A Lignin-Derived Carbonaceous Acid for Efficient Catalytic Hydrolysis of Cellulose

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ABSTRACT

A solid acid catalyst was prepared from masson pine alkali lignin in waste liquor of soda pulping by a combined process of chemical activation, carbonization, and sulfonation. The lignin-derived solid acid (LDSA) was characterized by FESEM, XRD, FTIR, TGA, XPS, BET analyses, and acid-base back titration. The carbonaceous material had high thermal stability and large specific surface area (488.4 m²/g), and the structural analyses showed that it was composed of amorphous carbon bearing -SO3H, -COOH, and phenolic -OH groups. The lignin-derived catalyst was then applied to the hydrolysis of a microcrystalline cellulose (MCC) in aqueous system, and the yield of total reducing sugars was found to be 46.1%. It was proposed that good adsorption capacities of cellulose and desorption property of glucose on LDSA probably contributed to efficient catalytic hydrolysis.

Keywords: Lignin; Cellulose; Carbon-based solid acid; Catalysis; Hydrolysis

1. INTRODUCTION

Cellulose is the most abundant component of natural lignocellulosics. The effective hydrolysis of cellulose into glucose is crucial to the conversion of renewable lignocellulosic biomass into value-added biochemicals and biofuels. As is known, the utilization of catalysts plays a vital role in the energy-and cost-efficient hydrolysis of cellulose. Compared with conventional homogenous acidic catalysts and biological enzymes, the heterogeneous solid acid catalyst possesses a number of advantages such as being less expensive, easier to be recycled, and having a comparable catalytic activity.

Global researchers have been focusing on producing carbon-based solid acid catalysts for replacing traditional catalyst systems during the process of cellulose hydrolysis. Due to the high-crystalline structure of cellulose and its insolubility in water and most organic liquids, the yield of total reducing sugars (TRS) can be significantly enhanced via cellulose solvation in an immobilized acidic ionic liquid, or using bifunctional strategy for structural design of catalysts bearing cellulose-binding sites (-Cl, phenolic -OH and – COOH groups) and catalytic active sites (-SO3H group). All of these developments have contributed to an increase in catalytic performance through decreasing cellulose crystallinity and improving solid-solid interaction. Lignin is, second to cellulose, the most abundant, environmentally friendly and renewable natural biopolymer. In China, a large amount of lignin can be separated from black liquor discharged without reutilization during pulp production process. Actually, owing to its high carbon content and abundant aromatics possessing -COOH, -OH and phenolic -OH groups, lignin is considered as a good precursor for activated carbon. Thus, alkali lignin from black liquor could be a better carbon source (e.g., at a lower cost) for the preparation of carbonaceous acid, in comparison with other carbon precursors such as active carbon, glucose, and grapheme oxide. However, to the best of our knowledge, there is little information available in literature concerning the preparation of lignin-derived solid acid (LDSA) that can facilitate cellulose hydrolysis in aqueous medium.

In this study, we synthesized a LDSA from alkali lignin in black liquor of soda pulping by a combined process of chemical activation with phosphoric acid, carbonization in nitrogen atmosphere, and sulfonation in concentrated sulfuric acid. The solid acid was characterized by FESEM, XRD, FTIR, TGA, XPS, BET analyses, and acid-base back titration. Its catalytic performance was evaluated in terms of the hydrolysis of microcrystalline cellulose (MCC) in H₂O system. In addition, the possible catalytic mechanism of LDSA was also discussed by comparing with other solid acid catalysts.

2. EXPERIMENTAL

2.1 Materials

Masson pine alkali lignin (MAL), supplied by Nanping paper-making Co., Ltd (Fujian Province, China), was separated and purified from masson pine pulping black liquor by acidic treatment. MCC with a mean particle size of 25 μm was purchased from Aladdin Chemistry Co., Ltd (Shanghai, China). Nitrogen gas (99.9% of purity) was purchased from Chenggong Gas Co. Ltd (Xiamen, China). Amberlyst-15 was purchased from Aladdin Chemistry Co. Ltd (Shanghai, China). Cellobiose, glucose, sodium hydroxide, concentrated sulfuric acid...
(98%), and phosphoric acid were of analytical grade and obtained from Aladdin Chemistry Co. Ltd (Shanghai, China). All other reagents were of analytical-reagent grade and used without further purification. Dinitrosalicylic acid (DNS) reagent was prepared according to Wu et al.\textsuperscript{12}

### 2.2 Synthesis of lignin-derived solid acid

MAL was mixed with a 40% phosphoric acid solution at the phosphoric acid-to-lignin mass ratio of 1.5:1. The mixture was transferred into a tube furnace in which carbonization was carried out at a heating rate of 3 °C/min and a constant nitrogen flow of 75 mL/min for 90 min at 450 °C. Upon cooling down to room temperature, the carbonized mixture was washed several times with hot deionized water to a pH of 7. Then, the sample was dried at 105 ºC in an oven for 12 h to obtain the lignin-derived carbonaceous material (LDCM). Subsequently, the LDCM was sulfonated in concentrated sulfuric acid (m/v, 1 g/20 ml) at 180 ºC for 12 h. Finally, the slurry was repeatedly washed several times with hot deionized water (80 ºC) until no sulfate ion (SO₄²⁻) in the filtrate was detectable by barium sulfate gravimetric method, and then dried at 80 ºC overnight to obtain the LDSA sample. All experiments were repeated twice.

### 2.3 Characterization

TGA analysis of MAL and MAL activated by phosphorylation (MAP) using Thermal Gravimetric Analyzer (DTG-60H, Shimadzu, Japan) was performed at 30-800 ºC under N₂, atmosphere, at a heating rate of 10 °C/ min. FTIR analyses was conducted by sampling of KBr-based pellets, spectra were collected with a spectrophotometer (Nicolet iS50 Microscope, Thermo Fisher Scientific, USA) in a wavenumber range of 4000 to 400 cm⁻¹, with 32 scans for each sample. X-ray diffraction analysis was performed on a scanning X-ray microprobe using monochromatic Al Kα radiation source (E=1486.6 eV), with a scanning speed of 4 °/min. XPS analysis was performed on a scanning X-ray microprobe using monochromatic Al Kα radiation source (E=1486.6 eV), while high-resolution scans of the O 1s, C 1s and S 2p regions were acquired with a pass energy of 20 eV. The loading amounts (mmol/g) of -SO₃H group (C\textsubscript{S0D}), -COOH group, and Phenolic -OH group (C\textsubscript{COOH}+\textsubscript{-OH}) in the catalysts were determined by following the previously reported acid-base back titration method, with tailored modifications in terms of procedures.\textsuperscript{13}

### 2.4 Hydrolysis of MCC and determination of TRS yield

The hydrolysis of cellulose was carried out in a 25 mL teflon-lined stainless steel reactor. 0.025 g of cellulose, 0.1 g of LDSA, 5 mL of deionized water were loaded into the PTFE lining and shaken (200 rpm) for 5 min. Subsequently, the mixture was heated to 180 ºC for 4 h in the sealed container under self-generated pressure. Upon completion of the reaction, the reactor was placed into a mixture of ice and water to cool down to room temperature. The suspension was then filtered using a 0.22 μm filter membrane, and the TRS yield in filtrate was determined using DNS colorimetry.\textsuperscript{14} All experiments were repeated three times.

### 2.5 Determination of saccharide adsorption on catalyst

0.1 g of LDSA was added into a 10 mL of cellubiose or glucose solution, and the mixture was oscillated at room temperature. The supernatant was then determined by following the DNS method to calculate the adsorption capacity. Amberlyst-15 was treated in the same manner to investigate its adsorptive behavior toward cellubiose or glucose. Each reported number (average value) of adsorption was based on three parallel experiments.

### 3 RESULTS AND DISCUSSION

#### 3.1 Characterization

TGA profiles of MAL and MAP are shown in Figure 1. For MAL and MAP, three stages of weight loss can be seen. For MAL (Figure 1(a)), the first stage pertains to a temperature of 150 ºC, and the weight loss was around 8%, which is caused by the evaporation of adsorbed water. The second stage a with weight loss of 67.5% occurred at 150-600 ºC which is probably due to the losses of volatiles and tar. However, it was found that the stage of weight loss of MAP was in advance in comparison with that of MAL. As shown in Figure 1(b), there are significantly different peak reductions at 101.01 ºC and 178.22 ºC, respectively. The weight loss of MAP is obviously higher than that of MAL. It is possible that the dehydration of phosphoric acid exacerbates the dehydration and volatilization of low boiling volatile matters, thus leading to the phosphorylation of alkali lignin and an increase in its crosslinking reaction as well as the formation of micropore structure. Meanwhile, the weight loss of MAP is lower than that of MAL within 250-600 ºC, and the maximum weight loss occurs at 305.2 ºC, which might be attributed to carbonization and aromatic structure, thus effectively inhibiting the continuous pyrolysis of alkali lignin and generating more aromatic compounds via incomplete carbonization of MAL.\textsuperscript{15} It is proposed that the activation process pertaining to the use of phosphoric acid plays an important role in the improvement of pyrolysis characteristics of MAL.
Figure 2 shows the XRD patterns of LDCM and LDSA. The patterns exhibit two weak and broad diffraction peaks in the 2θ range of 15–30° and 35-50° attributed to amorphous carbon (002) and (004), which represents aromatic carbon sheets oriented at random\textsuperscript{16}. The lower and wider these peaks are, the higher degree of amorphous aromatic carbon sheets are. Furthermore, compared with LDCM, the diffraction peak of LDSA has a slight right-shift, which confirms the introduction of -SO\textsubscript{3}H group into LDCM via sulfonation.

The FESEM image of LDSA is shown in Figure 3. As can be seen, the catalyst was composed of irregular particles with a size of several nanometers, and their aggregates had a relatively rough and fluffy surface. Moreover, using BET method, the surface area of LDSA was estimated to be 488.4 m\textsuperscript{2}/g, and its pore diameter was 2.3 nm (BJH method) (Figure 4). These results are consistent with the FESEM image.
In the FTIR spectrum of LDSA (Figure 5), the broad absorption band at 3400 cm−1 is attributed to O‒H stretching vibration. The vibration bands at 1030 cm−1 and 598 cm−1 are assigned to O=S=O stretching mode and C=S stretching mode in -SO3H groups, respectively. The results indicated that -SO3H groups were introduced successfully into LDCM during sulfonation process. Additionally, the band at 1701 cm−1 pertains to the stretching vibration of C=O in -COOH groups. Moreover, the XPS spectra of LDSA exhibited the peak of S 2p with binding energy of 168.2 eV due to -SO3H groups (Figure 6(a)) and the peak of C 1s spectrum with binding energy of 288.6 eV assigned to -COOH groups (Figure 6(b)). The results further confirmed the existence of -COOH and -SO3H groups in LDSA.

3.2 Catalytic mechanism

The hydrolysis of cellulose in water was investigated using LDSA as catalyst, and the result pertaining to the comparison of catalytic performances is shown in Table 1. As can be seen in Table 1, the TRS yield (46.1%) of the carbonaceous acid prepared in this work was obviously larger than that of other typical solid acids reported in literature, and TRS was undetectable when using Amberlyst-15 as the catalyst in this work, demonstrating the highly-efficient catalytic performance of LDSA for the hydrolysis of cellulose in water. Moreover, as shown in Table 1, although BC-SO3H-1 had a much higher acidity density (5.54 mmol/g) than other solid acids, its lower yield of TRS was mainly due to its very small specific surface area (<5.0 m²/g). Meanwhile, although AC-SO3H had a much larger specific surface area (941.0 m²/g) than LDSA (488.4 m²/g), its lower acidity density (1.63 mmol/g) led to a lower TRS yield of 43.0% than LDSA (46.1%). Therefore, LDSA with a large BET surface area (488.4 m²/g) contained a high density of phenolic –OH and –COOH groups (2.64 mmol/g) as well as a certain amount of –SO3H groups (0.88 mmol/g), which probably largely contributed to its comparable catalytic activity for the conversion of cellulose into TRS.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>S_{BET} (m²/g)</th>
<th>C_{SO3H} (mmol/g)</th>
<th>C_{COOH+–OH} (mmol/g)</th>
<th>TRS yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC-SO3H-1</td>
<td>&lt;5.0</td>
<td>1.98</td>
<td>3.56</td>
<td>19.8</td>
</tr>
<tr>
<td>Fe₃O₄-SBA-SO3H</td>
<td>464.0</td>
<td>0.60</td>
<td>0.49</td>
<td>26.0</td>
</tr>
<tr>
<td>AC-SO3H</td>
<td>941.0</td>
<td>0.44</td>
<td>1.19</td>
<td>43.0</td>
</tr>
<tr>
<td>Amberlyst-15</td>
<td>38.0</td>
<td>4.50</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>LDSA</td>
<td>488.4</td>
<td>0.88</td>
<td>2.64</td>
<td>46.1</td>
</tr>
</tbody>
</table>
It is widely believed that improving the solid-solid contact area between cellulose and catalyst is crucial to the efficient hydrolysis of cellulose. Increase in adsorption capacity of cellulose on catalyst would be beneficial to its catalytic performance. Catalysts with cellulose binding sites are thought to be superior at adsorbing cellobiose which is often used for the modeling of cellulose hydrolysis. Since -COOH and -OH groups are considered as strong hydrogen bond acceptors that can destroy hydrogen bonds between the hydroxyl groups of cellulose structure. Compared with other solid acid catalysts, LDSA had a high content of oxygen functional groups. To further clarify the catalytic mechanism, the adsorption of cellobiose and glucose on LDSA were investigated.

As shown in Figure 7, the adsorption capacity of cellobiose on LDSA was compared with that on Amberlyst-15, and results indicated that the former (12.97%) is much larger than the latter (2.80%), highlighting the reasonable mechanism for the higher TRS yield using LDSA as catalyst in cellulose hydrolysis. Furthermore, as indicated by the results shown in Figure 7, LDSA also had a positive effect on the desorption property of glucose. It was proposed that the stronger electrophilicity of -COOH and phenolic -OH groups in comparison to -SO3H group probably resulted in a better adsorption capacity of cellulose on solid acid surface.

4 CONCLUSIONS

A low cost, green, porous, and carbonaceous solid acid was developed through chemical activation, carbonization and sulfonation of alkali lignin. This solid acid exhibited higher efficiency for the hydrolysis of microcrystalline cellulose, as compared with other previously reported solid acids. The maximum TRS yield of 46.1% was achieved. In addition, both the large specific surface area of 488.4 m²/g and the high density of acidity including phenolic –OH and –COOH groups (2.64 mmol/g) and –SO₃H group (0.88 mmol/g) were mainly responsible for the comparable catalytic performance of lignin-derived solid acid. Production of lignin-derived solid acids from biomass solid waste could not only offer a feasible way for the high-value utilization of lignin, but also reduce the cost of catalysts as well as the environmental pollution. This approach would provide a promising strategy for the hydrolysis of cellulose-rich biomass.

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