

NiMo/HBETA as Catalysts with Dual Functions Beneficial to Waste Tyre Pyrolysis

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The world is running out of petroleum with the increasing demand in the fuel consumption. Oil from waste tyres is one of interesting fuels to be developed, and pyrolysis is one of the suitable processes to utilize these waste tyres. In the pyrolytic oil from waste tyres, sulphur compounds are largely present in the form of polar-aromatics such as thiophene, benzothiophene, and dibenzothiophene, which can cause poisoning of the active sites on the catalyst. Moreover, if sulphur-containing oils are used as fuels, SO₂ that is a pollutant can be produced during combustion. In our previous work, Ni/HBETA was proven to be a potential waste tyre pyrolysis catalyst; thus, since NiMo is one of good desulphurization catalyst, it was also expected to have both pyrolysis and sulphur removal activities beneficial to waste tyre pyrolysis. The purposes of this work were to study the cracking ability as well as the desulphurization ability of NiMo loaded on HBETA catalyst for tyre pyrolysis, and to study the change of sulphur compounds when the compositions of the bimetallic catalysts are varied. The results showed that 5%Ni with 20%Mo catalyst had both good cracking and desulphurization abilities. The pyrolytic oil obtained from the catalyst had lower polar-aromatic and sulphur contents than those from the other catalysts. It was mainly composed of full-range naphtha which had large amounts of saturated hydrocarbons and mono-aromatics. Moreover, the sulphur compounds in the pyrolytic oils were analyzed by GC-MS (TOF). It was found that sulphur compounds were mainly in the kerosene range (C₁₀–C₁₃) such as benzo[b]thiophene, 2,7-dimethyl, benzo[b]thiophene, 2-ethyl-7-methyl- and dibenzothiophene.

1. Introduction

The increases in petroleum demand and price have driven the world to seek for alternative fuels. Waste tyres discarded in a gigantic quantity are an adequate supply for producing oil substitute through pyrolysis process. Waste tyre pyrolysis is the thermal degradation of waste tyre in the absence of the oxygen. Three products; pyrolytic gas, oil, and char (Chang, 1996) can be obtained. Pyrolytic oil can be used directly as a chemical feedstock or fuel oil substitute. In the pyrolytic oil from waste tyres, sulphur compounds are largely present in the form of polar-aromatics such as thiophene, benzothiophene, and dibenzothiophene (Pakdel et al., 2001), which can cause poisoning of the active sites of a catalyst. Moreover, if fuels contain sulphur, SO₂ that is a pollutant is produced during combustion. With this reason, many countries limit the amount of sulphur content in transportation fuels. Therefore, not only are the cracking of heavy hydrocarbons to light hydrocarbons as well as hydrogenation and ring-opening needed, but hydrodesulphurization is also important in the pyrolysis process. There were many researchers that used catalysts to improve the quality and quantity of the pyrolytic products. Bifunctional catalysts (metals supported on zeolites) become interesting to order to improve the efficiency of catalytic pyrolysis. Noble metals supported on acidic zeolite were used to optimize the high value products because noble metals can promote hydrogenation and ring opening (Du et al., 2005). For examples, Pt/HBETA showed good ability for polar-aromatic reduction, leading to a decreasing amount of sulphur in the pyrolytic oil (Düng et al., 2009). With the high prices of the noble metals, some of non-noble metals were used instead of noble metals. Ni based catalysts have been effective for many reaction such as pyrolysis and partial oxidation

(Tagawa et al., 2013). Saeaeah et al. (2012) found that Ni loaded on HBETA zeolite increased the cracking ability of HBETA in tyre pyrolysis because it increased the gas yield with a consequent decrease in the oil yield. They also found that the sulphur content in oil was further reduced by using Ni/HBETA catalyst. Ni/HBETA also increased the quality of the pyrolytic oil by decreasing long residue and then increasing the full range naphtha. They found that some of non-noble metals can be used to substitute noble metals when used in a higher amount. Moreover, bimetallic catalysts, such as NiMo, NiW, CoMo, and CoW (Mo and W as second metals doped to Ni and Co) supported on Al_2O_3 are normally used in hydrodesulphurization process (Torres-Mancera et al., 2005). Therefore, in this work, Mo was chosen as a second metal promoter on Ni/HBETA since the pyrolysis of waste tyre requires both cracking and desulphurization functions of the catalyst. The purposes of this work were, therefore, to study the cracking ability as well as the desulphurization ability of modified Ni/HBETA catalysts (bimetallic NiMo) in tyre pyrolysis, and to study the change of sulphur compounds when the compositions of the bimetallic catalysts were varied. Ni was fixed at 5 wt%, whereas the loading of Mo was varied to 10 and 20 wt%. Types and amounts of sulphur compounds in the oil were also studied.

2. Experimental

2.1 Catalyst Preparation

The zeolite, which is HBETA ($\text{Si}/\text{Al} = 13.5$) obtained from Tosoh Company in Singapore, was calcined at 600 °C for 5 h with a heating rate of 2 °C/min. To prepare the bimetallic catalysts, NiMo/HBETA, appropriate amounts of nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and ammonium heptamolybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot \text{H}_2\text{O}$) were loaded on the HBETA zeolite by incipient wetness impregnation technique. The composition of bimetallic catalysts was varied as 10 and 20 wt% of Mo with the fixed amount of Ni at 5 wt%. After that, the samples were dried at 110 °C for 3 h in an oven, and calcined at 500 °C for 3 h with the heating rate of 5 °C/min and further reduced at 800 °C for 1 h to obtain the catalysts in the bimetallic form.

2.2 Catalyst Characterization

X-ray Diffraction (XRD) was used to verify the metallic form of catalysts. X-ray diffraction (XRD) patterns were taken by using a Bruker X-ray diffractometer system (D8 Advance) equipped with a 2.2 kW Cu anode long fine focus ceramic X-ray tube for generating a $\text{CuK}\alpha$ radiation (1.5405 Å). The detector scans the peak position from the sample as a function of 2θ by starting at the 10° to 60° (2θ) range and a scan speed of 0.02° (2θ)/0.6 s. The XRD patterns were matched to the standards to identify crystalline phases. Temperature-programmed reduction (TPR) was used to identify the reducibility of the impregnated catalysts and the metal-metal interaction. The TPR experiments were conducted from 30 °C to 850 °C.

2.3 Pyrolysis Experiment

There are 2 zones of pyrolysis reactor; that are, catalytic zone (the upper zone) and pyrolytic zone (the lower zone). The pyrolysis experiments were conducted according to the procedure in Dũng et al. (2009). First, 30 g of the waste tyre with sizes in the range of 8-18 mesh was loaded into the lower zone with a heating rate of 10 °C/min from the room temperature to final temperature. The final temperature of this zone was controlled at 500 °C and then kept for 90 minutes at the atmospheric pressure. In the catalytic zone of the reactor, 7.5 g of pellet catalyst was loaded and controlled at 350 °C. N_2 flow rate was controlled at 30 ml/min for purging the oxygen out of the system prior to pyrolysis and subsequently for carrying the pyrolysis product through two condensers and then to a gas sampling bag. These condensers were placed into the ice bath in order to collect the condensable products (pyrolytic oils). The gas sampling bag collected the non-condensable products (pyrolytic gases). Non-decomposable components of the tyres were collected as pyrolytic chars.

2.4 Product Analysis

Pyrolytic gases were analyzed by using a Gas Chromatography, Agilent Technologies 6890 Network GC system, using HP-PLOT Q column: 30 m x 0.32 mm ID and 20 µm film thicknesses. A detector was FID type using He as the carrier gas. Pyrolytic oil was separated into asphaltene (n-pentane insoluble) and maltene (n-pentane soluble), and then the maltene solution was fractionated using specific solvents (Šebor et al., 1999) into 5 fractions, which are saturated hydrocarbons, mono-aromatics, di-aromatics, poly-aromatics and polar-aromatics in a liquid chromatography column. The liquid fraction was analyzed using a Varian CP-3800 stimulated distillation gas chromatograph (SIMDIST GC) equipped with an FID, according to the ASTM D2887 method. Each fraction was classified according to its boiling point range, which are full range naphtha (< 200 °C), kerosene (200 - 250 °C), light gas oil (250 - 300 °C), heavy gas

oil (300 – 370 °C) and long residue (> 370°C). The sulphur compounds in the pyrolytic oil were determined using a Gas Chromatography equipped with a mass spectrometry of Time of Flight type (GC-TOF).

3. Results and Discussion

3.1 Characterization

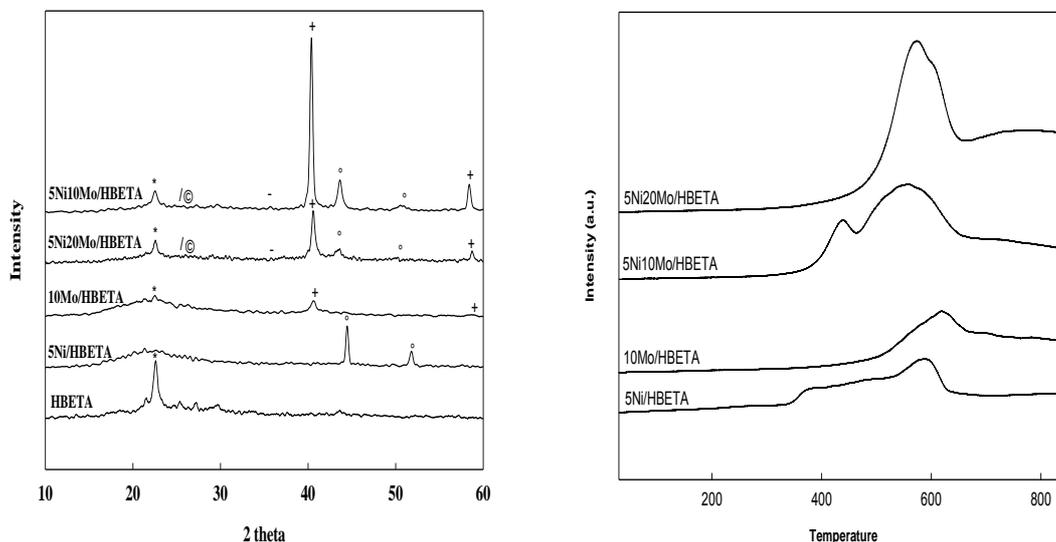
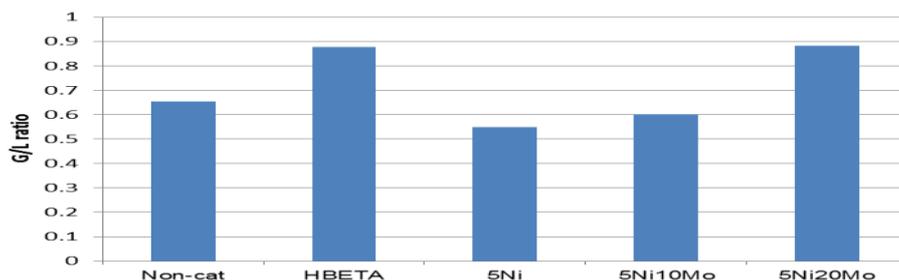


Figure 1: XRD (left) and TPR (right) obtained from modified Ni/HBETA catalysts in comparison with 10Mo/HBETA

Figure 1 illustrates XRD and TPR obtained from the modified Ni/HBETA catalysts. The XRD confirms that the bimetallic NiMo clusters (+ and 0) are formed on the zeolite. The TPR profile of 5Ni20Mo/HBETA catalysts show a strong Ni-Mo interaction peak whereas that of the 10 % Mo doping shows two strong interaction peaks. The strong interaction is believed to be responsible for the cracking and desulphurization abilities of 5Ni20Mo/HBETA catalyst.

3.2 Cracking ability

The results exhibit the qualities and quantities of the pyrolytic products from the Mo-doped Ni/HBETA catalysts. The product distribution can be shown by the ratio of gas to liquid in Figure 2. The solid product remains constant at about 40 wt%.



- * 5Ni = 5 wt% Ni on HBETA
- ** 5Ni10Mo = 5 wt% Ni- and 10 wt% Mo- loaded HBETA
- *** 5Ni20Mo = 5 wt% Ni- and 20 wt% Mo- loaded HBETA

Figure 2: G/L ratio obtained from modified Ni/HBETA catalysts

Figure 2 shows the ratio between gas and liquid obtained from the modified Ni/HBETA catalysts as compared to that of pure HBETA zeolite and the non-catalytic case or non-cat (thermal pyrolysis). The higher G/L ratio gave the higher the cracking ability because the heavy molecules can be cracked into

lighter molecules over the acid sites of the catalysts. For the 5Ni/HBETA catalyst, the reduction of the G/L ratio can be resulted from the interaction between the metal and the support. However, with using the bimetallic catalysts (NiMo), the G/L ratio increases with the increase of the amount of the Mo loading, which indicates that, the modified Ni/HBETA catalysts (5Ni10Mo/HBETA and 5Ni20Mo/HBETA) can increase the cracking ability from the monometallic 5Ni/HBETA catalyst. 5Ni20Mo/HBETA has the highest cracking ability among the others because it had the highest G/L ratio (0.88). Nevertheless, although Mo can enhance the cracking ability of the Ni/HBETA catalyst, the bimetallic catalysts still have the same cracking ability as the parent HBETA zeolite. Therefore, the doping of Mo to Ni/HBETA catalyst helps maintain the cracking activity of the parent zeolite.

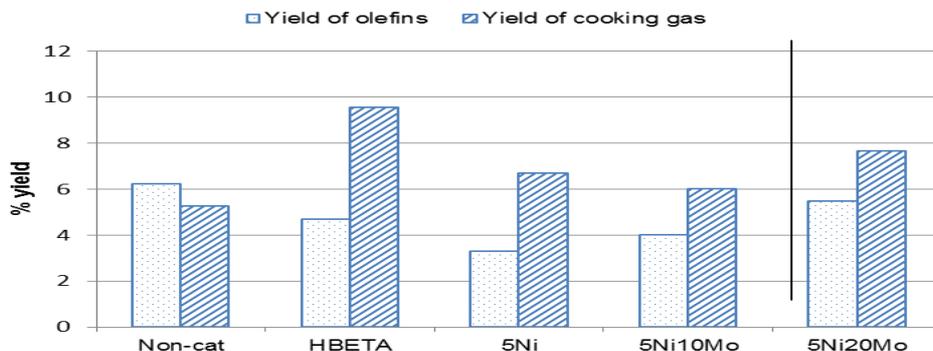


Figure 3: Yield of olefins and cooking gas obtained from pyrolysis with modified Ni/HBETA catalysts

Non-condensable gases are composed of gases in the range of C₁-C₅. Some of these gases are valuable petrochemical products such as olefins (ethylene and propylene), and cooking gas (propane mixed with mixed C₄). Figure 3 show the yield of these petrochemical gases obtained from modified Ni/HBETA catalysts. The results indicate that the non-catalytic case gives 6.25 and 5.27 wt% yield of olefins and cooking gas, respectively. With using the catalysts, the yields of olefins decrease in accordance with the increase in the yield of cooking gases. 5Ni/BETA gives the lowest yield of olefins; however, when the modified Ni/HBETA catalysts are used, the yields of olefins increase significantly. The yield of olefins increases with the increasing contents of Mo. The pure HBETA gives the highest yield of cooking gas (9.6 %) among the other catalysts; including the non-catalytic case. 5Ni/HBETA gives about 6.7 wt% yield of cooking gas. 5Ni10Mo/HBETA does not increase the yield of cooking gas whereas using 5Ni20Mo/HBETA increases the yield of cooking gas significantly. This can be concluded that although the bimetallic catalysts, especially 5Ni20Mo/HBETA, do not enhance the cracking ability, they can increase the yield of the valuable gases.

3.3 Quality of the pyrolytic oil

After asphaltene was separated from the liquid products of waste tyre pyrolysis, the maltene solutions were separated into 5 fractions; saturated hydrocarbons, mono-aromatics, di-aromatics, poly-aromatics and polar-aromatics, as shown in Figure 4, by using liquid column chromatography (Šebor et al., 1999). These 5 fractions were analyzed by using a SIMDIST-GC for the true boiling point curves that later were cut to the petroleum fractions; naphtha (< 200 °C), kerosene (200 - 250 °C), light gas oil (250 - 300 °C), heavy gas oil (300-370 °C), and long residue (> 370 °C)..

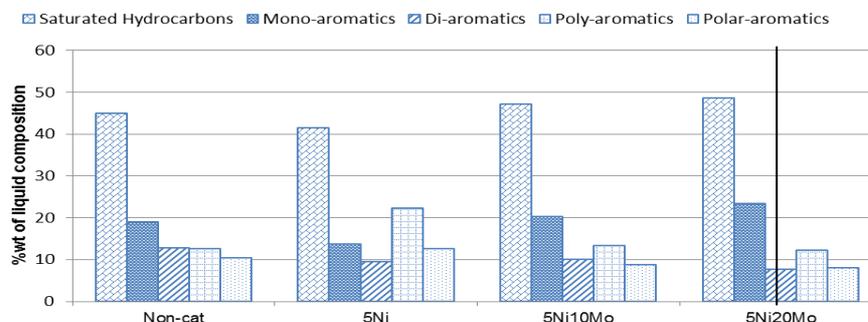


Figure 4: Chemical compositions in maltenes from using modified Ni/HBETA catalysts

Figure 4 indicates the chemical compositions in maltenes from various catalysts. With using 5Ni/HBETA, the light components (saturated hydrocarbons and mono-aromatics) decrease in conjunction with the increase in the heavy components (poly- and polar-aromatics). However, when the bimetallic catalysts (NiMo on HBETA) are used, saturated hydrocarbons and mono-aromatics increase dramatically in the same trend; resulting in the consequently decreases in poly- and polar-aromatics, which indicates the good abilities in cracking and ring-opening of the large aromatic molecules. The NiMo/HBETA catalyst, especially 5Ni20Mo/HBETA, gives the highest concentration of saturated hydrocarbons and mono-aromatics, which are about 48.6 % and 23.5 % by weight. It can be concluded that the modification of Ni/HBETA catalyst with Mo can increase the qualities of the pyrolytic oils because it can help to convert the heavy components such as poly- and polar aromatics to the lighter components (saturated hydrocarbons and mono-aromatics with a lower average carbon number) as compared with the non-catalytic case (Nor et al., 2013). Figure 5 shows the petroleum fractions in maltenes obtained from using modified Ni/HBETA catalysts. It can be seen that using the 5Ni/HBETA catalyst can increase the amount of full range naphtha. The results show that the bimetallic NiMo catalysts are likely to produce the light oils since 5Ni20Mo/HBETA gives the highest amount of the full range naphtha while 5Ni10Mo/HBETA gives the highest amount of kerosene. It can be seen that the higher the loading of the second metal (Mo), the higher full range naphtha is obtained. In addition, pure HBETA produces the heavier oils than all other catalysts. Therefore, it can be concluded that the promotion of Mo in the Ni/HBETA catalyst can improve the quality of oil.

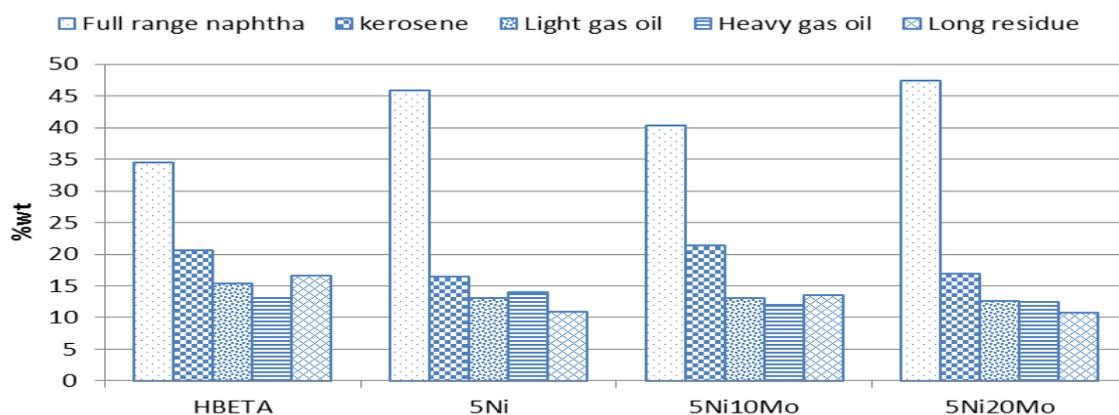


Figure 5: Petroleum fractions in maltenes obtained from using modified Ni/HBETA catalysts

3.4 Desulphurization ability

The sulphur contents in pyrolytic oil and sulphur deposition on spent catalysts were determined by a CHNS analyser, and the sulphur compounds in the pyrolytic oils were analyzed by GC-MS (TOF).

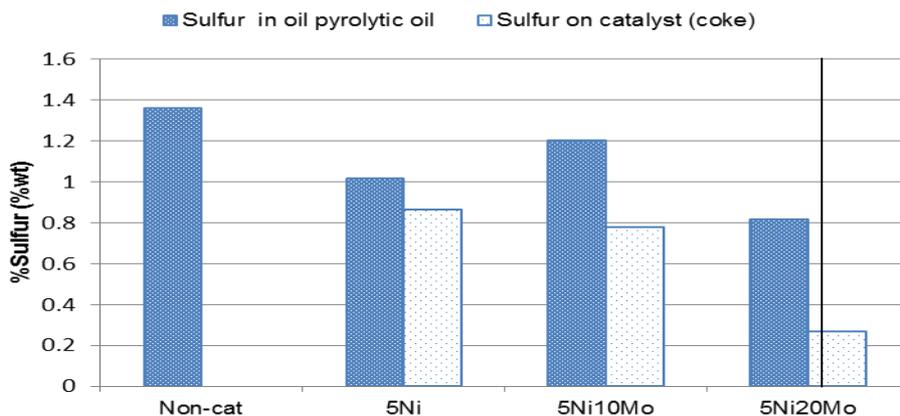


Figure 6: Sulphur contents (%wt) on spent catalysts and in the pyrolytic oils obtained from modified Ni/HBETA catalysts

Figure 6 shows the presence of sulphur contents obtained from the modified Ni/HBETA catalysts. The sulphur content in pyrolytic oil is about 1.36 %wt when none of the catalyst used. 5Ni/HBETA and all of modified Ni/HBETA catalysts show good hydrodesulphurization ability because they can reduce the sulphur content in the pyrolytic oil. When 5Ni/HBETA is used, it can reduce the sulphur content in the pyrolytic oil to 1.02 wt%, and sulphur content on the spent catalyst (coke) is reduced to 0.87 wt%. Using 5Ni10Mo/HBETA, the sulphur content in the pyrolytic oils increases in conjunction with the decrease in sulphur content on the spent catalyst, whereas 5Ni20Mo/HBETA gives the lowest sulphur contents in the pyrolytic oil (0.82 wt%) and the lowest sulphur contents on the spent catalysts (0.27 wt%) among all others. 5Ni20Mo/HBETA is a good catalyst for the sulphur reduction as indicated by the lowest sulphur contents in oil. This can be suggested that 5Ni20Mo/HBETA can breakdown the C-S bonds due to the hydrodesulphurization activity (Songdong et al., 2012). Moreover, it can be concluded that 5Ni20Mo/HBETA catalyst can produce high quality of oil that contains low sulphur content.

The sulphur compounds in the pyrolytic oils were analyzed by GC-MS (TOF). The sulphur compounds in the oil obtained from 5Ni20Mo/HBETA are mainly in the range of C₅-C₉, such as thiophene, 2-(1-methylethyl)-, benzo[b]thiophene, 4-methyl and benzo[b]thiophene whereas the sulphur compounds from the non-catalytic case are mainly in the range of C₁₀-C₁₃, such as benzo[b]thiophene, 2,7-dimethyl, benzo[b]thiophene, 2-ethyl-7-methyl- and dibenzothiophene.

4. Conclusions

The effects of modified Ni/HBETA catalysts on the quantity and quality of pyrolysis products were investigated. The results showed that the modification of Ni/HBETA catalyst with both 10 % and 20 %wt of Mo can increase the quality of pyrolytic oil, which contained a high amount saturated hydrocarbons and light petroleum fractions. Moreover, 5Ni20Mo/HBETA also had a good desulphurization ability because it gave the lowest sulphur contents in oil (0.82 wt%).

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