

Catalytic performances of HZSM-5, NaY and MCM-41 in two-stage catalytic pyrolysis of pinewood

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Abstract. Experiments were carried out in an atmospheric two-stage fixed bed reactor to investigate the catalytic cracking of pinewood pyrolysis vapour over three single catalysts, HZSM-5, NaY and MCM-41. The pinewood was pyrolyzed in the first stage reactor at a heating rate of 10 °C min⁻¹ from room temperature to 700 °C, and the resultant vapour was cracked through the second reactor at a temperature of 500, 600 or 700 °C with and without catalyst. Both the gases and liquid compounds were thoroughly determined. It was found that all three catalysts had significant catalytic effects on the vapour cracking especially in the range of 500–600 °C. However, three catalysts showed dissimilarity to each other with respect to the distributions of products. Among three catalysts, HZSM-5 displayed the highest selectivity for the formation of olefins and light aromatics, with the least deposit of coke, though NaY showed the strongest capability of deoxygenation. The HZSM-5 cracking at 600 °C was preferred to balance the yield and quality of bio-products. MCM-41 behaved as a worse catalyst in the deoxygenation, and its resultant liquid product contained more heavy aromatics.

1. Introduction

With the non-sustainability of fossil energy, the conversion of renewable lignocellulosic biomass to a viable alternative for traditional fuels has drawn considerable attentions [1]. Lignocellulosic biomass can be utilized via various thermochemical processes. Pyrolysis is such an important process that can convert biomass to gaseous, liquid and solid products of more energy-intensive and more convenient form. However, the crude bio-oil derived from pyrolysis are chemically complex and unstable because the pyrolysis is generally terminated by a number of non-equilibrium state reactions [2]. The excessive presence of oxygen in pyrolysis bio-oil is a critical problem, which causes the bio-oil to have several drawbacks of low calorific value, acidity, viscosity and instability [3].

The deoxygenation of bio-oil is a key technical way to upgrading the pyrolysis bio-oil and converting it to more valuable chemicals. Several upgrading processes have been put forward by researchers, which mainly include pressurized treatment [4], hydroprocessing [5] and catalytic cracking [6]. Catalytic upgrading has some advantages over hydroprocessing of on need for expensive hydrogen and over pressurized treatment of operating at an atmospheric pressure [7]. It is widely proved that a large variety of oxygenate compounds derived from biomass could be converted into hydrocarbons over acidic zeolite catalysts at the expense of a low yield of bio-oil [7]. Williams *et al.*

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observed that the yield of oil obtained from the pyrolysis of rice husks at the temperature of 550 °C reduced from 28.5 wt. % to 4.4 wt. % through the ZSM catalyst bed at the temperature of 500 °C. Adjaye and Bakhshi compared HZSM-5, HY and a silica alumina catalyst in production of hydrocarbons by upgrading of a fast pyrolysis bio-oil [8]. Iliopoulou et al investigated the effect of Al-MCM-41 on the biomass pyrolysis behaviour [9]. It appears that the yield and quality of bio-oil can be largely tailored using different catalysts.

In this work, we have examined the catalysis of three typical catalysts, HZSM-5, NaY and MCM-41 for cracking of pinewood pyrolysis vapour in a two-stage fixed bed reactor. We have tried to determine a wide spectrum of products including gases (CO, CO₂, CH₄, H₂, C₂~C₃) and main liquid products (water, small molecule oxygenates, light aromatic hydrocarbons, etc.). Therefore, a comprehensive evaluation can be performed with respect to their catalytic effects on bio-oil deoxygenation, aromatization and the selective formation of olefins.

2. Experimental

Table 1. The properties of pine wood.

Proximate analysis (wt. %, dry basis)			Ultimate analysis (wt. %, daf. basis)				
Ash	Volatile	Fixed carbon	C	H	O ^a	N	S
0.50	85.01	14.49	51.71	6.17	42.02	0.10	0.00

^a By difference.

Table 2. The properties of zeolites.

Zeolites	Components (wt. %)			BET surface area (m ² g ⁻¹)	Average pore width (nm)	Acidity (mmol H ⁺ g ⁻¹)	WA/SA ratio ^a
	SiO ₂	Al ₂ O ₃	Na ₂ O				
HZSM-5	83.69	7.05	0.08	224.67	1.756	1.81	2.84
NaY	66.04	17.96	6.29	383.87	1.905	2.83	5.41
MCM-41	99.09	0.61	0.00	1291.52	3.167	0.45	0.87

^a WA/SA ratio, the ratio of weak acidity (100~400 °C) to strong acidity (400~700 °C).

The properties of the pinewood sample and three catalysts used in this study are listed in Table 1 and Table 2, respectively. The dried pinewood sample was composed of 10.5% hemicellulose, 48.6% cellulose and 25.3% lignin, with 15.5% extractives. And the catalysts were provided by Yuanli Ltd, Co in China. The schematic diagram of the apparatus used for pyrolysis and vapour cracking was illustrated in our previous paper [10]. The main part of the apparatus was the two coupled stainless steel tubular reactors, which were heated independently with two electric furnaces. In each run, a 2.2 g sample of dried pinewood was wrapped in a piece of wire mesh and placed in a lower (first) reactor. Pinewood was pyrolyzed at a heating rate of 10 °C min⁻¹ from room temperature to 700 °C. The resultant volatiles were purged with argon to the upper (second) reactor where the temperature was pre-set at 500, 600 or 700 °C. In the case of catalytic cracking, a 70 mm (about 6.4g of HZSM-5 and NaY, about 2.1g of MCM-41) high bed of catalyst wrapped in wire mesh was tightly inserted in the reactor. The space time of vapour through the hot catalyst bed was about 2.9~2.3s. The liquid product was captured in the cold traps (-12~-8 °C), the non-condensable gas was collected in thirteen gas bags, and the char product and catalyst were recovered at the end of experiment. Comparative experiments were also conducted without catalyst.

The four major gases (H₂, CO, CH₄ and CO₂) and the four light hydrocarbon gases (C₂H₄, C₂H₆, C₃H₆, C₃H₈) were quantitatively determined using a GC-TCD analyzer (Agilent 6820) and a GC-FID analyzer (Haixin, GC-950), respectively. The water content in the liquid product was determined by a Coulometry trace moisture analyzer (Mettler Toledo, C20). The quantitative determination of typical liquid compounds was carried out on a GC-FID analyzer (Haixin, GC-950), by an external calibration method. The distributions of PAHs in liquid product were measured by a fluorescence spectrophotometer (Lengguang, F97Pro). An elemental analyzer (Elementar Vario EL III) was used to

characterize the elemental analysis of chars and pine wood. A Micromeritics ASAP 2020 instrument was used to measure the pore surface area of catalyst. The composition of catalyst was measured using a Sequential X-Ray Fluorescence Spectrometer (Shimadzu, XRF-1800). The acidities of three catalysts were measured by a NH_3 -TPD method with the use of a Micromeritics ASAP 2920 instrument.

3. Results and discussions

3.1. Release rates of gaseous products

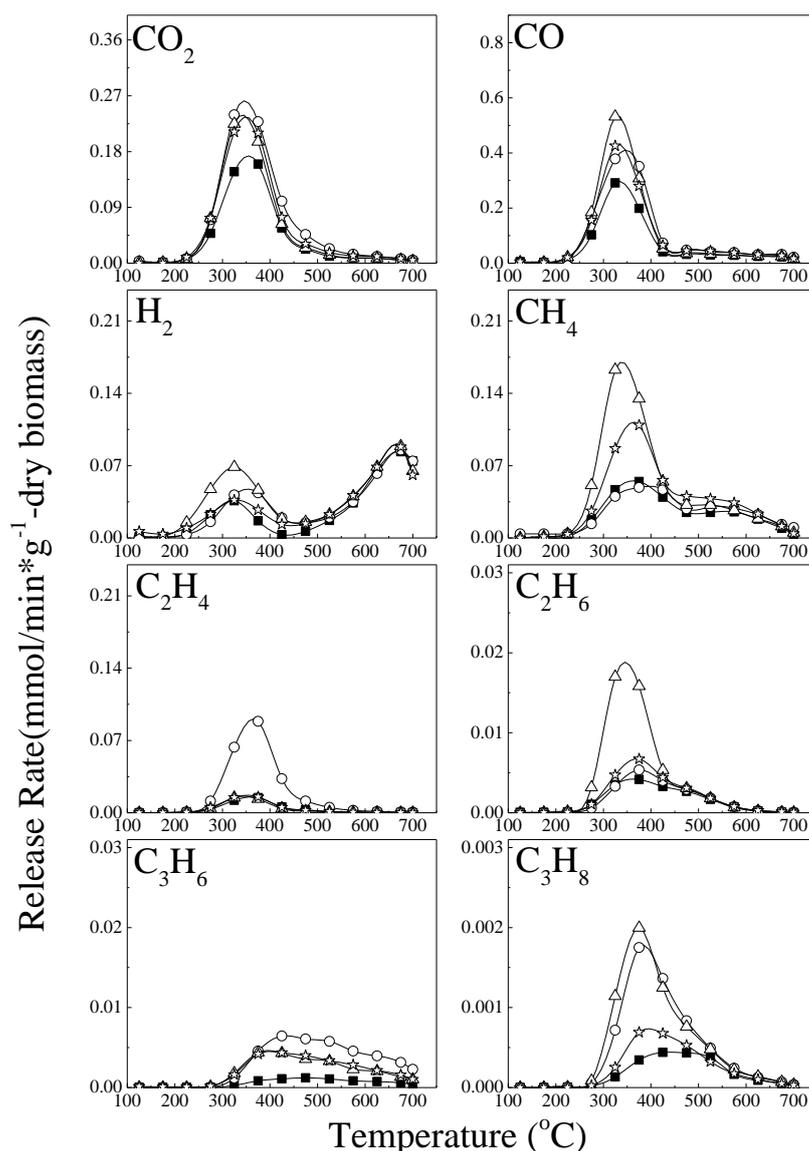


Figure 1. The release rates of gases from NC (■), HZSM-5 (O), NaY (Δ) and MCM-41 (\star) at varying pyrolysis temperatures. The cracking temperature, 600 °C.

Figure 1 shows the curve of release rate versus pyrolysis temperature for eight gases obtained at the cracking temperature of 600 °C with three types of catalyst and without catalyst. In the presence of each catalyst, the release rate of CO_2 and CO were increased significantly at the pyrolysis temperature range of 275–475 °C, where the pyrolysis volatiles were violently generated from pinewood [11]. The increase occurred mainly as the pyrolysis temperature increased from 325 °C to 375 °C, where the

cellulose decomposed largely. It was interesting that the order of CO release rate at 325 °C was: NaY >>MCM-41 >HZSM-5, while the order at 375 °C became: HZSM-5 >NaY ≈MCM-41. It was also found that NaY was strongly inclined to produce H₂ at 225-525 °C, while HZSM-5 and MCM-41 showed an increase rate of H₂ at a later temperature range of 375-525 °C. This meant that NaY had a catalytic effect on dehydrogenation of volatiles derived during the entire pyrolysis process, whereas this effect of HZSM-5 and MCM-41 occurred only on the volatiles derived after 375 °C, where the pyrolysis reactions were composed primarily of the decomposition of lignin and non-ligninic residues. HZSM-5 showed distinct increase in the release rate of C₂H₄ at 275-475 °C and C₃H₆ at 325-700 °C, indicating its selectivity for production of olefins. In contrast, NaY and MCM-41 showed marked increases in the release rates of CH₄ and C₂H₆ at 275-425 °C. Moreover, the increase of CH₄ over MCM-41 was lasted to 575 °C. It could be inferred that this large pore size catalyst had a catalytic effect on demethanation of lignin-derived volatile matter.

3.2. Overall distribution of products

The yields of four categories of products including gas, liquid, coke and char, which were produced under various cracking conditions, are shown in Figure 2. Due to the same condition of pyrolysis in the down reactor, the yields of char were close to each experiment. At the cracking temperatures of 500 °C and 600 °C, all three catalysts exhibited the catalytic effects on the deduction in the yield of liquid product, accompanied by the increases in the yield of gas and the yield of coke deposit. In sharp contrast, the cracking at 500 °C and 600 °C without catalyst only resulted in slight changes in the yields of products. Sun et al. [12] observed from a similar thermal cracking experiment that the elevation of temperature from 500 °C to 600 °C resulted in a significant degradation of some non-evaporated compounds to some evaporated compounds in the bio-oil. At the cracking temperature of 700 °C, the gaps in the yields of products with and without catalysts were no longer significant. It could be deduced that thermal effect became dominant at a higher cracking temperature. In addition, the yields of both coke deposit and liquid products decreased with increasing the cracking temperature. Among these three zeolites, the degree of coking was: NaY > MCM-41 >HZSM-5.

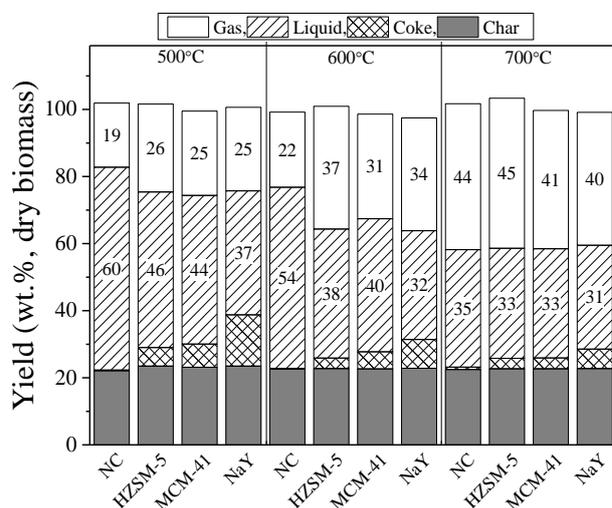


Figure 2. Yields of gas, tar, water, coke and char obtained at different cracking temperatures with and without zeolite catalysts

3.3. Yields of individual gas products

Table 3 shows the yields of eight gases obtained with three types of catalyst and without catalyst at different cracking temperatures. Under all cracking conditions, CO₂ and CO were the main gases. At the cracking temperature of 500 °C, through the catalyst beds, both the yields of CO₂ and CO increased to some extent, consistent with the increase in total gaseous product as shown in Figure 2. Increasing the cracking temperature from 500 °C to 700 °C gradually enhanced the yields of CO

whether the catalyst was used or not, while the changes in the yields of CO₂ were different to each other. For instance, the marked increases of CO₂ with HZSM-5 and without catalyst were occurred at 500-600 °C and 600-700 °C, respectively; the yield of CO₂ gradually increased over MCM-41 from 500 °C to 700 °C, while that over NaY remained almost constant.

Among six hydrogen-containing gases, H₂ and CH₄ were the main gases at the cracking temperature of 500 °C without catalyst. Through the catalyst beds, the yield of all these gases slightly increased over MCM-41, while the yields of C₂H₄ and C₃H₆ over HZSM-5 and the yields of CH₄ and C₂H₆ over NaY increased significantly. At the cracking temperature of 600 °C, all these hydrogen-containing gases showed some increases in their yields for each catalyst. The yields of H₂ and CH₄ obtained with and without catalyst exhibited large gaps at this temperature. In addition, the yield of C₂H₄ over HZSM-5 and the yield of C₂H₆ over NaY increased significantly. At the cracking temperature of 700 °C, the gaps in the yields of H₂ and CH₄ obtained with and without became smaller due to the dominated thermal cracking effect at a higher cracking temperature. However, HZSM-5 still had a promoting effect on the formation of C₂H₄ and C₃H₆, in contrast to the inhibitory effect of NaY and MCM-41 on the formation of C₂H₄.

Table 3. Cumulative yields of gases at different cracking temperatures with and without zeolites. NC, no catalyst. (wt. %)

Cracking conditions		Gaseous yields (wt.%, dry biomass)							
		CO ₂	CO	H ₂	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈
500 °C	NC	9.57	7.28	0.29	1.51	0.21	0.17	0.05	0.03
	HZSM-5	10.66	11.00	0.26	1.49	1.27	0.17	0.75	0.14
	NaY	12.07	8.91	0.33	2.42	0.46	0.36	0.27	0.09
	MCM-41	11.76	10.58	0.31	1.72	0.40	0.20	0.11	0.04
600 °C	NC	9.25	9.97	0.35	1.90	0.51	0.23	0.14	0.04
	HZSM-5	14.61	14.67	0.41	2.15	2.76	0.28	0.63	0.13
	NaY	12.07	15.63	0.48	3.77	0.48	0.62	0.46	0.12
	MCM-41	12.41	13.95	0.40	3.03	0.54	0.30	0.49	0.05
700 °C	NC	12.31	22.99	0.62	4.19	2.53	0.42	0.18	0.04
	HZSM-5	14.71	20.49	0.72	4.71	3.08	0.41	0.58	0.04
	NaY	11.66	20.88	0.86	3.32	1.71	0.55	0.34	0.05
	MCM-41	13.21	20.77	0.62	4.91	1.08	0.43	0.17	0.04

3.4. Yields of main liquid products

Table 4. Yields of eight groups of compounds in bio-oil obtained with three types of catalysts at 600 °C (mg g⁻¹, dry biomass).

Groups	NC	HZSM-5	NaY	MCM-41
Acids	20.25	0.45	2.08	5.98
Ketones	5.08	1.86	0.34	3.06
Esters	4.75	0.29	2.49	1.66
Furans	8.07	0.05	0.24	2.33
Guaiacols	0.11	0.11	0.02	0.09
Phenols	6.83	3.71	5.03	8.23
MAHs	2.57	30.67	3.08	2.98
DAHs	3.54	6.89	1.02	3.14
TAHs	0.37	0.57	0.25	0.87

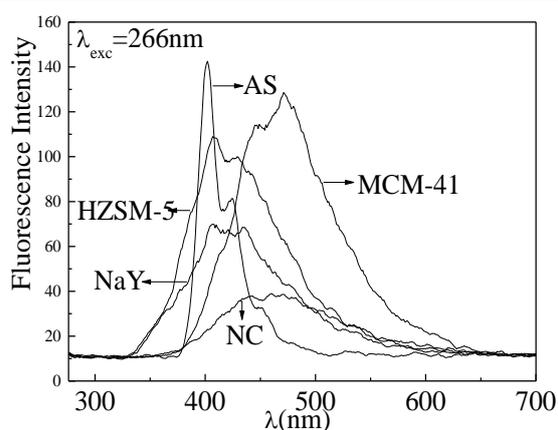


Figure 3. Fluorescence emission spectra of the liquid products produced with three types of catalyst (HZSM-5, NaY and MCM-41) and without catalyst (NC) at 600 °C by reference to the spectra of a mixture of PAH reagents. Exciting wavenumber, 266 nm.

The quantitative determination of nineteen compounds was carried on a GC-FID by using an external standard method. And other eighteen compounds were semi-quantitatively determined based on the effective carbon number method appropriate for FID signals. These compounds could be divided into nine groups, acids (methanoic acid, acetic acid and propanoic acid), ketones (hydroxyacetone and 2-cyclopenten-1-one), esters (methyl formate, 1,2-ethanediol,manoacetate and methyl acetate), furans (furfural, 2-furanmethanol and benzofuran), guaiacols (2-methoxyphenol, and 4-methyl-2-methoxyphenol), phenols (phenol, cresols, 1,2-benzenedi15ol and 2,4-xyleneol), MAHs (benzene, toluene, m-xylenes, o-xylene, ethylbenzene and 1,2,3-trimethylbenzene), DAHs (indane, indene, naphthalene and 2-methylnaphthalene), and TAHs (fluorene, phenanthrene and anthracene). The yields of these groups of compounds obtained with three different catalysts at 600 °C are listed in Table 4. In the absence of catalyst with the cracking temperature of 600 °C, the main oxygen-containing compounds were still significantly present, such as acids, ketones, esters and furans. The acids were the main composition of the bio-oil, with the amount of 20.25 mg g⁻¹-dry biomass. Interestingly, using three zeolite catalysts reduced the main oxygen-containing compounds dramatically, but the extent of the catalytic effects by three catalysts was different. HZSM-5 showed the strongest ability on the degeneration of acids, esters and furans, while NaY showed the strongest ability on the degeneration of ketones and guaiacols. MCM-41 displayed a worst deoxygenation among three catalysts, with the highest content of acids, ketones and furans, due to its lowest acidity. However, MCM-41 promoted the generation of phenols. It could be deduced that these extra phenols were generated from the decomposition of the large molecule guaiacols in the large pore of MCM-41. In the presence of HZSM-5, interestingly, the yields of both MAHs and DAHs were significantly enhanced via the catalytic cracking. In the presence of NaY, the yields of both DAHs and TAHs were decreased, but the yield of MAHs was increased. In the presence of MCM-41, the yields of both MAHs and TAHs were increased, but the yield of DAHs was decreased. From these results, it could be inferred that HZSM-5 had a strong ability on the formation of monocyclic aromatic hydrocarbons and dicyclic aromatic hydrocarbons, and MCM-41 had a strong ability on the formation of tricyclic aromatic hydrocarbons, but NaY only had a slight ability on the formation of monocyclic aromatic hydrocarbons.

Figure 3 shows the UV-excited ($\lambda=266$ nm) fluorescence spectra of some typical liquid products obtained with three types of catalyst and without catalyst. we examined the fluorescence spectra of five mixtures dissolved in acetone, which contained a mixture of acetic acid, hydroxyacetone, furfural and 2-furanmethanol, a mixture of phenol, o-cresol, p-cresol, 2,4-xyleneol and 2-methoxyphenol, a mixture of benzene, toluene and m-xylene, a mixture of indene, naphthalene and 2-methylnaphthalene, and a mixture of fluorene, phenanthrene and anthracene, respectively. It was observed that the former four solutions had no fluorescence at the excited wavelength. Only the last solution did the fluorescence occur, as shown in the figure (sample AS). Compared to the spectra of the liquid product obtained without catalyst, those of the liquid products obtained with HZSM-5 and NaY showed stronger intensity, particularly at a lower wavenumber which mainly corresponded to the fluorescence of tricyclic aromatics. In contrast, the spectrum of liquid product obtained with MCM-41 was peaked at a higher wavelength, reflective of the larger molecule aromatics. The spectrum of this liquid product was similar to that of liquid product obtained without catalyst, but with higher intensity. These results indicated the catalytic aromatization of all three catalysts. However, HZSM-5 and NaY were favourable for producing smaller molecule aromatics, unlike MCM-41.

4. Conclusions

HZSM-5 shows a better catalytic effect on the selective deoxygenation of bio-oil as well as the production of olefins and light aromatics. NaY also shows a strong ability on the deoxygenation of bio-oil, but with less light aromatics. MCM-41 displayed the worst ability on the deoxygenation and the formation of heavy aromatics among three catalysts. HZSM-5 showed less coking compared to NaY and MCM-41. Through the catalytic cracking with HZSM-5 at 600 °C, the yield of liquid product

was 38.5 wt. %, with 24.0 wt. % water content (not shown) and 14.5 wt. % of bio-oil; the yield of monocyclic aromatic hydrocarbons was 3.0wt. % (all dry biomass basis).

Acknowledgments

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