Supporting Information

Effective saccharification of lignocellulosic biomass over hydrolysis residue derived solid acid under microwave irradiation

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Figure S1. SEM of CSA derived from corncob hydrolyzed residue.

Figure S2. HPLC analysis of corncob hydrolyzed solution.
Figure S3. XRD patterns of cellulose and corncob.

Figure S4. FT-IR of the CSA reintroduced -SO$_3$H groups.
Figure S5. Adsorption of cellobiose on the surface of CSA, Amberlyst-15, and H-ZSM-5.

Adsorption condition: 1.5g catalyst was mixed with 30 mL cellobiose solution (510 ppm, and then stirred at about 350 r/min at room temperature. CAS (particle size, 5-30 um); ground Amberlyst-15 (particle size, 10-50 um); H-ZSM-5 (particle size, about 5um). Silica-alumina and H-beta showed almost no adsorption.

Figure S6. Filter papers (cellulose >99%) after soaking in solid acid-water suspensions (solid acid, 0.3g, water 2 mL) at room temperature. CAS (particle size, 5-30 um); ground Amberlyst-15 (particle size, 10-50 um).

After soaking the filter paper in a solid acid-water suspension for 10 min, the filter paper with solid acid particles was rinsed several times in 100 mL of distilled water in an ultrasonic bath (100 W) for 15 min. The CSA can adsorb tightly on the surface of filter paper and can be observed visually. The ground Amberlyst-15 particles (gray color) can not be visually observed to adsorb on the filter paper surface.
Figure S7. Corncob (the raw material used in this research) after soaking in solid acid-water suspensions (solid acid, 0.3g, water 2 mL) at room temperature.

After soaking the corncob in a solid acid-water suspension for 10 min, the corncob with solid acid particles was rinsed several times in 100 mL of distilled water in an ultrasonic bath (100 W) for 15 min. The CSA can also adsorb tightly on the surface of corncob and can be observed visually. The ground Amberlyst-15 particles (gray color) can not be visually observed to adsorb on the corncob surface.
Figure S8. Temperature programme desorption of: a. Corncob hydrolysis residue without NH₃ adsorption; b. CSA without NH₃ adsorption; c. CSA-D; d. CSA-R1 e. As prepared CSA.

Reaction condition: The sample was prepared at 373 K for 1 h in flowing argon. After that, the sample was cooled to 323 K and saturated with ammonia. Then the program was carried out from 323 to 1173 K at a rate of 10 K/min. The desorbed ammonia was monitored continuously with a gas chromatograph equipped with a TCD detector.

It is found the distribution of acid sites (desorption temperatures) is different between the CSA-D (c) and as-prepared CSA (e), the surface acid sites can be resumed by reintroduction of SO₃H groups (CSA-R1, d).

Figure S9. FT-IR spectra of different samples. a. the spectrum between 700-4000 cm⁻¹; b. comparison spectra of the different samples at about 1035 cm⁻¹ (vibration of SO₃H).

The vibration of SO₃H of CSA-D is different from as-synthesized CSA and CSA+corncob hydrolysis residue, which indicated that after hydrolysis, acid sites of...
the CSA had been modified during the reaction. The results agreed with that of NH$_3$-TPD.

**Table S1.** The additional results of corncob hydrolysis.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample</th>
<th>GY (%)</th>
<th>XY (%)</th>
<th>AY (%)</th>
<th>TSY (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Traditional heating$^a$</td>
<td>8.9</td>
<td>31.4</td>
<td>51.2</td>
<td>20.6</td>
</tr>
<tr>
<td>2</td>
<td>Microwave irradiation$^b$</td>
<td>34.6</td>
<td>77.3</td>
<td>85.2</td>
<td>55.1</td>
</tr>
<tr>
<td>3</td>
<td>Silica-alumina (Si/Al=4.9)$^c$</td>
<td>14.9</td>
<td>28.3</td>
<td>76.1</td>
<td>23.8</td>
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<tr>
<td>4</td>
<td>H-beta(Si/Al=13)$^c$</td>
<td>18.5</td>
<td>65.1</td>
<td>92.1</td>
<td>41.8</td>
</tr>
<tr>
<td>5</td>
<td>H-ZSM-5(Si/Al=38)$^c$</td>
<td>17.3</td>
<td>71.2</td>
<td>85.3</td>
<td>43.4</td>
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<tr>
<td>6</td>
<td>Amberlyst-15$^c$</td>
<td>23.3</td>
<td>75.4</td>
<td>77.6</td>
<td>47.8</td>
</tr>
</tbody>
</table>

Reaction condition: $^a$ CSA 0.2g, corncob 0.2g, 2 mL H$_2$O, 403 K, heated by oil bath for 60 min; $^b$ CSA 0.2g, corncob 0.2g, 2 mL H$_2$O, 403 K, heated by microwave irradiation for 60 min; $^c$ catalyst 0.2g, corncob 0.2g, 2 mL H$_2$O, 403 K, heated by microwave irradiation for 60 min.