Catalytic pyrolysis of xylan-based hemicellulose over zeolites

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Abstract: Xylan was selected as model compound of hemicellulose to investigate its thermal behavior over zeolites by using TG-FTIR. The chemical structure of xylan and characterization of catalysts were first studied. All the three catalysts, HZSM-5, H-β and USY, had obvious influence on deoxygenation and fragmentation reactions during xylan pyrolysis. The dehydration in the initial stage was enhanced and the char formation was suppressed. USY had the best effect on dehydration with the consumption of oxygenated compounds, such as acids and furans. The presence of HZSM-5 and H-β catalyzed the formation of water, CO2 and alkanes, with the degradation of char residues.

Key-Words:-catalytic pyrolysis; xylan; hemicellulose; zeolites; acids; furans; TG-FTIR

1 Introduction
Hemicellulose is a group of polysaccharides found in plant cell walls and can be extracted from different plant sources with heterogeneity [1]. In contrast to cellulose that is crystalline and strong, hemicellulose has a random and amorphous structure with little strength and cross-link to cellulose and lignin. As the major component of biomass, the content of hemicellulose is 10~15 % in softwood, 18~23 % in hardwood and 20~25 % in herbaceous plant. The saccharides contained in hemicellulose are pentose, hexose, and/or uronic acids, including xylose, mannose, galactose, glucose, and arabinose etc. [2]. Other sugars such as rhamnose and fucose may also be present in small amounts and the hydroxyl groups of sugars can be partially substituted with acetyl groups. Xylan is the most relevant component in hemicellulose, and being the most abundant [3]. Its dominant structure is shown in Fig.1, in which O-acetyl xylan and 4-O-methylglucuronoxylan are primary units in hardwood species, while arabinoxylan and 4-O-methylglucuronoxylan are rich in softwood plant [4, 5].

Fig.1 Chemical structure of xylan

The decomposition of xylan mainly occurred at the range of 220~315 °C with a rapid weight loss rate to produce more CO2 [6]. The successive reactions model and independent parallel reactions model were deduced to obtain the kinetic parameters respectively, and the former had a better fit at 10 and 80 °C/min [7]. The distribution of the main products (bio-oil, gas and char) generated by degradation of xylan were investigated in the studies [8-10]. The yields of gas, tar, water and char from xylan gasification at 800 °C are 14.1 wt%, 54.3 wt%, 11.5 wt% and 20.1 wt% respectively, and furans are the most abundant compounds in tar [8]. Meanwhile, hemicellulose has significant influence on pyrolysis behaviors of biomass [6, 11, 12], through the interactions between cellulose and lignin [13-15]. Recently, catalytic pyrolysis of biomass and its components are widely studied to investigate the possibility of direct production of high-quality fuels from biomass. Bridgwater [16] proposed that the pyrolysis vapors of biomass could be cracked into aromatics and other hydrocarbon products over zeolites, and then further converted into gasoline or diesel. In the presence of zeolites, the volatiles released from cellulose pyrolysis underwent various deoxygenation reactions including dehydration, decarboxylation, and decarbonylation, resulting in the production of hydrocarbons and carbonaceous solids-coke [17]. The conversion of lignin to phenols was also optimized over zeolites with an increased octane number [18]. Various treatments were used to produce sugars from hemicellulose hydrolysis such
as acid hydrolysis, hydrothermal treatments, ionic liquids, supercritical fluids etc. [5], but the report on catalytic pyrolysis of hemicellulose was rarely.

To further understanding the thermal behaviors of hemicellulose and biomass, xylan was selected as model compound of hemicellulose to study the decomposition of xylan over zeolites by using the thermogravimetric analyzer coupled with Fourier transform infrared spectrometer (TG-FTIR). And the decomposition model was deduced in combination with structure analysis of xylan and catalysts.

2 Experimental Methods

2.1 Materials
Xylan as the model compound of hemicellulose was purchased from Sigma Corporation. It was Poly (β-D-xylopyranose [1→4]) extracted from the beechwood. The three zeolite catalysts, HZSM-5 (SiO2/Al2O3=25), H-β and USY, were representative of zeolites. Each catalyst and xylan was well ground and screened to less than 200 μm, and then dried at 105 °C in an oven to remove the absorbed water before experiments.

2.2 Methods
The chemical structure of xylan was measured by FTIR first. The sample was prepared using the KBr pellet and FTIR spectra were measured using a Nicolet Impact 830D spectrometer manufactured by Thermo Fisher Scientific Inc. in USA. Measurements were taken at wave numbers from 400 to 4000 cm−1 with a resolution of 4 cm−1, and each spectrum was based on the average of 36 scans. BET surface area and other textural properties of zeolites were measured by N2 adsorption-desorption isotherms at 77 K on a Micromeritics TriStar 3000 apparatus. A Mettler–Toledo TGA/SDTA851e thermo-balance coupled with a Nicolet NETXUS 670 FTIR spectrometer was used to study the pyrolysis behaviors of xylan. Nitrogen was as carrier gas with the purity over 99.99 % to ensure the inert atmosphere. Experiments were operated on the TGA at a linear heating rate of 20 °C/min within the temperature range from 30 °C to 800 °C at a steady nitrogen flow rate of 30 ml/min. The volatiles released during pyrolysis would be swept into FTIR gas cell quickly. For the detection of volatiles, a deuterated triglycine sulfate pyroelectric detector was adopted for its quick response and low noise. The spectral range was covered from 400 to 4000 cm−1, and the resolution factor was selected as 1 cm−1. In order to reduce the influence of sample amount on the intensity of IR absorption, the weight of each sample without catalysts was about 10±0.05 mg, the total weight was controlled at 20±0.05 mg. so the mass ratio of mixed catalyst and sample was 1:1.

3 Results

3.1 Structural Analysis of Xylan
The chemical structure of xylan is shown in Fig.1 and its FTIR spectrum is described in Fig.2. The characteristic functional groups are all identified in the xylan spectrum, corresponding to the chemical structure. For example, the strong (s) bond vibrations of O-H at 3600~3200 cm−1 and C-O at 1320~1210 cm−1 represent alcoholic hydroxyl, which is carboxyl combined with middle (m) bond stretch of C=O at 1725~1705 cm−1; the strong stretch at 1150~1070 cm−1 corresponds to C-O-C linkage; the middle unsymmetrical shrinkage of –CH2-cyclopentane is at 3000~2800 cm−1; and the weak (w) bond vibration at 2250 cm−1 is related to -O-Ac structure. Therefore, it is concluded that xylan contains O-acetyl and 4-O-methylglucurono units.

![Fig.2 FTIR spectra of xylan](image)

3.2 Characterization of the Catalysts
Zeolite has most of the acid sites located within the micro porous crystal structure, thus the acid sites are an integral part of their structure not at the surface terminating the individual crystallites [19].

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m²/g)</th>
<th>Total pore volume (cm³/g)</th>
<th>Average pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HZSM-5</td>
<td>484.45</td>
<td>0.3567</td>
<td>2.87</td>
</tr>
<tr>
<td>H-β</td>
<td>497.54</td>
<td>0.3981</td>
<td>3.20</td>
</tr>
<tr>
<td>USY</td>
<td>476.54</td>
<td>0.3040</td>
<td>2.55</td>
</tr>
</tbody>
</table>

The physical property of zeolite is shown in Table 1. It is found that all the three catalysts have similar high BET surface area and large pore volume, which provide large amount of acid sites to the reactants. The results calculated by using BET method are in
the range of previous analysis [20, 21], in spite of little difference due to the unique of each catalyst.

### 3.3 Pyrolysis Behavior Analysis

#### 3.3.1 Thermal Degradation

Fig. 3 shows the TG/DTG curves of xylan pyrolysis with zeolites. The decomposition of all samples is divided into four stages, which are the initial stage in the temperature range 30–200 °C, the main stage in 200–350 °C, the third stage in 350–500 °C, and the final stage after 500 °C. The maximal weight loss rate is observed at 260 °C. The initial stage is attributed to water release by evaporation and dehydration [22], so it can be concluded that the three zeolites all catalyze the dehydration of xylan. The main stage is ascribed to the cleavage of the glycosidic bonds and the decomposition of side-chain structure and even the fragmentation of other depolymerized units. It is found that the presence of USY inhibits the further degradation of xylan, which results in a low yield of volatiles. In the third stage, the weight loss of pure xylan and xylan with HZSM-5 or USY was a smooth shoulder, but xylan with H-β was a peak due to the secondary cracking of monomeric residues. It may be caused by the special catalytic effect on acetyl groups and 4-O-methyl-α-d-glucopyranosyluronic acid linkage, which are both thermal stable linkage in native xylan [23]. In the final stage, pure xylan and xylan with USY retained a char yield of 26 %, and xylan with HZSM-5 and H-β kept a char yield 16 %.

![Fig.3 TG/DTG curves of xylan pyrolysis with zeolites](image)

#### 3.3.2 Product Release

The characteristic release from xylan pyrolysis with zeolites is shown in Fig. 4. The unique peak release of xylan with or without zeolites is all at 262 °C, which is similar to the tendency of DTG curves. Based on the comparison of standard spectrum of certain compound (shown in Table 2) with the original spectra of xylan, the major products are identified by the appearance of characteristic absorption bonds, such as CO with two continuous peaks at 2280-2144 cm⁻¹ and 2144-1950 cm⁻¹. The main products from xylan pyrolysis include water, CO₂, CO, benzene, methanol, formic acid, acetic acid, 2-furaldehyde and furan, 2-methyl etc. at 262 °C. The major products from xylan pyrolysis with zeolites are similar to pure xylan just with different release intensity.

The weight loss peak of xylan with H-β appeared in 350–500 °C corresponds to the largely formation of ethylene unexpectedly. The detailed evolution of the typical products can be investigated by their unique infrared spectrum peak (shown in Table 2), as the intensity of absorbance reflects the concentration of the products [24].

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Compounds</th>
<th>Characterized peak (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3964-3038, 2098-1593-1233 (2)</td>
<td>H₂O</td>
<td>3735</td>
</tr>
<tr>
<td>2406-2215</td>
<td>CO₂</td>
<td>2366</td>
</tr>
<tr>
<td>2280-2144-1950 (2)</td>
<td>CO</td>
<td>2178</td>
</tr>
<tr>
<td>3280-1960-1812-1523-1360, 1153-803</td>
<td>Ethylene</td>
<td>950</td>
</tr>
<tr>
<td>3683-3461, 3055-2840, 1861-1670, 1163-990, 763-483</td>
<td>Formic acid</td>
<td>1123</td>
</tr>
<tr>
<td>3630-3513, 1858-1658, 1483-1329-1236-1113-1043-920 (5), 741-464</td>
<td>Acetic acid</td>
<td>1184</td>
</tr>
<tr>
<td>3100-2600, 1600-1313-1178-929-830 (4)</td>
<td>Methanol</td>
<td>1061</td>
</tr>
<tr>
<td>3036-2787, 1646-556 (12)</td>
<td>Furan, 2-methyl</td>
<td>720</td>
</tr>
<tr>
<td>2898-2676, 1812-547 (13)</td>
<td>2-Furaldehyde</td>
<td>747</td>
</tr>
</tbody>
</table>

![Fig.4 FTIR spectra of xylan pyrolysis with zeolites at maximal volatile release](image)
3.3.3 Evolution of the Typical Products
By the integration of intensity and temperature, the yield of certain compound can be approximately evaluated. Fig.5 shows the evolution of typical products from xylan pyrolysis. The intensity of acids is the sum of formic acid and acetic acid, and the intensity of furans corresponds to 2-furaldehyde and furan, 2-methyl. The release of water and CO₂ is more complex and is divided into three stages: the initial stage in 30~200 °C, the main stage in 200~350 °C and the last stage in 350~800 °C, which agrees well with the tendency of DTG curves. Pyrolysis of xylan with USY yields the most of water in the initial stage, but the subsequent maximal values are all obtained from pyrolysis of xylan with H-β. The formation of oxygenated compounds is concentrated in 200~500 °C, except for xylan with H-β in 100~500 °C. Pyrolysis of pure xylan produces more acids and furans, and less water and CO₂ than xylan pyrolysis with zeolites. After the addition of HZSM-5, H-β, and USY, the yield of water increases by 29.06 %, 289.69 %, and 116.42 % respectively; the yield of CO₂ increased by 58.11 % and 226.15 %, and decreases by 47.80 %; the yield of acid compounds decreased by 67.39 %, 47.16 % and 94.39 %; and the yield of furans decreased by 60.09 %, 12.94 % and 83.19 % respectively. A large amount of ethylene is produced from xylan pyrolysis with H-β in 400~550 °C. Therefore, it can be concluded that the presence of H-β efficiently promotes the decomposition of xylan to form small molecular gases, such as water, CO₂ and alkanes. The catalytic effect of USY is primarily related to the deoxygenation of oxygenated compounds, which has been identified by Wang [25].

3.4 Discussion on Decomposition Model
The thermal decomposition of typical xylan units is proposed and summarized in Fig.6. It starts with the depolymerization of polymer first. The formation of acetic acid is involved with the primary elimination reaction of the active O-Ac groups in the side chain of O-acetyl xylan [26], and furfural is obtained through the cleavage of the bond between O-C₅ and ring forming between C₂-C₅ positions on the main chain of xylan [27]. The other pathway for furfural formation is related to the decomposition of 4-O-methylglucuronic xylan along with the release of CO₂ and methanol. Moreover, alkanes are obvious obtained from the depth deoxygenation of C₂ or C₃ oxygenated compounds, such as acetaldehyde,
acetone, ethanol, and glycolaldehyde etc. It is observed that the cleavage of chemical bonds in the side chains is easier than these in the sugar ring. In the presence of zeolites, the formation of furfural is restrained and the fragmentation reaction becomes intense to produce more water, CO₂, CO and alkanes. Meanwhile, the cleavage of O-acetyl group is affected by the zeolites significantly, as acetic acid is mainly formed from it. USY is best for acidic oxygenated compounds removal and H-β prefers to thorough deoxygenation at higher temperature.

Fig.6 The conjectural chemical routes of thermal decomposition of typical xylan units

4 Conclusions
In the present study, TG-FTIR technique was used to study the catalytic effect of zeolites on hemicellulose pyrolysis. Xylan was selected as model compound of hemicellulose. It was observed that xylan contained the characteristic 4-O-methylglucurono and O-acetyl groups from wood and its components during pyrolysis. Formation of the main degradation compound and USY, catalyzed the dehydration in the initial stage and inhibited the formation of char residues. The proposed order was USY>HZSM-5>H-β related to the enhancement of dehydration, and inverse to the suppression of char residues. It was also found that the presence of catalysts decreased the yield of oxygenated compounds and increased the formation of small molecular gaseous products such as water, CO₂ and alkanes. USY had the best effect on deoxygenation in xylan pyrolysis. H-β induced a formation peak of ethylene at 350-510 °C, caused by the secondary cracking of depolymerized compounds.

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References:


