Catalytic upgrading of biomass fast pyrolysis vapors using ordered mesoporous ZrO$_2$, TiO$_2$ and SiO$_2$

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Abstract

Ordered mesoporous ZrO$_2$, TiO$_2$ and SiO$_2$ (SBA-15) were prepared and employed for catalytic cracking of biomass fast pyrolysis vapors using the analytical pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) technique. The three catalysts displayed different catalytic capabilities, and the ordered mesoporous ZrO$_2$ was the best catalyst to alter the distribution of the pyrolytic products, so as to improve the fuel properties of the products. It was effective to convert the lignin-derived oligomers to monomeric phenolic compounds. Moreover, it was capable to decrease the anhydrosugars, linear aldehydes and linear acids, and meanwhile, increase the linear ketones, hydrocarbons and cyclopentanones. The ordered mesoporous TiO$_2$ was also able to improve the fuel properties of the pyrolytic products, while the SBA-15 was not so promising.

Keywords: biomass; fast pyrolysis; catalytic cracking; ordered mesoporous catalyst; analytical Py-GC/MS

1. Introduction

Liquid bio-oil from fast pyrolysis of biomass is a low-grade liquid fuel containing many undesirable compounds, including water, acids, aldehydes and large molecular oligomers. In-situ catalytic cracking of biomass fast pyrolysis vapors is a promising way to upgrade bio-oil, and the key problem is the selection of proper catalyst. Traditional microporous catalysts, such as zeolites, are unable to convert large molecular compounds (mainly lignin-derived oligomers), and thus, will be deactivated quickly. Recently, ordered mesoporous catalysts, such as SBA-15, MCM-41 and MSU, have attracted some interest for their potential to convert large molecules. However, these materials are pure silica, lack of catalytic activity, and should be treated to create active sites by incorporation of proper metals. In this study, two ordered
non-silica mesoporous catalysts, TiO$_2$ and ZrO$_2$, were prepared for catalytic upgrading of biomass fast pyrolysis vapors, and their catalytic effects were compared with an order mesoporous silica of SBA-15.

2. Experimental

Poplar wood particles with the size of 0.2-0.3 mm were dried and used as the feedstock in this study. Its chemical composition was 49.8% cellulose, 24.4% hemicellulose, 23.3% lignin, 2.2% extractive and 0.3% ash. Its elemental composition on the dry basis was 49.58% C, 6.33% H, 0.08% N and 0.09% S.

The ordered mesoporous SBA-15, TiO$_2$ and ZrO$_2$ were prepared according to previous studies [1-3]. They were characterized by the X-ray diffraction (XRD) analysis and nitrogen adsorption/desorption isotherms measurement.

Analytical Py-GC/MS experiments were performed with the CDS Pyroprobe 5200HP pyrolyser connected with the Perkin Elmer GC/MS (Clarus 560). To prepare experimental samples, 0.50 mg poplar wood was placed in the middle of the quartz tube, and certain amount of catalyst was placed at both sides of the poplar wood (0.20 mg, 0.30 mg, 0.40 mg or 0.50 mg at each side). The analytical pyrolysis was conducted at 500 °C for 20 s with the heating rate of 20 °C/ms. The pyrolysis vapors were directly analyzed by the GC/MS. The experimental details can be found in our previous study [4]. For each sample, the experiments were conducted at least three times. The peak area and peak area% of each pyrolytic product were recorded, and the average and standard deviation values were calculated and used for discussion. For each product, its yield changing can be determined via comparison of its average peak area values obtained under different conditions, and its content changing (the content among the detected products) can be determined via comparison of its average peak area% values.

3. Results and discussion

3.1. Catalyst characterization

The N$_2$ adsorption-desorption isotherms, small-angle and wide-angle XRD patterns of the ordered mesoporous SBA-15, ZrO$_2$ and TiO$_2$ are shown in Fig.1. The isotherms of three catalysts exhibited typical irreversible type IV adsorption isotherms with a H1 hysteresis loop, and the small-angle XRD patterns exhibited typical diffraction peaks matched well the literature data [1-3], which confirmed the ordered mesoporous structure of the three catalysts. According to the wide-angle XRD patterns, the SBA-15 only showed a broad diffuse peak of the amorphous SiO$_2$, while the TiO$_2$ and ZrO$_2$ were crystallized into anatase phase and tetragonal phase, respectively.

![Fig. 1. (a) N$_2$ adsorption-desorption isotherms; (b) Small-angle XRD patterns; (c) Wide-angle XRD patterns](image_url)

3.2. Comparison of the catalytic effects of the three catalysts
Analytical Py-GC/MS experiments did not allow product collection, and thus, could not quantitatively determine the pyrolytic products. However, it is able to preliminarily estimate the yield changes of the detected compounds by comparing the corresponding total peak area values under different reaction conditions. Fig.2(a) gives the peak area of the total detected compounds from the three catalysts with the catalyst/wood ratio of 1.2. It is seen that the total peak area, representing the total product yield, did not show significant changes under the ZrO2 catalysis, but decreased remarkably under the TiO2 and SBA-15 catalysis, especially the SBA-15.

![Graph showing total peak area of detected compounds under different catalysts](image)

Fig. 2. Total peak area and the product distribution from fast pyrolysis of poplar wood with or without catalysts

Table 1. Peak area% of each product group from fast pyrolysis of poplar wood with or without catalysts

<table>
<thead>
<tr>
<th>Catalyst/wood ratio</th>
<th>Phenolics</th>
<th>Linear aldehydes</th>
<th>Linear ketones</th>
<th>Linear acids</th>
<th>Furans</th>
<th>Anhydratosugars</th>
<th>Hydrocarbons</th>
<th>Cyclopentanones</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poplar wood/25.34</td>
<td>25.34</td>
<td>12.78</td>
<td>8.05</td>
<td>15.09</td>
<td>7.06</td>
<td>8.20</td>
<td>0.76</td>
<td>4.75</td>
<td>3.12</td>
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<tr>
<td>SBA-15/1.2</td>
<td>28.95</td>
<td>10.85</td>
<td>8.97</td>
<td>16.16</td>
<td>7.46</td>
<td>6.26</td>
<td>1.04</td>
<td>5.35</td>
<td>3.10</td>
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<tr>
<td>TiO2/1.2</td>
<td>31.32</td>
<td>3.68</td>
<td>13.66</td>
<td>15.87</td>
<td>9.49</td>
<td>6.61</td>
<td>2.00</td>
<td>8.02</td>
<td>1.76</td>
</tr>
<tr>
<td>ZrO2/0.8</td>
<td>29.05</td>
<td>10.40</td>
<td>9.21</td>
<td>14.19</td>
<td>8.09</td>
<td>6.72</td>
<td>1.02</td>
<td>5.26</td>
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<tr>
<td></td>
<td>1.2</td>
<td>30.19</td>
<td>9.55</td>
<td>10.48</td>
<td>13.49</td>
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<td>8.84</td>
<td>6.25</td>
<td>2.30</td>
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</tbody>
</table>

All the detected products could be classified into nine groups, their peak area values (representing the yield of each group) are shown in Fig.2(b), and peak area% values (representing the content of each group) are given in Table 1. According to Fig.2(b), the peak area of the phenolics, representing the phenolics yield, was increased obviously under the ZrO2 catalysis, indicating the ZrO2 was capable to convert the lignin-derived oligomers (pyrolytic lignins) to monomeric phenolic compounds, which was very essential for catalytic upgrading of biomass fast pyrolysis vapors. Moreover, the yields of the linear aldehydes, linear acids and anhydrosugars were decreased after the ZrO2 catalysis, while the yields of the linear ketones, cyclopentanones and hydrocarbons were increased. These yield changes resulted in the corresponding content changes of these product groups, as shown in Table 1. According to the peak area% results, the contents of the phenolics, linear ketones, furans, hydrocarbons and cyclopentanones were increased after catalysis, while the contents of the linear aldehydes, linear acids and anhydrosugars were decreased. These changes could help to reduce the oxygen content, viscosity and acidity of the obtained bio-oil, so as to improve its fuel properties. The TiO2 did not show promising capabilities to convert the lignin-derived oligomers (Fig.2(b)), but it was also able to improve the fuel properties of the
pyrolytic products (Table 1). However, the SBA-15 did not show promising catalytic effects to upgrade the pyrolysis vapor.

3.3. Catalytic effects of the ordered mesoporous ZrO$_2$

The catalytic effects of the ordered mesoporous ZrO$_2$ were further determined, by investigating the effects of the ZrO$_2$/wood ratio on the distribution of the pyrolytic products. The peak area values of the total products and each product group are shown in Fig. 3, and the peak area% values are given in Table 1. Based on the peak area values in Fig. 3, the rising of the ZrO$_2$/wood ratio resulted in different yield changes of the product groups. These effects on the fuel properties of the obtained bio-oil can be determined according to Table 1. As the rising of the ZrO$_2$/wood ratio, the contents of the linear aldehydes, linear acids and anhydrosugars were gradually decreased, while the contents of the linear ketones, furans, hydrocarbons and cyclopentanones were increased. These changes were beneficial to improve the fuel properties of the bio-oil. In regard to the specific pyrolytic products, their peak area and peak area% were also determined, and the details are not shown here.

4. Conclusions

Ordered mesoporous ZrO$_2$, TiO$_2$ and SiO$_2$ (SBA-15) were employed for catalytic upgrading of biomass fast pyrolysis vapors. The ZrO$_2$ was confirmed to be the best catalyst. It exhibited promising capability to convert the lignin-derived oligomers to monomeric phenolic compounds, which was every essential for biomass fast pyrolysis vapors upgrading. Moreover, catalytic upgrading by the ZrO$_2$ decreased the yields of the linear aldehydes, linear acids and hydrocarbons, and meanwhile increased the yields of linear ketones, furans, hydrocarbons and cyclopentanones. These catalytic effects would improve the fuel properties of the obtained bio-oil.

References

Biography

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