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Catalytic Fast Pyrolysis of Biomass into Aromatic Hydrocarbons over Mo-Modified ZSM-5 Catalysts

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Abstract: Mo-modified ZSM-5 catalysts were prepared and used to produce aromatic hydrocarbons during catalytic fast pyrolysis (CFP) of biomass. The composition and distribution of aromatics were investigated on pyrolysis–gas chromatography/mass spectrometry (Py-GC/MS). The reaction factors, such as the Mo content, the reaction temperature and the catalyst/biomass mass ratio, were also optimized. It was found that the 10Mo/ZSM-5 catalyst displayed the best activity in improving the production of monocyclic aromatic hydrocarbons (MAHs) and decreasing the yield of polycyclic aromatic hydrocarbons (PAHs) at 600 °C and with a catalyst/biomass ratio of 10. Furthermore, according to catalyst characterization and the experiment results, the aromatics formation mechanism over Mo/ZSM-5 catalysts was also summarized and proposed.

Keywords: biomass; fast pyrolysis; Mo/ZSM-5 catalyst; aromatic hydrocarbons

1. Introduction

In recent years, fast pyrolysis of biomass has proved to be an effective method to produce liquid bio-oil [1–6]. The bio-oil was composed of hundreds of chemical compounds, such as sugars, phenols, acids, aldehydes and ketones, aromatics and so on [7–9]. The complexity of bio-oil has limited its further use for petroleum oils or chemicals; therefore various catalysts have been introduced to upgrade the bio-oil to valuable chemicals [10–14].

Aromatic hydrocarbon is one of the important chemicals in bio-oil and it is widely used as a raw material in modern industry. Catalytic upgrading of the bio-oil was considered as a feasible technology to produce aromatics. Zeolite catalysts, especially ZSM-5 zeolites, due to their unique structure and chemical properties, were extensively researched during catalytic fast pyrolysis (CFP) of biomass to aromatics [15–20]. Inaba et al. reported that the H-ZSM-5 and H-Beta zeolites were effective in improving the formation of aromatic hydrocarbons in catalytic fast pyrolysis of woody biomass [16]. Jia et al. reported that, compared to microporous zeolites, the desilicated zeolites with mesopores displayed higher selectivity to monocyclic aromatic hydrocarbons (MAHs) and stability upon coke deposition [19]. However, the aromatics produced from ZSM-5 catalysts contain certain amounts of polycyclic aromatic hydrocarbons (PAHs), which are undesirable and toxicant products; therefore there is a need to maximize the yields of MAHs and minimize the productivity of PAHs with high efficiency ZSM-5 catalysts in the CFP processes.

It was reported that transition metals-modified zeolite catalysts could significantly enhance MAH yields and facilitate the transformation of PAHs to MAHs [21–25]. Li et al. modified zeolites with Fe, Zr, and Co metals and investigated the effect on bio-oil characteristics. It was concluded that Fe favors naphthalene and 1-methyl-naphthalene formation, Zr enhances the yields of ketones and aromatics, and Co results in higher production of anhydrous sugars and has the highest selectivity to toluene and p-xylene [22]. In our previous literature [26], we also found that the introduction of Fe to ZSM-5 catalysts improves the yields of MAHs. Furthermore, the metal Mo was also introduced to modify ZSM-5 zeolites to improve the yields of aromatic hydrocarbons. Thangalazhy-Gopakumar et al. studied the effect of hydrogen pressure on aromatics yield during catalytic pyrolysis of biomass over Mo/ZSM-5 catalysts. It was found that due the promotion effect of hydrogenation reactions caused by the metal Mo, Mo/ZSM-5 led to higher aromatics yield than HZSM-5 at 400 psi [27]. Liu et al. researched and characterized the acid sites of Mo/HZSM-5 and the interaction between the Mo species and HZSM-5, and concluded that a certain amount of Brønsted acid sites on the Mo/HZSM-5 surface was good for methane dehydrogenation and aromatization reactions [28]. Cheng et al. reported that 4%Mo-2%Co/HZSM-5 showed a robust ability in the catalytic cracking of prairie cordgrass (PCG) with the highest yield of hydrocarbons at 41.08% [29]. However, systematic research on CFP of biomass to aromatic hydrocarbons with Mo-modified ZSM-5 catalysts has not been reported.

In this work, Mo-modified ZSM-5 catalysts were prepared and characterized by various methods, including X-ray diffraction (XRD), scanning electron microscopy (SEM) and pyridine infrared spectroscopy (Py-IR). The effects of Mo loading, reaction temperature and catalyst/biomass mass ratio on the distribution of aromatic hydrocarbons were investigated by pyrolysis–gas chromatography/mass spectrometry (Py-GC/MS) experiments. The actual yields of five major aromatic hydrocarbons were identified by an external calibration method. The catalytic mechanism of Mo-modified ZSM-5 catalysts for producing aromatic hydrocarbons was also summarized based on catalyst characterizations and the experiment results.

2. Results and Discussion

2.1. Catalyst Characterizations

2.1.1. XRD

The XRD patterns of the ZSM-5 and Mo/ZSM-5 catalysts are displayed in Figure 1.

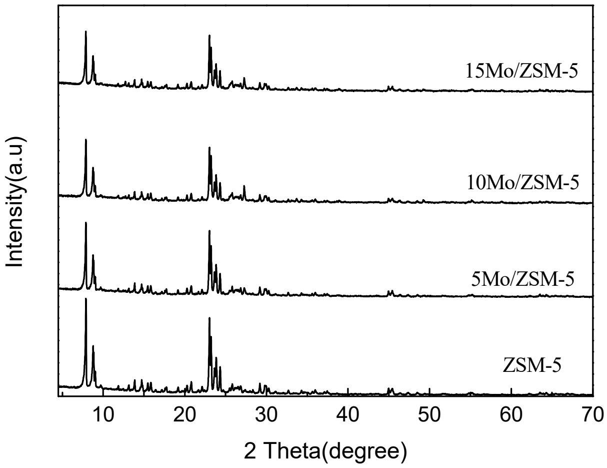

Figure 1. X-ray diffraction (XRD) patterns of the ZSM-5 and Mo/ZSM-5 catalysts.

According to Figure 1, the peaks' intensities of an MFI type zeolite (2θ = 7–9° and 23–25°) were reduced, but the structures remained after the introduction of Mo into ZSM-5 zeolites. In addition, there are no metal Mo oxides peak areas indicating the well distribution of Mo on ZSM-5 catalysts.

However, compared to the ZSM-5 catalyst, the peak intensities of Mo/ZSM-5 catalysts decreased with the increase of Mo loadings.

2.1.2. SEM

The SEM images of the ZSM-5 and Mo/ZSM-5 catalysts are shown Figure 2. Compared to the morphologies of ZSM-5, the Mo/ZSM-5 catalysts keep the cubic shape of ZSM-5 zeolites. In addition, more small crystal particles are distributed on the surface of ZSM-5 catalysts, with a Mo content increase from 5% to 15%, which may be attributed to the Mo species distributed on the external surface of the Mo/ZSM-5 catalysts.

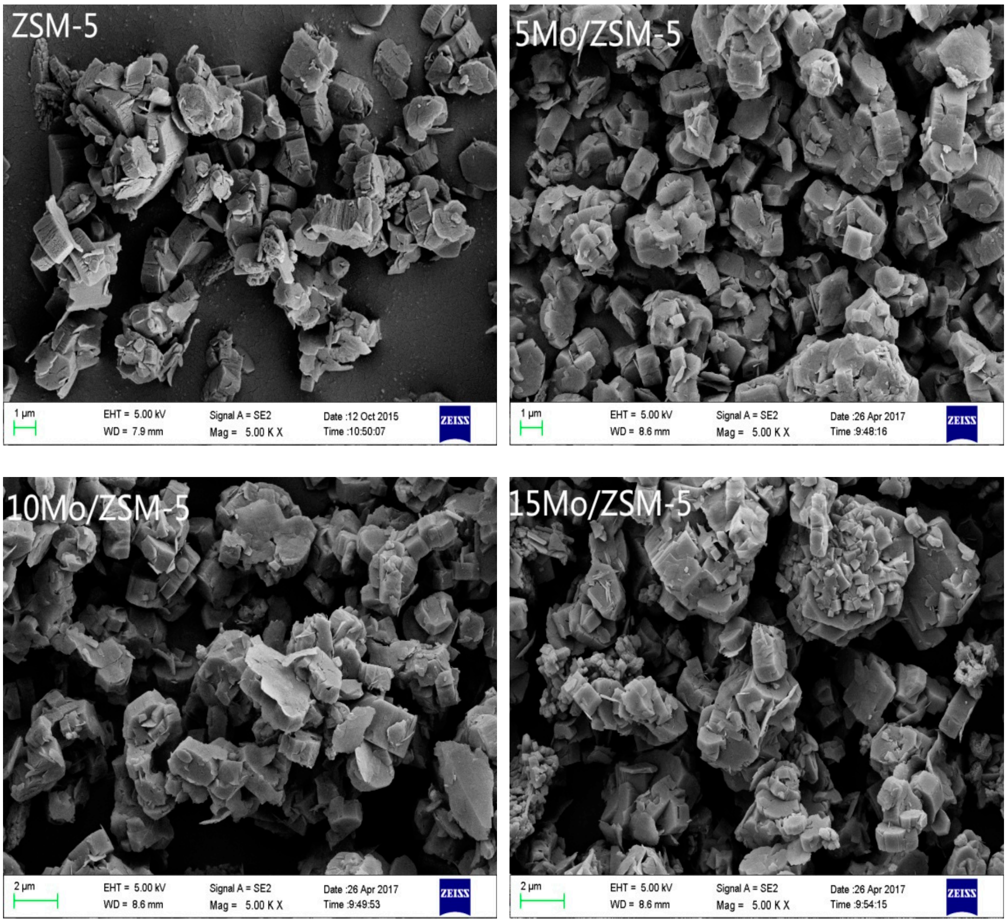

Figure 2. The scanning electron microscopy (SEM) images of the ZSM-5 and Mo/ZSM-5 catalysts.

2.1.3. Py-IR

Figure 3 shows the Py-IR of the ZSM-5 and Mo/ZSM-5 catalysts. The pyridine adsorption peaks are classified into three categories: (1) Lewis acid sites (L, 1450 and 1610 cm^{-1}), (2) Brønsted acid sites (B, 1542 and 1640 cm^{-1}), and (3) the coexistence of L and B acid sites (1490 and 1597 cm^{-1}). According to Figure 3, the adsorption peaks of B acid sites and the coexistence of L and B acid sites are significantly decreased with the load of Mo on ZSM-5 catalysts. In addition, the B/L ratio decreases from 3.79 to 1.03, indicating that the B acid sites on the ZSM-5 surface are covered by metal Mo oxides. It has been reported that the polymerization reactions easily occurred on the B acid sites [30]; the decrease of B/L ratio might be favored to the production of MAHs and thereby inhibit the formation of PAHs.

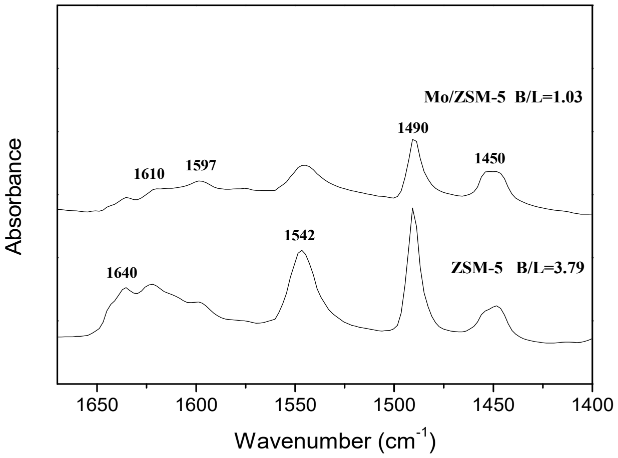

Figure 3. Pyridine infrared spectroscopy (Py-IR) of the ZSM-5 and Mo/ZSM-5 catalysts.

2.2. Catalytic Performances

2.2.1. FP of Biomass over ZSM-5 and Mo/ZSM-5 Catalysts to Aromatics

Aromatic hydrocarbons were classified into two categories, (1) MAHs, such as benzene, toluene, and xylene and (2) PAHs, such as naphthalene and 2-methyl-naphthalene. Figure 4 shows the distribution of aromatics produced from the CFP of biomass over different catalysts. According to Figure 4, the yields of the PAHs all decreased, while the yields of the MAHs increased by the three Mo/ZSM-5 catalysts. The 10Mo/ZSM-5 catalyst displayed the best activity in the increase of yields of MAHs among the three Mo/ZSM-5 catalysts. The above results indicate that the modification of ZSM-5 with metal Mo promoted the decomposition of PAHs into small molecules and other intermediates, and then accelerated the aromatization reactions. Compared with the ZSM-5 catalyst, higher MAHs selectivity (67.4% vs. 52.7%), and lower yield (decreased by 82.0%) and selectivity (10.3% vs. 40.2%) of PAHs were obtained with the 10Mo/ZSM-5 catalyst. Therefore, the 10Mo/ZSM-5 catalyst was selected to further investigate the effects of temperature and catalyst/biomass mass ratio on the yield and selectivity of aromatics during CFP of biomass.

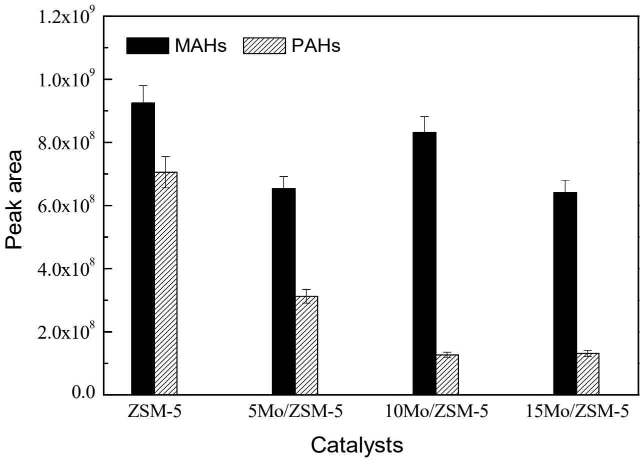

Figure 4. *Cont.*

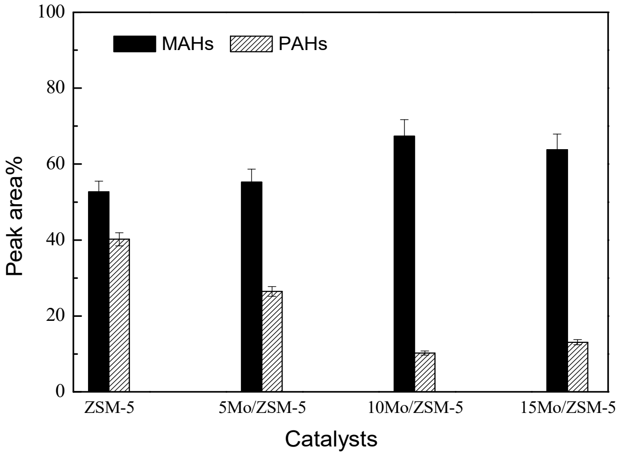

Figure 4. Distribution of aromatics produced from catalytic fast pyrolysis (CFP) of biomass over different catalysts (T = 600 °C, catalyst/biomass mass ratio = 10).

2.2.2. Effects of Reaction Temperature on Aromatics Yield and Selectivity

The effects of reaction temperature on aromatics yield and selectivity are displayed in Figure 5. At the low reaction temperature of 400 °C, the biomass was not completely disintegrated, resulting in a very low yield of aromatics. The yields of both the MAHs and the PAHs increased with the temperature increasing from 400 to 600 °C, but then decreased with the rise of temperature from 600 to 700 °C. It may be because the higher reaction temperature resulted in the decomposition of aromatics and transformed them into small molecule gases.

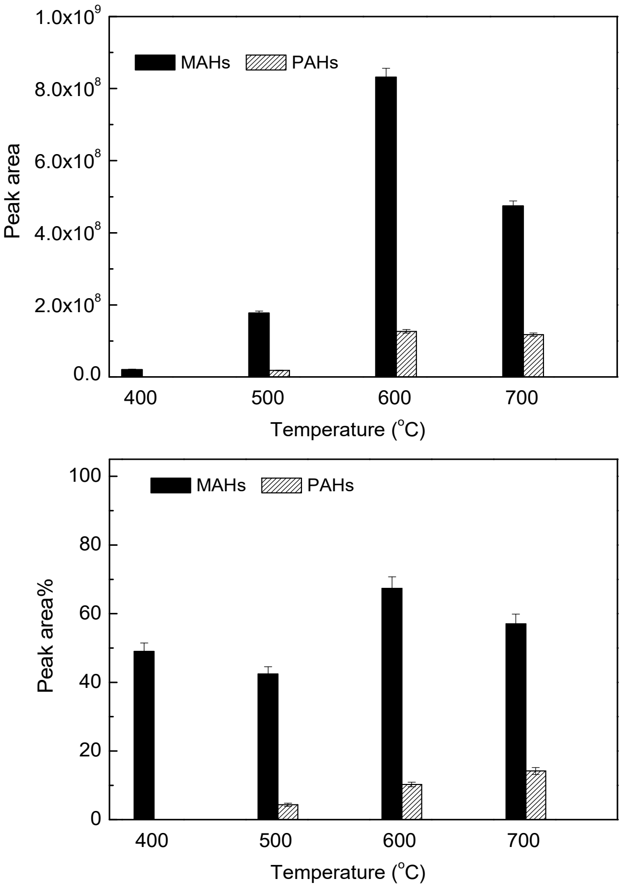

Figure 5. Effects of reaction temperature on the yield and selectivity of aromatics. (10Mo/ZSM-5, catalyst/biomass mass ratio = 10).

2.2.3. Effects of Catalyst/Biomass Mass Ratios on Aromatics Yield and Selectivity

Figure 6 shows the effects of catalyst/biomass mass ratios on the yield and selectivity of aromatic hydrocarbons. According to Figure 6, the catalyst/biomass mass ratio significantly influences the yield and selectivity of aromatic hydrocarbons. The yields of aromatics, both MAHs and PAHs, are very low at the catalyst/biomass mass ratio of 1/1, and increase at a ratio of 5/1. However, when the catalyst/biomass mass ratio changes from 5/1 to 10/1, both the yields of MAHs and PAHs are significantly increased, but the growth range of MAHs is higher than that of PAHs. It can be concluded that due to the presence of more active sites for aromatization, with higher contents of catalysts, high catalyst/biomass mass ratio was favored to increase the yields of aromatic hydrocarbons during CFP of biomass.

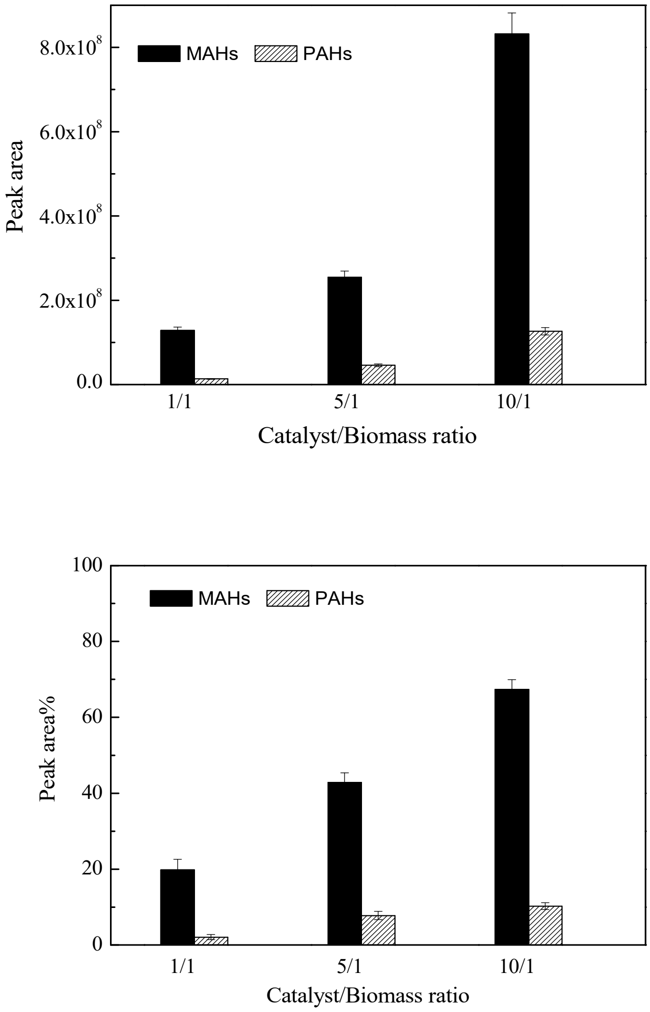

Figure 6. Effects of catalyst/biomass mass ratios on the yields and selectivity of aromatics. (10Mo/ZSM-5, T = 600 °C).

2.2.4. Quantitative Analysis of Five Major Aromatic Hydrocarbons

The five major aromatic hydrocarbons, i.e., benzene, toluene, xylene, naphthalene and 2-methyl-naphthalene, were mainly produced during CFP of biomass; their actual yields were qualified and determined by an external calibration method [24,25]. Figure 7 shows the actual yields of five major aromatics under different catalyst/biomass ratios. According to Figure 7, the peak area and actual yields of five aromatic hydrocarbons both increased when the catalyst/biomass ratios varied from 1/1 to 10/1. The above results indicate that the peak area values can be used to determine the change of actual yields of aromatics.

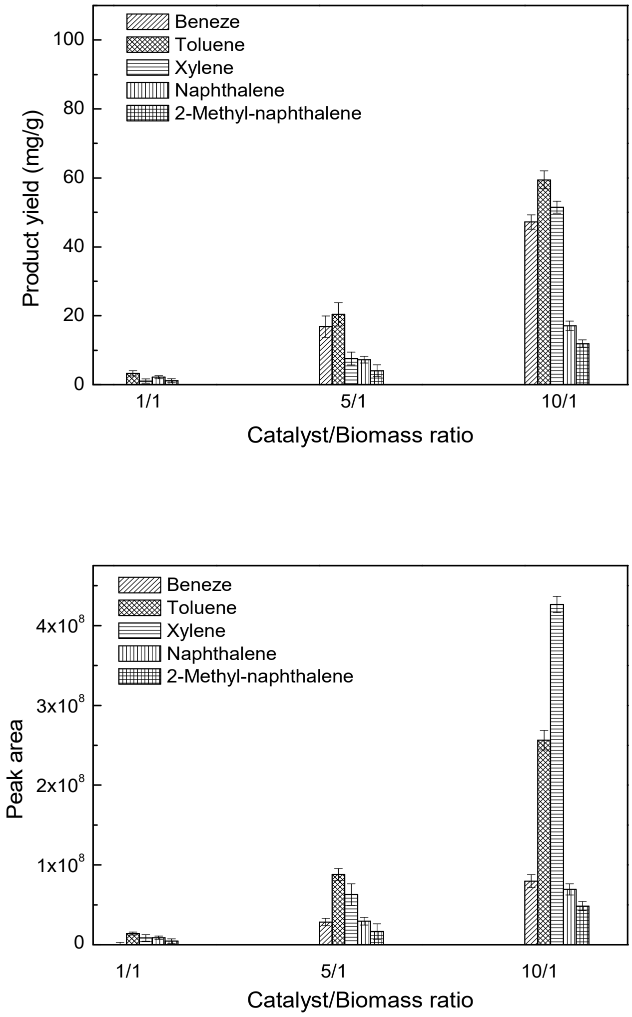

Figure 7. The actual yields of five major aromatic hydrocarbons (10Mo/ZSM-5, T = 600 °C).

At the catalyst/biomass ratio of 10, the actual yields of benzene, toluene, xylene, naphthalene and 2-methyl-naphthalene are 47.2, 59.4, 51.5, 17.1 and 11.9 mg/g biomass, respectively. It can be deduced that the total actual yields of the aromatics are 187.2 mg, including 158.2 mg/g MAHs and 29.0 mg/g PAHs. Then the selectivity of MAHs can be calculated to be 84.5%. However, the total yields of aromatics produced over the ZSM-5 catalytic were 250.5 mg (126.4 mg MAHs and 124.1 mg PAHs), with the selectivity of MAHs of only 50.5% under the same reaction conditions. In general, it was confirmed that the ZSM-5 catalysts modified with the metal Mo displayed good ability in transforming PAHs to MAHs and improving the yield and selectivity of MAHs, on the basis of the above results.

2.3. *The Aromatics Formation Mechanism*

Based on the above catalyst characterizations and the experiment results, Mo-modified ZSM-5 catalysts displayed an excellent ability in producing MAHs. It was deduced that the Mo/ZSM-5 catalyst greatly improved the quality of aromatic hydrocarbons by restraining the formation of PAHs and converting pyrolysis products to MAHs during CFP of biomass. Recently, CFP of biomass to produce aromatic hydrocarbons with Mo-supported ZSM-5 catalysts was investigated, and the mechanism of aromatic formation was put forward and summarized. Firstly, it was reported that Mo oxides have good ability to crack the biomass and simultaneously remove oxygen. Yang et al. studied the integration of biomass catalytic pyrolysis and methane aromatization over Mo/HZSM-5 catalysts, and found that it promoted deoxygenation of lignin-derived phenols [31]. The biomass was decomposed into intermediate products (alcohols, acids, furans, aldehydes and ketones) with the catalytic effect of metal

Mo. Secondly, by the action of ZSM-5 zeolites, the intermediate products were further cyclized and aromatized to aromatic hydrocarbons on both the surface and pores of the ZSM-5 catalysts, which were effective in the aromatization reaction [32]. Finally, the synergistic effect between Mo and the ZSM-5 catalysts results in the high yield and selectivity of the production of MAHs during CFP of biomass to aromatics.

3. Materials and Methods

3.1. Catalysts Preparation

Wood sawdust was selected as the biomass material (Shandong, China). Commercial ZSM-5 zeolites were bought from Nankai University (Tianjin, China). The different Mo/ZSM-5 catalysts were prepared by the impregnation method. Firstly, the ammonium molybdate ($(NH_4)_6M_{O7}O_{24}\cdot 4H_2O$) purchased from Sinopharm (Beijing, China) was dissolved into deionized water, and then impregnated onto the ZSM-5 zeolites for 4 h. Secondly, the above mixture was dried at 100 °C for 12 h and calcined at 550 °C for 4 h. As the last step, the powder was crushed and sieved for use. The catalysts with Mo loadings of 5, 10 and 15wt% were named as 5 Mo/ZSM-5, 10Mo/ZSM-5 and 15Mo/ZSM-5, respectively. The catalysts with Mo loadings of 5, 10 and 15wt% were named as 5Mo/ZSM-5, 10Mo/ZSM-5 and 15Mo/ZSM-5, respectively. A detailed description about the materials and catalyst preparation method was reported in our previous literature [26].

3.2. Catalyst Characterization

XRD patterns were recorded by a Rigaku D/max-RB (Tokyo, Japan) by using Cu Ka radiation at 40 kV and 40 mA. SEM was performed to examine the morphologies of the catalysts on a Carl Zeiss AG SUPRA 55 (Oberkochen, Germany). The acid distributions were studied by Py-IR analyses on a Thermal Nicolet 380 Fourier transforming infrared spectrum (FT-IR) spectrometer (Woodland, CA USA).

3.3. Py-GC/MS Experiments

Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) analyses were conducted on the CDS Pyroprobe 5200HP pyrolyser (Oxford, PA USA) with the Agilent 7890A/5975C GC/MS (Santa Clara, CA USA). The detailed experiment parameters and methods were clearly shown in our previous study [14–26]. The amounts of biomass materials were fixed at 0.5 mg in every experiment. Because the quantity of biomass material was identical in each experiment, the chromatographic peak area and peak areas percent values of one compound were used to consider with its yield and selectivity [12–22]. Furthermore, an external calibration method was used to quantify the actual yields of aromatics [24,25]. For example, different peak area values of benzene could be obtained by injecting a series of benzene standard solutions into GC/MS. According to the peak area value and the corresponding quantity of benzene, a standard curve was fitted. The real yield of benzene in each experiment was then calculated according to the peak area and standard curve.

4. Conclusions

A series of Mo/ZSM-5 catalysts were prepared and applied for CFP of biomass to obtain aromatic hydrocarbons by Py-GC/MS. The experiment results showed that at 600 °C and with a catalyst/biomass ratio of 10, the 10Mo/ZSM-5 catalyst displayed the best ability in the production of MAHs among the catalysts. Under the above optimal reaction conditions, the yields of MAHs and PAHs from the 10Mo/ZSM-5 catalysts were 158.2 mg/g and 29.0 mg/g, respectively, with a MAHs selectivity of 84.5%. It is concluded, based on the combination of the catalyst characterization and the experiment results, that the distribution of aromatics rich in MAHs and low in PAHs by the Mo/ZSM-5 catalysts was attributed to the synergistic effect of metal Mo and ZSM-5 zeolites during CFP of biomass reactions.

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Conflicts of Interest: The authors declare no conflict of interest.

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