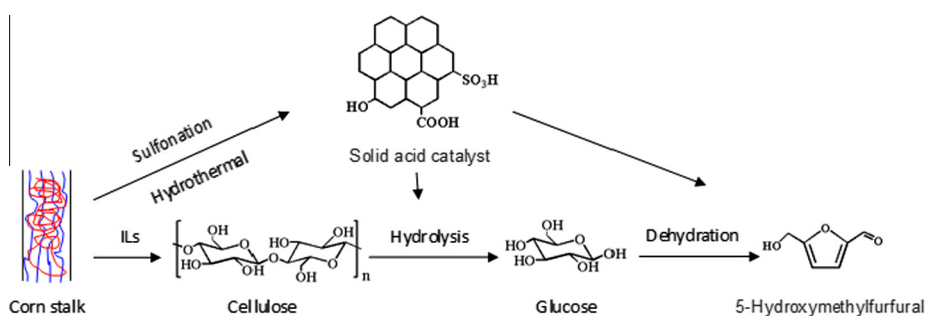
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HIGHLIGHTS

- Carbonaceous material was prepared from hydrothermal carbonization of corn stalk.
- The solid acid catalyst is efficient for the production of 5-HMF from corn stalk.
- A 5-HMF yield of 44.1% could be achieved at 150 °C in 30 min reaction time.
- A green and efficient strategy for crude biomass utilization is developed.

GRAPHICAL ABSTRACT



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ABSTRACT

A carbonaceous solid acid was prepared by hydrothermal carbonization of corn stalk followed by sulfonation and was characterized by FT-IR, XRD, SEM and elemental analysis techniques. The as-prepared corn stalk-derived carbonaceous solid acid catalyst contained $-\text{SO}_3\text{H}$, $-\text{COOH}$, and phenolic $-\text{OH}$ groups, and was used for the one-step conversion of intact corn stalk to 5-hydroxymethylfurfural (5-HMF) in the ionic liquid 1-butyl-3-methyl imidazolium chloride ([BMIM][Cl]), where a 5-HMF yield of 44.1% was achieved at 150 °C in 30 min reaction time. The catalytic system was applicable to initial corn stalk concentration of up to ca. 10 wt.% for the production of 5-HMF. The synthesized catalyst and the developed process of using corn stalk-derived carbon catalyst for corn stalk conversion provide a green and efficient strategy for crude biomass utilization.

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1. Introduction

With growing concerns on environmental issues and energy crisis, biomass resources have attracted much attention as a renewable source of fuels and chemicals (van Putten et al., 2013). Among the possible biomass-derived chemicals, 5-hydroxymethylfurfural (5-HMF), an acid-catalyzed dehydration product of hexose, is one of the versatile platform chemicals that has an important role in the production of biofuel and other chemicals, such as

2,5-bis (hydroxymethyl)-furan (BHF), 2,5-dimethylfuran (DMF) (Hu et al., 2014) and levulinic acid (LA) (Ya'aini et al., 2013).

In the past few years, intensive efforts have been conducted on the production of 5-HMF from biomass (van Putten et al., 2013). Generally, fructose could be efficiently converted to 5-HMF by acid-catalyzed dehydration with excellent yields above 70% (Chinnappan et al., 2014; Qu et al., 2012). Unfortunately, the high cost of fructose restricted its large-scale application. Therefore, recently many researchers have turned their attentions to glucose and cellulose as the starting material (Hu et al., 2013; Jimenez-Morales et al., 2014; van Putten et al., 2013), which is the most abundant monosaccharide and polysaccharide in nature, respectively. A pioneering work was carried out by Zhao et al. (2007)

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who studied the conversion of glucose into 5-HMF in an ionic liquid 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) using CrCl_2 as catalyst, and obtained a 5-HMF yield of nearly 70% from glucose. Inspired by this work, many efforts have been devoted to the transformation of glucose or cellulose into 5-HMF. For example, Liu et al. (2013a) investigated the direct conversion of cellulose into 5-HMF under microwave irradiation in ionic liquids catalyzed by ZrCl_4 , and an optimal 5-HMF yield of 51.4% was obtained from cellulose in 3.5 min under MI at 400 W.

Although the production of 5-HMF from the model compounds such as fructose, glucose, sucrose and cellulose have been broadly studied in a variety of efficient catalytic processes, the direct preparation of 5-HMF from inedible crude lignocellulosic biomass such as wood, rice straw or corn stalk would be preferable. It still remains a challenge and more works are needed to convert the intact lignocellulosic biomass into 5-HMF from a practical perspective.

In this work, a carbonaceous material bearing $-\text{SO}_3\text{H}$, $-\text{COOH}$ and phenolic $-\text{OH}$ groups was prepared by hydrothermal carbonization of corn stalk followed by sulfonation with concentrated H_2SO_4 , and then it was used as solid acid catalyst in the one step production of 5-HMF from corn stalk as starting material in ionic liquid 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]). This work may provide a promising strategy for the comprehensive utilization of crude lignocellulosic biomass.

2. Methods

2.1. Materials

Sulfuric acid (99%), ethyl acetate and ethanol were purchased from Jiangtian Chemical Technology Co., Ltd. (Tianjin). Ionic liquid 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]) (99%) was purchased from Henan Lihua Pharmaceutical Co., Ltd. (Xinxiang), and 5-hydroxymethylfurfural (98%) was purchased from the Acros Organics company (Geel). All chemicals were used as received without further purification. Corn stalk was local material (Tianjin, North China) that was milled to pass 180 mesh, and dried at 105 °C for 24 h before use.

2.2. Preparation of carbonaceous solid acid catalyst from corn stalk

The corn stalk-derived solid acid catalyst was prepared by hydrothermal treatment of corn stalk followed by sulfonation according to the following procedure. Typically, 10 g corn stalk (CS) with 50 mL deionized water was loaded into a 100-mL stainless steel autoclave with Teflon container. Then, the autoclave was sealed and heated to 250 °C, and kept for 4 h at the autogenous pressure (ca. 3.9 MPa). After cooling the autoclave to room temperature, the precipitate was centrifuged, collected and washed repeatedly with distilled water and ethanol for several times. The obtained solid (denoted as HCS) was dried at 80 °C for 12 h and ground into powder. Then, 10 g of HCS material was heated in a concentrated sulfuric acid (100 mL) at 200 °C for 10 h under a nitrogen atmosphere. After cooling to room temperature, the black precipitate was washed with deionized water until no sulfate ions could be detected in the leachate. The obtained black sample was dried at 80 °C for 12 h and ground into powder, which is denoted as HCSS.

2.3. Catalyst characterization

The obtained samples were characterized by SEM (JSM-7500F, JEOL), FT-IR (MAGNA-560, NICOLET), X-ray diffraction (XRD,

D/max-2500, RIGAKG), elemental analysis (Vario EL cube, Elementar) and ICP (ICP-9000, Thermo Jarrell-Ash Corp., USA).

2.4. Typical experimental procedure for production of 5-HMF from corn stalk

In a typical reaction, 0.05 g corn stalk was dissolved in 1 g of [BMIM][Cl] and then 0.05 g catalyst was added. The reaction mixture was heated at 150 °C for a given reaction time in an oil bath. After the desired reaction time elapsed, the reactor was cooled to room temperature with cold water bath and 1 mL deionized water was added to the reactor. The 5-HMF product was extracted from the reaction mixture with ethyl acetate and analyzed with a Cary-50 Model spectrophotometer (Varian Inc.) at 284 nm using standard curve method. All results were replicated at least 3 times and average values were adopted. Reproducibility of the 5-HMF yield was within 5% in standard deviation. The yield of 5-HMF was calculated on the basis of a cellulose content of 36% in the corn stalk and as defined below:

$$\text{5-HMF yield (mol\%)} = \frac{\text{5-HMF concentration in product}}{\text{Hexose concentration in the loaded sample}} \times 100\% \quad (1)$$

3. Results and discussion

3.1. Characterization of the catalyst

Fig. S1 shows the XRD patterns of the raw corn stalk (CS) and the obtained carbonaceous material from the hydrothermal carbonization of corn stalk following with sulfonation (HCSS). It can be seen that the XRD pattern of the untreated corn stalk exhibited two characteristic diffraction peaks of crystalline cellulose at 2θ angle of around 16° and 22° (Zhang et al., 2013). By contrast, XRD pattern for HCSS sample exhibited one strong diffraction peak at 2θ angle of around 23° and one broad, but weak peak at around 43°, which are typical diffraction peaks for amorphous carbon that consist of aromatic carbon sheets oriented in a considerably random fashion (Nakajima and Hara, 2012). It indicates that the crystalline structure of cellulose in the raw corn stalk was destroyed and underwent significant changes by the hydrothermal and sulfonation treatment.

SEM images of CS, HCS and HCSS are given in Fig. S2. It can be seen that the raw corn stalk mainly consisted of rod-shaped fibers and large size particles. The obtained solid material (HCS) from the hydrothermal carbonization of CS exhibited a decrease in size for the particles and rod-shape fibers, and some carbonaceous microspheres could be found. When the HCS sample was further treated by sulfonation, the obtained carbonaceous material (HCSS) exhibited irregular morphology.

The chemical composition of the CS, HCS and HCSS samples was analyzed, and the results are listed in Table 1. The sample HCS showed a carbon content of 70.3%, which is much higher than that in the raw corn stalk (43.3%). The increase of carbon content in the HCS was mainly ascribed to the deoxygenating reactions such as dehydration and decarboxylation occurred during the hydrothermal reaction (Kang et al., 2012). After the HCS material was heat

Table 1
Elemental compositions of the CS, HCS and HCSS samples.

Sample	C (wt.%)	H (wt.%)	N (wt.%)	S (wt.%)
CS	43.3	6.22	0.48	0.04
HCS	70.3	6.20	1.72	0.04
HCSS	56.9	2.51	0.87	0.87

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