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Impact of HY as an Additive in Pd/HBETA Catalyst on Waste Tire Pyrolysis Products

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Addition of HY as a zeolite additive into Pd/HBETA used in the catalytic pyrolysis of waste tire was studied in this work. Pd/HBETA was used as the main catalyst because of its ability on improving the quality and quantity of light fractions (full range naphtha, and kerosene). Due to the different porosity and acid properties of the two zeolites, HY was therefore used as the additive in the main catalyst to improve the cracking performance and the quality of oil product. The amount of Pd on HBETA was fixed at 1 %wt whereas the amount of HY was varied at 10 and 20 %wt. The obtained products were analyzed via gas chromatograph, liquid chromatograph, and SIMDIST-GC, while the catalysts were characterized by SAA, and TG-DTA. The results indicated that the HY as a catalyst itself can improve the quality and quantity of oil product in the range of naphtha fraction. After adding HY as the additive in Pd/HBETA, the quality and quantity of light gas oil fraction were improved with the increasing saturated hydrocarbons in this fraction. In addition, the light olefins production was gradually enhanced when the HY was added in Pd/HBETA. These results revealed that the nature of HY and specific pore volume were two important factors influencing the products.

1. Introduction

Due to the growth of transportation, a numerous number of waste tires mainly from private vehicles are generated and dumped in the landfills that create many problems, and affect to the environment. One of the most commonly found problems of waste tire is the non-biodegradability of tires. As a result, waste tires which consist of heavy hydrocarbon compounds may possibly be processed to lighter products used in some applications. One of the methods for dealing with the tire's problems is pyrolysis process. Pyrolysis is the thermal degradation in the absence of oxygen that generates gas, oil, and char from waste tires. Pyrolytic gases can be used to provide process energy. Pyrolytic oils can be used as a fuel substitute or chemical feed stock, whereas char can be used as a smokeless fuel or low-grade activated carbon. In refineries, acidic zeolite catalysts are widely used in the fluid catalytic cracking unit because they have potential to convert heavy feed into lighter products by cracking reactions on the acidic sites. Williams and Brindle (2002) reported that the presence of catalysts increased the yield of gas and coke formation on the catalyst with a consequently reduced yield of oil, whereas the yield of char remained constant. Furthermore, the binary and multi systems of molecular sieve have potential for FCC gasoline upgrading (Fan et al., 2005). They succeeded in using a quadruple composite catalyst composed of SAPO-11/HMOR/HBETA/HZSM-5, which can increase the liquid yield and lower the coke content. The Y-BETA binary zeolites, which Y zeolite was the main zeolite whereas BETA zeolite was the additive in this binary zeolite, had a suitable potential for the

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hydrocracking of vacuum gas oil which can increase the heavy naphtha and jet fuel yields (Zhang et al., 2010). Bifunctional catalysts have become interesting in the pyrolysis of tires with the fact that the noble metals, especially Pt and Pd, can promote hydrogenation, dehydrogenation, heteroatom removal, and ring-opening reactions. In addition, they can also reduce the catalyst deactivation. Pt/HBETA has high polar-aromatic reduction activity because Pt metal sites promote hydrogenation reaction which the polar-aromatics are converted to saturated hydrocarbons, and then, the saturated products are further cracked on the acidic sites (Dũng et al., 2009). Moreover, Pintoo (2008) showed that Pd/HBETA can reduce heavy fractions to lighter fractions, which resulted in a high amount of saturated hydrocarbons, suitable for kerosene production. Taking the advantage of composite catalysts, HY (Si/Al = 7.5) was selected in this work as the additive in the Pd/HBETA (Si/Al = 13.5) catalyst proven effective for tire pyrolysis. Since HBETA used as the support in Pd/HBETA has a higher Si/Al ratio (higher acid strength but lower acid density), mixing HY into the Pd/HBETA catalyst was therefore expected to provide a number of acid sites to Pd/HBETA. The purpose of this work was thus to investigate the addition of a second microporous zeolite (HY) as an additive into the main catalyst (Pd/HBETA), expectedly influencing to the pyrolysis products, especially light oil fractions. The loaded amount of Pd metal was fixed at 1 wt% on HBETA whereas the amount of HY additive was varied at 10 wt% and 20 wt%. The pyrolysis products were investigated in terms of the quality and quantity of the gas and liquid products.

2. Experimental

2.1 Catalyst preparation

The zeolites, HBETA (Si/Al = 13.5) obtained from Tosoh Company in Singapore were calcined at 600 ºC for 5 h with a heating rate of 2 ºC/min for HBETA and at 500 ºC for 3 h with a heating rate of 5 ºC/min for HY. To prepare the bi-functional catalyst (1 wt% Pd/HBETA), the appropriate amount of palladium (II) nitrate dihydrate was loaded on the HBETA zeolite by incipient wetness impregnation technique. After that, the sample was dried at 110 ºC for 3 h in the oven, and calcined at 500 ºC for 3 hr with the heating rate of 5 ºC/min and further reduced at 400 ºC for 2 h to obtain the bi-functional catalyst in the metal form. To prepare composite catalysts, 10 wt% and 20 wt% of HY (Si/Al = 7.5) also purchased from Tosoh were physically mixed with the reduced Pd/HBETA catalyst thoroughly prior to use.

2.2 Pyrolysis experiments

The pyrolysis was performed in the similar reactor as conducted in Dũng et al., 2009. A 30 g of a scrap tire thread sample (Turanza GR-80 215/55R16) was introduced to the lower zone of the reactor whereas the upper zone contained 7.5 g of 40-60 mesh catalyst granules. The temperature of pyrolytic zone was ramped from room temperature to 500 ºC with a heating rate of 10 ºC/min, while the temperature of catalytic zone was controlled at 300 ºC and kept for 90 minutes at atmospheric pressure. The controlled N_2 flow rate of 30 ml/min was continuously flown to sweep the oxygen out of the system and to carry the pyrolytic products through a condenser system and a gas sampling bag. The condensers were placed into the ice-bath to collect the condensable products. The non-condensable products were passed through the condenser system and collected in the Tedlar® gas sampling bag.

2.3 Product analysis

Pyrolysis gas samples 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. A liquid product was separated into asphaltene (n-pentane insoluble) and maltene (n-pentane soluble), which then the latter was fractionated using specific solvents (Šebor et al., 1999) into saturated hydrocarbons, mono-aromatics, di-aromatics, poly-aromatics and polar-aromatics in a liquid chromatography column. The liquid fraction were further analyzed using a Varian CP-3800 stimulated distillation gas chromatograph (SIMDIST GC) equipped with an FID, according to the ASTM D2887 method, for the true boiling point curves. Each fraction was classified according to it boiling point range, which are full range naphtha (<200 ºC), kerosene (200-250 ºC), light gas oil (250-300 ºC), heavy gas oil (300 ºC-370 ºC) and long residue (>370 ºC).

2.4 Catalyst characterization

The amount of coke formation on spent catalysts was determined by using the Thermogravimetric/Differential Thermal Analysis (TG/DTA). The samples were heated from the room temperature to 800 °C with the heating rate of 10 °C/min. Nitrogen and oxygen flow rates were set to 100 ml/min and 200 ml/min, respectively. The surface area and specific pore volume were determined by using Thermo Finnigan, Sorptomatic 1990 system in the Brunaueer-Emmett-Teller (BET) and Horvath-Kawazoe method, respectively.

3. Results and discussion

The distribution of products, which are gas, liquid or oil, and solid, obtained from pyrolysis can be presented using G/L ratio as revealed in Figure 1. Since a higher gas production indicates a higher cracking activity of a catalyst, a high G/L ratio reflects a high cracking activity as well. The results represent that the HBETA zeolite can increase the G/L ratio from 0.40 (from thermal pyrolysis) to 0.63 whereas, the HY zeolite slightly increases the G/L ratio from that of the non-catalytic case. The reason why the G/L ratio of HBETA is higher than that of HY is because the HBETA zeolite has stronger acid strength (Si/Al ratio = 13.5) than the HY zeolite (Si/Al ratio = 7.5). Moreover, the use of Pd/HBETA as a bi-functional catalyst in pyrolysis drastically increases the value of G/L ratio to 0.94, which indicates the improvement of cracking activity by Pd loading. In contrast, the G/L ratio is drastically reduced to 0.88 and 0.85 with the addition of HY at 10 wt% and 20 wt% in Pd/HBETA (denoted as 1PB10Y and 1PB20Y, respectively). Since HBETA has higher acid strength than HY, the reduction in the G/L ratio is possibly caused by the reduction in acid strength as a result of the dilution by HY addition. Moreover, the lower carbon deposition on the spent composite catalysts in Table 1 also confirms the reduction of cracking activity with the addition of HY.

Table 1: Physical properties of fresh catalysts and coke deposition on spent catalysts

Catalyst	Si/Al	Surface area (m^2/g)	Specific pore volume* (cm^3/g)	Coke on spent catalyst (%wt)
HBETA	13.5	604.3	0.492	28.5
HY	7.5	590.4	0.576	34.5
Pd/HBETA	-	454.6	0.484	33.3
1%Pd/HBETA+10%HY (1PB10Y)	-	499.3	0.546	33.1
1%Pd/HBETA+20%HY (1PB20Y)	-	525.4	2.961	27.5

*analyzed by using Horvath-Kawazoe method

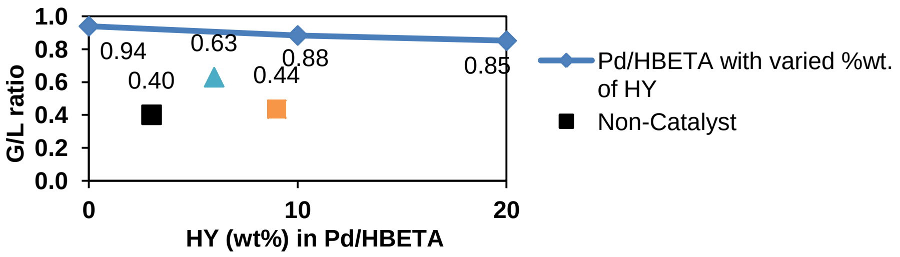


Figure 1: G/L ratio obtained from pyrolysis with varied percentages of HY in Pd/HBETA

A decrease in coke formation usually reflects a decrease in cracking activity; although, the increase in the pore volume would have allowed more coke to be formed. Despite of the slight reduction in cracking activity, the composite catalysts are expected to lead to the improvement of product qualities which is discussed below.

3.1 Gaseous products

The yield of light olefins and cooking gases (propane and mixed C4), which are considered as the valuable gas products, are illustrated in Figure 2. The results indicate that the Pd/HBETA catalyst itself produces the yield of light olefins (3.4 wt%) and cooking gases (11.2 wt%), which is improved from the pure HBETA and HY cases. Among all catalysts, HY gives the lowest light olefins and cooking gas yields. However, with the addition of 10 wt% and 20 wt% HY in Pd/HBETA, the yields of light olefins are gradually increased to 4.1 wt% and 4.3 wt%, respectively, which are also higher than those of both pure zeolite and the non-catalytic cases. Thus, it appears that the HY additive helps improving the light olefins yield, and the synergy between adding the zeolite additive with higher acid density into the pyrolysis catalyst having higher acid strength support is apparent as well. In contrast, it can be observed that the addition of HY does not improve the yield of cooking gas. According to Figure 2, the cooking gas yields obtained from the composite catalysts lie in between those of HBETA and HY; thus, it seems that no synergy between HBETA and HY occurs toward the production of cooking gas. In conclusion, Pd/HBETA without the additive seems to be the best catalysts for cooking gas production since it can produce the highest yield of cooking gas of 11.2 wt%, whereas 20 wt% of HY in Pd/HBETA is the best catalyst combination for light olefins production since it can produce the highest yield of light olefins of 4.3 wt%.

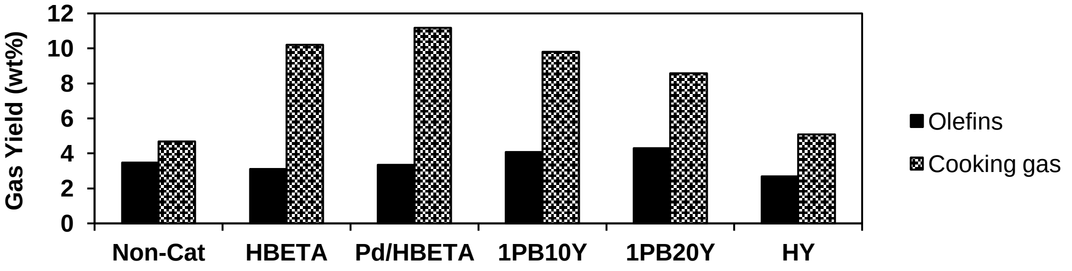


Figure 2: Yield of olefins and cooking gas in the gas products obtained from pyrolysis with varied percentages of HY in Pd/HBETA

3.2 Oil products

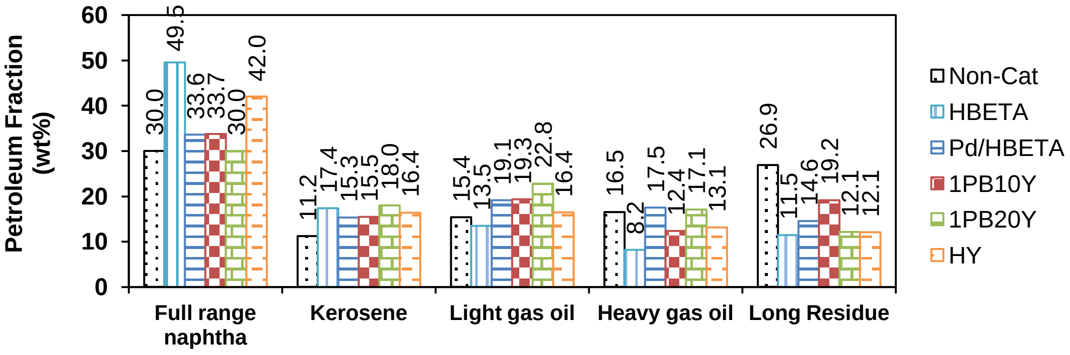


Figure 3: Petroleum fractions in derived oils obtained from pyrolysis with varied percentages of HY in Pd/HBETA

From Figure 3, the use of pure zeolites (both HBETA and HY zeolites) helps to improve the quantity of lighter products, which are the full range naphtha and kerosene fractions as compared to pyrolysis without a catalyst. Meanwhile, the use of bi-functional catalyst (Pd/HBETA) produces 33.6 wt% naphtha and 15.3 wt% kerosene, which are lower than the pure HBETA case. With the addition of HY in Pd/HBETA, naphtha production further decreases whereas light gas oil fraction increases. It suggests that the additive with higher acid density and lower acid strength results in a negative result on cracking activity and then on the light oil production. The Pd/HBETA catalysts with or without the addition of HY cause the lower cracking performance than the pure zeolites since the long residue fraction remains high as compared to the pure zeolites. Nevertheless, their cracking performance is improved as compared to the pyrolysis without a catalyst. Therefore, the use of Pd/HBETA catalysts with and without the addition of HY may not be as proper as the pure zeolites for full range naphtha production. However, they might be more appropriate for gas oils production since they can crack heavy fractions to gas oil fractions. Nevertheless, the quality of each fraction must be next investigated below for a suitable application.

The chemical compositions in Figure 4 indicate that the Pd/HBETA catalyst produces the highest concentration of saturated hydrocarbons among all Pd-loaded HBETA catalysts. The results clearly show that after adding 10 wt% and 20 wt% of HY in Pd/HBETA, the saturated hydrocarbon content is gradually reduced from 78.6 wt% to 76.5 wt% and to 58.1 wt%, whereas the mono-aromatics are increased from 4.1 wt% to 5.3 wt% and to 15.4 wt%, respectively. Nevertheless, these compounds must be considered along the range of petroleum fractions to determine the oil quality. For example, the full range naphtha must contain a sufficiently high quantity of saturated hydrocarbons for using as the feedstock for cracking process, or contains a sufficiently high quantity of aromatics compounds for using as the feedstock for aromatics separation or for blending in the gasoline pool. The analysis of the oil quality is further discussed below.

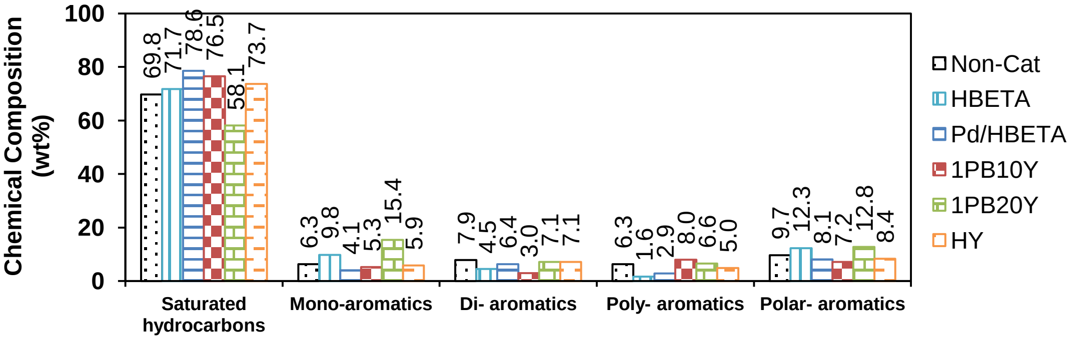
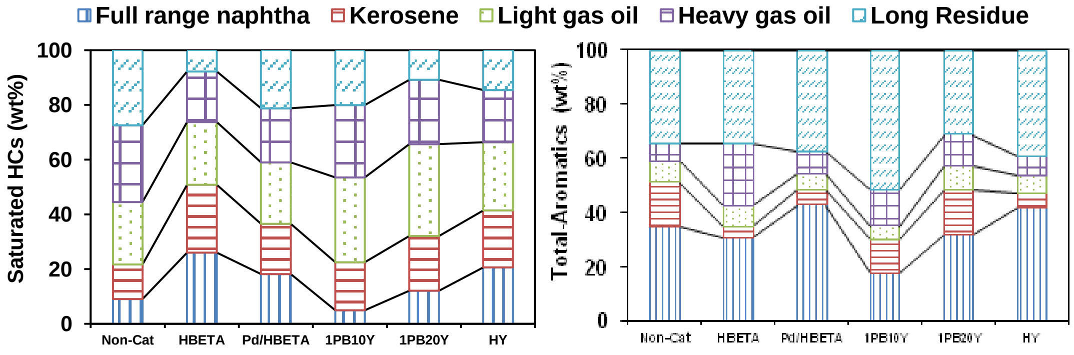


Figure 4: Chemical compositions of maltenes obtained from pyrolysis with varied percentages of HY in Pd/HBETA

In order to determine the quality of petroleum fractions, the saturated hydrocarbons and total-aromatics distributed in each petroleum fraction must be examined, which can be observed in Figure 5. As compared to the pure HBETA zeolite, the Pd/HBETA catalyst reduces the saturated hydrocarbons in light fractions (full range naphtha, kerosene, and light gas oil fractions), but it enhances the total aromatics in naphtha fraction instead. After adding an additive HY in Pd/HBETA, the quality of naphtha fraction is reduced because both of saturated hydrocarbons and total aromatics are reduced. However, saturated hydrocarbons in the light gas oil fraction are gradually improved with varied percentages of HY in Pd/HBETA. These can be stated that the addition of HY in Pd/HBETA can improve the quality of light gas oil fraction, which can be beneficial for the production of higher cetane number diesel. Therefore, it can be concluded that the addition of HY in Pd/HBETA can improve the quality of light gas oil fraction, which can be used for the diesel production. This enhancement of light gas oil quality by adding 20 wt% HY in Pd/HBETA can be applicable when the market demand for diesel is reached.

In summary, the addition of HY results in the increase in the total number of acid site and the enlargement of pore volume of the Pd/HBETA catalyst. Although the slight decrease in cracking activity is observed due to the decrease in overall acid strength, it enhances the light olefins production and the quality of gas oil which is contributed from the consequent increase in acid density (higher number of H^+ transfer) upon the HY addition. Moreover, the decrease in overall acid strength of the composite catalysts causes the reduction in coke deposition (although the increase in pore volume would have allowed a greater amount of coke to be formed) in conjunction with the increase in the production of large molecules, like mono-aromatics, from aromatization of saturated hydrocarbons.



4. *Figure 5: Distribution of saturated hydrocarbons (left) and total-aromatics (right) in petroleum fractions obtained from pyrolysis with varied percentages of HY in Pd/HBETA*Conclusions

The effects of 10 wt% to 20 wt% HY added in Pd/HBETA on the quantity and quality of pyrolysis products were investigated. The Pd/HBETA raises the total-aromatics content in naphtha fraction which can be used as feedstock for aromatics separation or blended in a low aromatics-containing gasoline pool. The addition of HY in Pd/HBETA reduced the cracking activity resulting to the reduction of naphtha quantity. However, the quality and quantity of gas oil fractions were improved instead, especially when 20 wt% HY was added in Pd/HBETA. Moreover, it enhanced the yield of light olefins despite the Pd/HBETA, pure zeolites, and non-catalyst case cannot do, which was caused by the synergy effect occurred by the addition.

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