CHAPTER VII
CATALYTIC PYROLYSIS OF WASTE TIRE OVER DOUBLE BEDS OF SILICA MCM-48 AND ZEOLITES

7.1 Abstract

Mesoporous have been used as a catalyst to decrease large aromatic hydrocarbons in tire-derived oil; however, the large pore size of catalyst does not have a shape-selectivity to enhance some desired products. Therefore, it is interesting to use the combination of mesoporous and microporous as a catalyst. In this work, mesoporous Si-MCM-48 was placed as a lower bed catalyst while a zeolite (HBETA, HY, or HZSM-5) was placed consecutively as an upper bed catalyst. The effects of zeolites properties, which are acidity (HBETA and HY) and pore size (HZSM-5 and HBETA), were investigated. The pyrolysis of waste tire was conducted in a bench-scale reactor. The catalysts were characterized by using SAXS, XRD, BET, TPD-NH_3, and TGA. Additionally, the products were analyzed by using GC×GC-TOF/MS, SIMDIST-GC, and S analyzer. As the results, the single bed of Si-MCM-48 decreased large molecules such as di- and poly-aromatic hydrocarbons in tire-derived oil due to its the large pore size. For the effect of acidity, the use of HY that had a higher acid density as the upper bed catalyst resulted in a higher formation of poly-aromatic hydrocarbons, and provided a lower concentration of petrochemicals than using HBETA in the same purpose. It can be explained that a higher density of acid sites of a catalyst in the second bed resulted in the undesirably-higher formation of large aromatic hydrocarbons than a lower acid density. Additionally, the sulfur content in tire-derived oil of both cases does not change significantly. For the effect of pore size, HZSM-5 (5Å) promoted the activity of cracking di- and poly-aromatic hydrocarbons, and gave a higher concentration of petrochemicals than HBETA (7Å) due to the medium pore size of HZSM-5 that has a limitation to form large molecules. Additionally, the strength of acid sites of HZSM-5 helped to promote cracking activity on the external surface.

7.2 Introduction

Waste tires, indegradable materials, are difficult to manage. The lifetime of waste tires in a landfill span in the period of 80 -100 years (Martinez *et al.*, 2013). Therefore, pyrolysis of waste tires is an interesting process to transform waste tires to valuable products, such as gas and oil. Tire-derived oil is remarkable product in the process. It is an aromatic-based hydrocarbon mixture; however, it usually consists of some large aromatic hydrocarbons, sulfur compounds and small amounts of petrochemicals. The oil consists of about 25 wt.% large aromatic hydrocarbons (di- and poly-aromatic hydrocarbons) in maltenes (Yuwapornpanit *et al.*, 2015). The presence of large aromatic hydrocarbons and sulfur compounds in fuels not only destroys the engines, but also increases the high amount of toxicity in the environment due to the incomplete combustion and SO_x emission. Moreover, petrochemicals such as benzene, toluene, xylenes, ethylbenzene, and cumene in tire-derived oil are interesting products because they are widely used as raw materials in petrochemical industry.

Previously, the uses of mesoporous MCM-41 and MCM-48 catalysts were successful in decreasing the large molecules in tire-derived oil. Dũng *et al.* (2009a) found that MCM-41 catalyst can reduce the amount of poly- and polar-aromatic hydrocarbons in tire-derived oil, similar to MCM-48 catalyst as reported by Witpithomwong *et al.* (2011). However, mesoporous catalysts do not have a shape-selectivity for small molecules due to its large pore size. On the other hand, zeolites that are microporous materials, are widely used in the variety of reactions because of their shape selectivity. Previously, several researchers used zeolites as catalysts in waste tire pyrolysis. Olazar *et al.* (2008) studied acid catalysts (HZSM-5 and HY) on pyrolysis of scrap tire. The authors found that HZSM-5 has a medium pore size and a fraction of strong acid sites. It was able to crack mono-aromatic hydrocarbons (C_{10}^-). Moreover, it can enhance the BTX production, resulting from olefins condensation in pores by Diel-Alder reaction; however, heavier aromatic hydrocarbons cannot be formed due to the limitation of pore size, whereas HY that has a larger pore size enhanced the formation of heavier aromatic hydrocarbons due to high hydrogen transfer capacity in pores. Muenpol *et al.* (2015) have studied the effect of pore size

catalyst (HZSM-5 and HBETA) in waste tire pyrolysis. They found that HBETA gave about 61 % petrochemicals in gasoline, which was more greatly than HZSM-5, indicating that the large pore size of HBETA was more suitable to produce petrochemicals in tire-derived oil than the medium pore size of HZSM-5. Moreover, in terms of sulfur removal, HZSM-5 significantly decreased benzothiophenes and benzothiazoles than HBETA because HZSM-5 has a medium pore size, which has less capacity to form heavier compounds.

Moreover, some researchers studied the design of double bed catalyst that takes advantage of performing reactions into two consecutive steps in one reactor. For examples, Beretta *et al.* (1996) used double bed of cesium-promoted $Cu/ZnO/Cr_2O_3$ and ZnO/Cr_2O_3 catalysts to improve the production of methanol and isobutyl alcohol mixtures from synthesis gas (H_2/CO). The first bed was packed with a $Cs/Cu/ZnO/Cr_2O_3$ catalyst, and the second bed was installed with $Cs/ZnO/Cr_2O_3$. They found that the first bed highly produced C1 - C3 oxygenated intermediates whereas the second bed helped to convert those intermediates into higher alcohols, especially isobutanol (1.88 mol/kg of catalyst/h). Moreover, Ning *et al.* 2000 also used double-bed catalysts to produce alcohol from synthesis gas. The authors found that Cu/Fe catalyst as the first bed and ZnO/Cr_2O_3 as the second bed highly improved the production of higher alcohols.

This work studied the double beds of mesoporous Si-MCM-48 and microporous (HBETA, HY, and HZSM-5) as catalysts by placing Si-MCM-48 as the lower bed, aiming to firstly decrease large aromatic hydrocarbons in tire-derived oil, and a zeolite was placed consecutively as the upper bed to investigate whether or not petrochemical productions and desulfurization in tire-derived oil can be enhanced. Moreover, as the upper bed catalysts, HBETA and HY were used to investigate the effect of acid density, and HZSM-5 and HBETA were used to investigate the effect of pore size and acid strength.

7.3 Methodology

7.3.1 Catalyst Preparation

NH_4-BETA (Si/Al=14), HY (Si/Al=7.5), and HZSM-5 (Si/Al=15) were purchased from TOSOH Company (Singapore). NH_4-BETA was calcined at 600 °C for 2 h with 2 °C/min. HY and HZSM-5 was calcined at 500 °C for 3 h with 10 °C/min.

For the synthesis of Si-MCM-48, tetraethoxysilane (TEOS), aluminum isoproproxide, cetyltrimethyl-ammonium bromide (CTAB), NaOH, aqueous ammonia (aq. NH_3), and ethanol were used as reactant. The Si-MCM-48 catalyst was synthesized at room temperature, following the a modified Stöber synthesis method (Kibombo et al., 2014). The molar composition of gel was 0.41 CTAB: 11 aq.NH_3: 1.0 TEOS: 53 Ethanol: 344 H_2O. Ethanol (25 ml), CTAB (1.2 g), aq. NH_3 (6 mL) and TEOS (1.8 mL) were sequentially added into deionized water (50 mL), and stirred for 4 h. After synthesis, the catalyst was filtrated and washed with deionized water. After that, the catalyst was dried in a 80°C oven for overnight, and calcined for 6 h in air at 540°C with the heating rate 2°C/min. Finally, all catalyst powders were pelletized, crushed, and sieved into the particle size range of 40-60 mesh.

7.3.2 Catalyst Characterization

The small-angled X-ray scattering pattern of mesoporous Si-MCM-48 was obtained using a Rikagu TTRAXIII diffractometer equipped with Cu Kα radiation at 50 kV and 300 mA. The experimental conditions were set with 0.02° of sampling width, 2°/min of scan speed, and 2.0-6.0° of scan angles. Additionally, the structures of zeolites were confirmed by using a Bruker X-ray diffractometer equipped with CuKα radiation operated at 40 kV and 30 mA. The diffraction peaks were scanned with 5 - 65° of scan angles and 5°/min of scan speed. The nitrogen adsorption/desorption isotherm, pore size distribution, pore diameter, specific surface area, and pore volume were determined by using a ThermoFinnigan/Sorptomatic 1990 instrument. TPD-NH_3 profiles were obtained using Thermo Finnigan, TPDRO 1100 Analyzer. The samples were pretreated at 300 °C for 3h under a Helium flow of

20 mL/min. After that, they were analyzed with 10 % NH_3 in Helium balance heated to 800 °C with the heating rate of 10 °C/min. The desorbed gases were analyzed by TCD detector. Thermogravimetric/Differential Thermal Analysis, TG/DTA was used to determine the amount of coke formation on spent catalysts. The temperature was ramped from 50 to 900 °C with 10 °C/min heating rate. LECO®Elemetal Analyzer (TruSpec®S) was used to measure the sulfur content in spent catalysts.

7.3.3 Waste Tire Pyrolysis

The same pyrolysis system was employed in the experiments, following the method set by Dũng *et al.* (2009b). 30 g of waste tyre sample was loaded into pyrolytic zone, and catalyst was loaded into the catalytic zone. In addition, there are two cases for placing the catalyst: that are, single bed and double bed catalyst. The upper bed catalyst was varied (HBETA, HY, or HZSM-5), and a lower bed catalyst was fixed to Si-MCM-48 as shown in Figure 7.1. Nitrogen was flown through the reactor at 30 ml/min. Heated with the heating rate of 10 °C/min from room temperature, the pyrolytic zone was operated at 500 °C, and the catalytic zone was operated at 350 °C catalytic zone. The liquid product was collected in condensers immersed in an ice bath. The gas product was collected in a gas sampling bag, whereas the solid product remained in the pyrolytic zone of reactor.
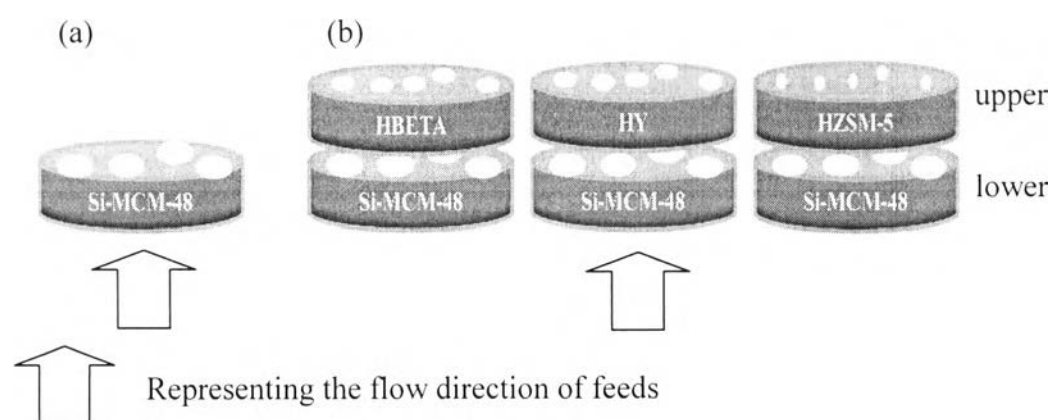

Figure 7.1 Placement of catalysts: (a) a single bed of Si-MCM-48, and (b) a double bed of Si-MCM-48 and a zeolite.

7.3.4 Product Analysis

The composition of gas was 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 thickness. A detector used was FID type. n-pentane was added into a liquid product in the liquid product/n-pentane weight ratio of 40:1 for 18 h to separate asphaltene out using a 0.45 um Teflon membrane in a vacuum system, and then a maltene solution was obtained. The components in maltenes were characterized by using a two-dimensional Gas Chromatography with Time of Flight Mass Spectrometer (GCxGC-TOF/MS) instrument, Agilent gas chromatograph 7890 system, combinded with a cryogenic modulator and a LECO Pegasus 4D TOF/MS. The PIANO standard purchased from Spectrum Quality Standards Ltd. was used to calibrate the concentration of petrochemicals such as benzene, toluene, p-xylene, ethylbenzene, and cumene in tire-derived oil. The concentration of petrochemicals in tire-derived oil was calculated from the areas of petrochemicals obtained from GCxGC-TOF/MS and percent of concentration of petrochemicals in a PIANO standard. The simulating true boiling point curves of maltene solutions were determined by using a Varian GC-3800 simulated distillation gas chromatograph (SIMDIST-GC), using ASTM D2887 method. The true boiling point curves were cut into petroleum fractions; that 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).
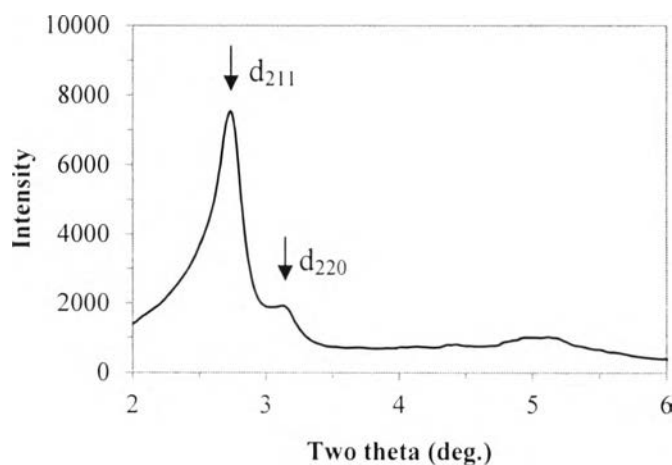
7.4 Results and Discussion

Figure 7.2 SAXS pattern of Si-MCM-48.

Si-MCM-48 catalyst that was used as the lower bed catalyst has the average pore diameter calculated from the BJH method is 2.78 nm. Figure 7.2 shows the small-angled X-ray scattering (SAXS) pattern of Si-MCM-48. There are two peaks at $2\theta = 2.5°$ and $2\theta = 3.0°$, corresponding to (211) and (220) diffractions, which are the characteristics of the parent MCM-48 (Kosslick *et al.*, 1998) indicating that Si-MCM-48 was successfully synthesized. Subsequently, it was placed as the bottom bed of catalysts together with a zeolite on the top in the order to study the effects of acidity and pore size of the zeolite on the top bed on tire pyrolysis products (Figure 7.1).

The liquid product was examined by using a GC×GC-TOF/MS, which has a high performance to separate the complex mixture. Figure 7.3 shows the good separation of compounds. Moreover, it shows the grouping of di-, poly-aromatics, and S-containing conpounds on the surface plots of total ion chromatogram in non-cat (a), Si-MCM-48 (b), Si-MCM-48/HBETA (c), Si-MCM-48/HY (d), and Si-MCM-48/HZSM-5 (e) case.
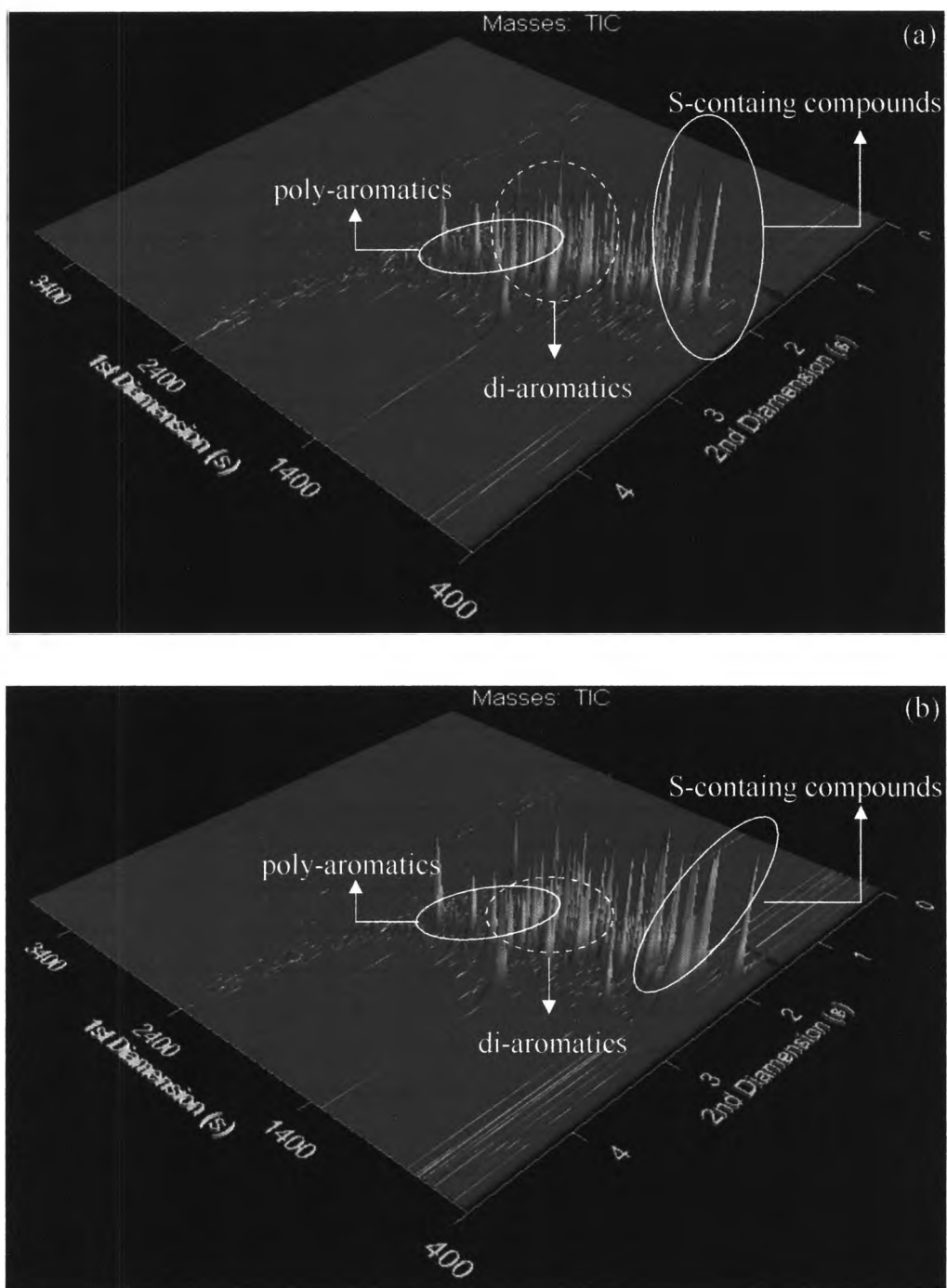
Figure 7.3 Total ion chromatograms (surface plot) (a) non-cat, (b) Si-MCM-48, (c) Si-MCM-48/HBETA, (d) Si-MCM-48/HY, and (e) Si-MCM-48/HZSM-5.
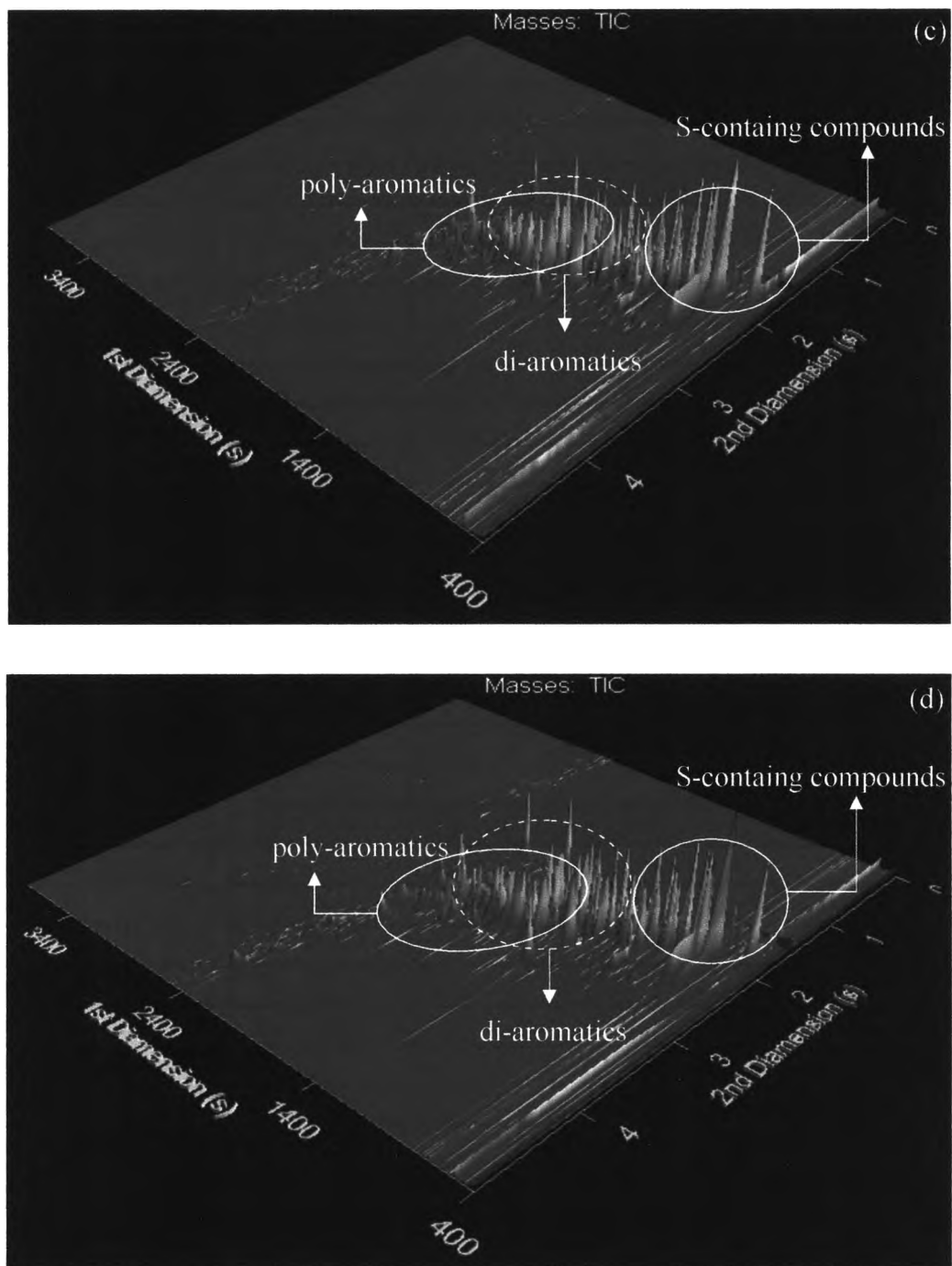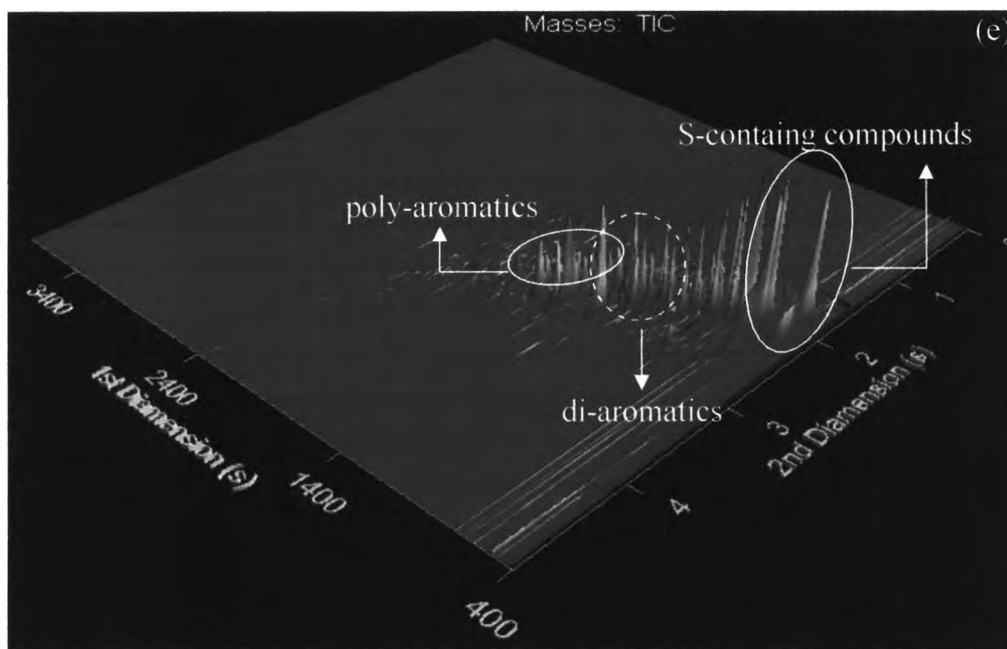
Figure 7.3 Total ion chromatograms (surface plot) (a) non-cat, (b) Si-MCM-48, (c) Si-MCM-48/HBETA, (d) Si-MCM-48/HY, and (e) Si-MCM-48/HZSM-5 (con't).

Figure 7.3 Total ion chromatograms (surface plot) (a) non-cat, (b) Si-MCM-48, (c) Si-MCM-48/HBETA, (d) Si-MCM-48/HY, and (e) Si-MCM-48/HZSM-5 (con't).

7.4.1 Effect of Acidity

HBETA (Si/Al = 14) and HY (Si/Al = 7.5) catalysts were individually used as a catalyst on the upper bed to study the effect of acidity. HY has a lower Si/Al ratio, corresponding to a higher density of acid sites than HBETA. The distribution of acid sites was determined by TPD-NH_3, and the TPD-NH_3 profiles of HY and HBETA are shown in Figure 7.4. The peaks of NH_3 desorped from HY and HBETA surfaces appear at the same temperature of approximately 190 and 525 °C for both zeolites, indicating that HY and HBETA have equal acid strength. Moreover, Table 7.1 shows the properties of HBETA and HY. It can be observed that both zeolites have similar properties of pore size and pore channel.
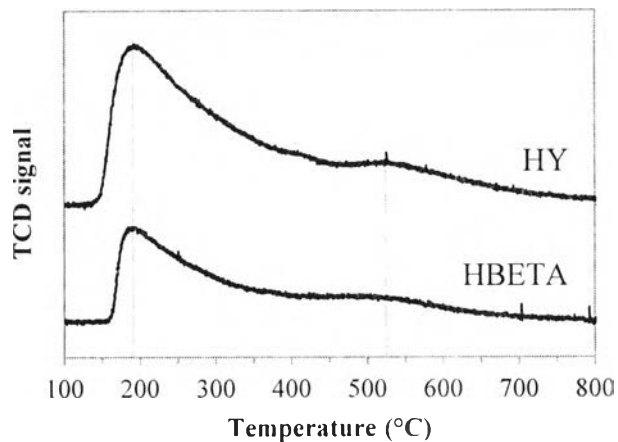
Figure 7.4 TPD-NH₃ profiles of HBETA and HY.

Table 7.1 Properties of HBETA and HY

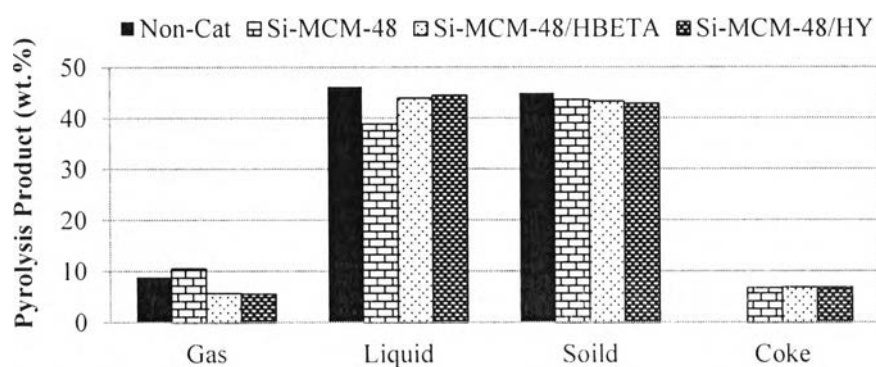| Zeolite	Si/Al Ratio	Pore Size	Pore Channel
HBETA	14	6.4 x 7.6	3D
HY	7.5	7.4	3D

Figure 7.5 Product distributions using the single bed of Si-MCM-48 and double beds of Si-MCM-48/HBETA and Si-MCM-48/HY.

Figure 7.5 shows the product distribution using the single bed of Si-MCM-48 and the double bed of Si-MCM-48 and HBETA or HY. It can be seen that the double beds of Si-MCM-48/HBETA and Si-MCM-48/HY decrease the gas yield while the liquid yield increase, indicating that HBETA and HY promote the combination of gas molecules, then forming larger molecules in the fraction of liquid products. Additionally, the double beds of Si-MCM-48/HBETA and Si-MCM-48/HY provide the same product distributions.

In tire-derived oil, the compounds were categorized into 7 groups; that are, paraffins (p), olefins (ole), naphthenes (nap), mono-aromatics (mono), di-aromatics (di), poly-aromatics (poly) and polar-aromatics hydrocarbons (polar) as shown in Figure 7.6. It shows that both double bed cases increased the formation of di- and poly- aromatic hydrocarbons whereas the amount of olefins and naphthenes decreased when compared to Si-MCM-48. Moreover, the group of polar-aromatic hydrocarbons does not change significantly. It can be explained that HBETA and HY as acid catalysts can promote aromatization of olefins and naphthenes, forming aromatic hydrocarbons via carbenium ion (Choudhary et al., 2000). In addition, the double bed of Si-MCM-48/HY gives about 13 wt.% poly-aromatic hydrocarbons in maltene, which is higher than the double bed of Si-MCM-48/HBETA that gives 9 wt.% in maltene. Furthurmore, the double bed of Si-MCM-48/HY provides a lower amount of mono-aromatic hydrocarbons than double bed of Si-MCM-48/HBETA by 6 wt.%, whereas the other groups including olefins, naphthenes, di-, and polar-aromatic hydrocarbons do not change significantly. It can be explained that a higher acid density of HY can promote the condensation of mono-aromatics, forming poly-aromatic hydrocarbons more greatly than HBETA (Meng et al., 2013).

From the GCxGC-TOF/MS results, the poly-aromatic compounds that significantly increased in the both double bed cases are 2-ethylbiphenyl (m/z =182) and dibenzylmethane (m/z = 196). The structure of these compounds consists of two benzene rings as shown in Figure 7.7. It was possible that olefins were aromatized with mono-aromatics to form 2-ethylbiphenyl and dibenzylmethane.
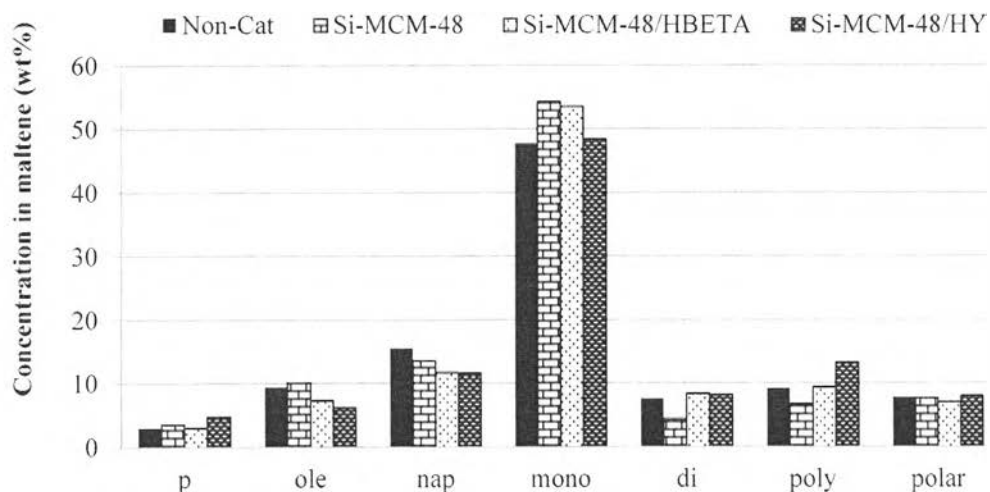
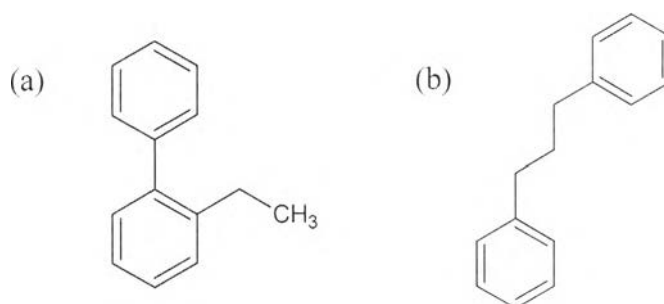**Figure 7.6** Concentration of each group of components in maltenes in the Si-MCM-48/HBETA and Si-MCM-48/HY cases.

Figure 7.7 (a) 2-ethylbiphenyl (m/z =182), and (b) dibenzylmethane (m/z = 196) in the Si-MCM-48/HBETA and Si-MCM-48/HY cases.

The valuable petrochemicals in tire-derived oil such as benzene, toluene, xylenes, ethylbenzene, and cumene are considered since they are important raw materials in petrochemical industry. The concentration of petrochemicals in maltenes by using Si-MCM-48, Si-MCM-48/HBETA, and Si-MCM-48/HY are 6.2, 7.2, and 5.9, respectively (Figure 7.8). The double bed of Si-MCM-48/HY gives a lower petrochemical production than double bed of Si-MCM-48/HBETA, resulting from a higher acid density of HY that promotes the aromatization of some petrochemicals and converts to larger aromatic compounds as seen in Figure 7.6. Moreover, the double bed of Si-MCM-48/HBETA gives a higher concentration of

benzene, toluene, p-xylene, and cumene and a lower concentration of ethylbenzene than single bed Si-MCM-48 and double bed of Si-MCM-48/HY.
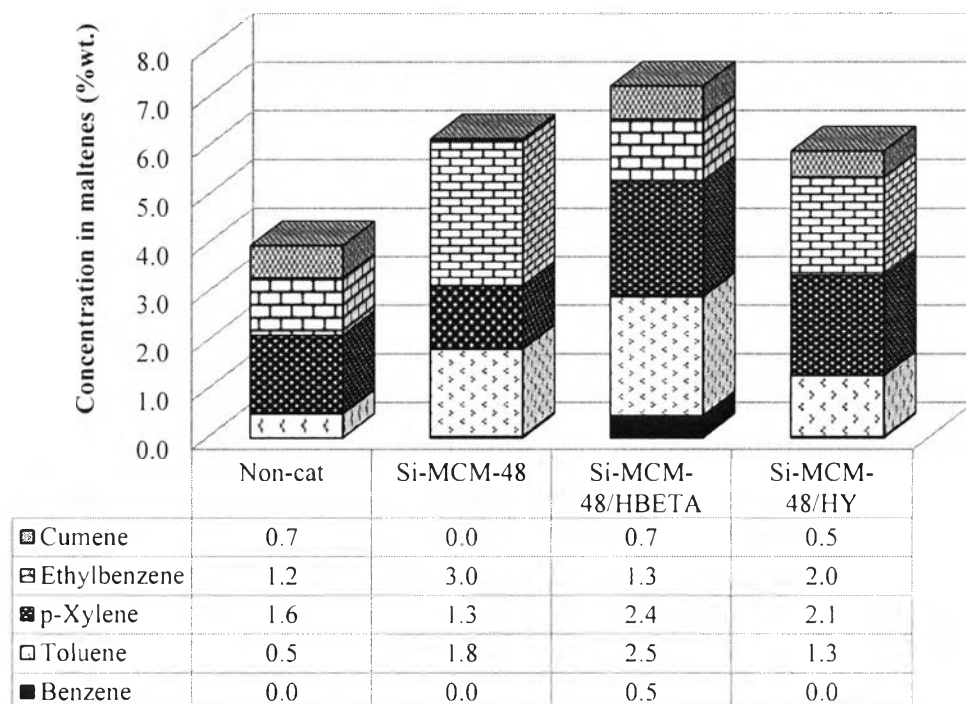

	Non-cat	Si-MCM-48	Si-MCM-48/HBETA	Si-MCM-48/HY
▨ Cumene	0.7	0.0	0.7	0.5
▣ Ethylbenzene	1.2	3.0	1.3	2.0
▨ p-Xylene	1.6	1.3	2.4	2.1
▢ Toluene	0.5	1.8	2.5	1.3
■ Benzene	0.0	0.0	0.5	0.0

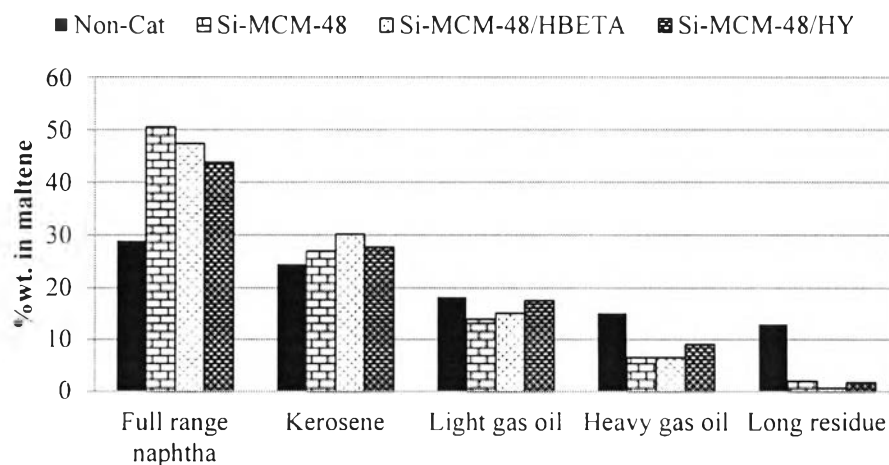**Figure 7.8** Concentration of petrochemicals in maltenes in the Si-MCM-48/HBETA and Si-MCM-48/HY cases.

Figure 7.9 Petroleum fraction in maltenes in the Si-MCM-48/HBETA and Si-MCM-48/HY cases.

The petroleum fractions of maltenes were cut into full range naphtha, kerosene, gas oil, and long residues as shown in Figure 7.9. The both double bed cases decrease naphtha fraction. Moreover, it is found that HY that has higher acid density gives a lower fraction of naphtha and kerosene and higher amount of heavier fractions, including light gas oil, heavier gas oil, and long residue than the double bed of Si-MCM-48/HBETA, indicating that the double bed of Si-MCM-48/HY promotes the combination of small to large molecules in the liquid product. It can be concluded that the liquid products are light in the rank of Si-MCM-48 > Si-MCM-48/HBETA > Si-MCM-48/HY.

In terms of sulfur removal, Figure 7.10 shows the sulfur distribution in pyrolytic products and Table 7.2 reports the sulfur content in oil. When compared to the single bed of Si-MCM-48, the double bed cases give a higher amount of sulfur deposited on spent catalysts. Moreover, both double bed cases decrease the amount of sulfur distributed in the gas products, and increase the amount of sulfur distributed in the oil products. It can be explained that the surface of HBETA and HY zeolite help to adsorp sulfur atom from H_2S. Furthermore, H_2S can interact with olefins to form thiophene and benzothiophene compounds in oils (Leflaive et al., 2002; Corma et al., 2001). Additionally, the double beds of Si-MCM-48/HBETA and Si-MCM-48/HY give a similar sulfur distribution in pyrolytic products, indicating that the different acid density of catalysts in the upper bed does not affect desulfurization.
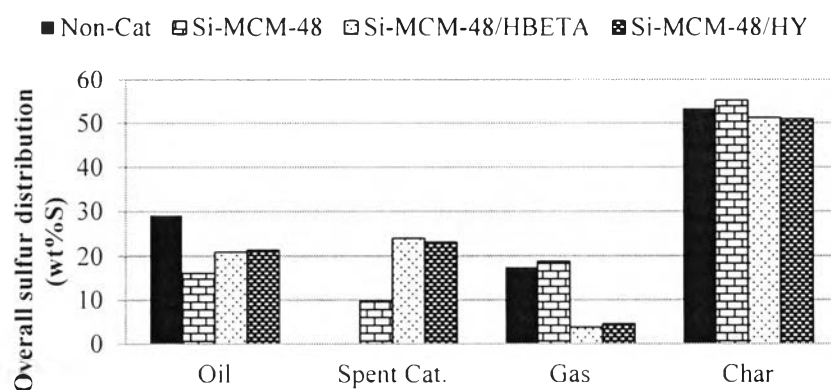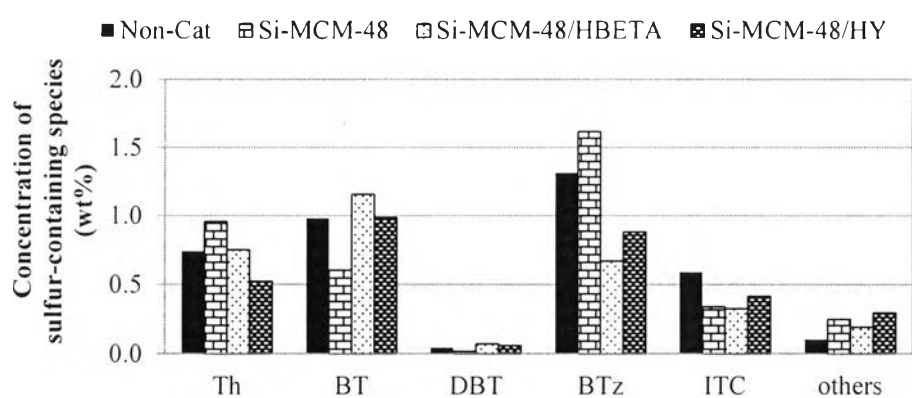

Figure 7.10 Overall sulfur distributions (wt%S) in the Si-MCM-48/HBETA and Si-MCM-48/HY cases.

Table 7.2 Sulfur content in oils (wt.%)

Catalyst	wt% Sulfur in Oil	Sulfur Removal (%)
No Catalyst	1.27 ± 0.04	-
Si-MCM-48	0.84 ± 0.01	33.9
Si-MCM-48/HBETA	0.96 ± 0.03	24.4
Si-MCM-48/HY	0.97 ± 0.03	23.6

Figure 7.11 Sulfur–containing compounds in maltenes in the Si-MCM-48/HBETA and Si-MCM-48/HY cases.

The sulfur species in the tire-derived oils are classified into five groups; that are, thiophenes (Ths), benzothiophenes (BTs), dibenzothiophenes (DBTs), benzothiazoles (BTz), and isothiocyanates (ITC) as shown in Figure 7.11. It can be seen that the double bed cases decrease the amount of thiophenes with increasing benzothiophenes and dibenzothiophenes. It can be suggested that benzothiophenes and dibenzothiophenes might be formed from olefins interacted with thiophenes (Corma *et al.*, 2001). On the other hand, benzothiazoles sharply decrease in the case of the double bed cases, indicating that HBETA and HY help the C-N bond to break.

7.4.2 Effect of Pore Size

HZSM-5 and HBETA were used as catalysts in the upper bed to study the effect of pore size. Table 7.3 shows the properties of HZSM-5 and HBETA. Both zeolites have a similarity of Si/Al ratio and pore channel. The Si/Al ratio corresponds

to the amount of acid sites. Figure 7.12 shows TPD-NH₃ profiles of HZSM-5 and HBETA. Two peaks appear in the TPD-NH₃ profiles of both zeolites. In the case of HZSM-5, the first peak present at 170 °C and the second peak present at 510 °C. In the case of HBETA, the first peak present at 190 °C and the second peak present at 525 °C. Moreover, the first peak in the lower temperature are assigned to weak acid sites whereas the second peak in the high temperature are assigned to strong acid sites. Thus, HZSM-5 has a lower acid strength than HBETA. Moreover, HZSM-5 has a higher number of strong acid sites than HBETA due to a higher area in the high temperature region as shown in Table 7.4.
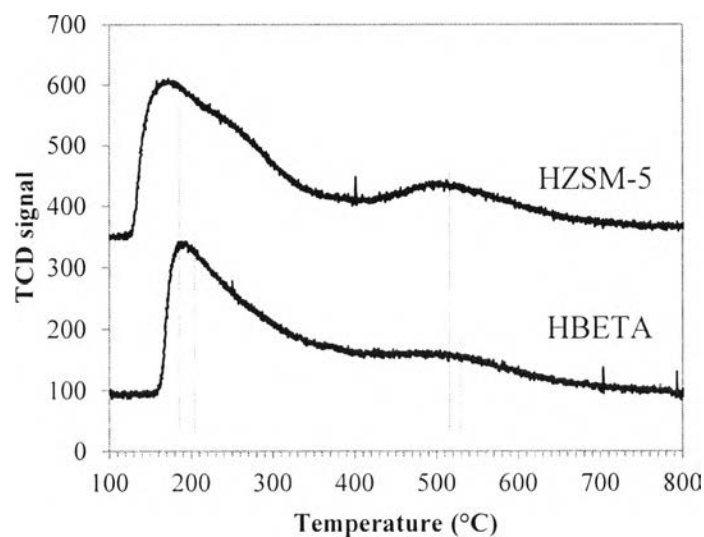

Figure 7.12 TPD-NH₃ profiles of HZSM-5 and HBETA.

Table 7.3 Properties of HZSM-5 and HBETA

Zeolite	Si/Al Ratio	Pore Size	Pore Channel
HZSM-5	15	5.3 x 5.6	3D
HBETA	14	6.4 x 7.6	3D

Table 7.4 Ammonia desorption temperature and area of catalysts

Catalyst	NH₃ Desorption Temperature		Area	
	Weak Acid Sites	Strong Acid Sites	Weak Acid Sites	Strong Acid Sites
HZSM-5	170	510	210568	85817
HBETA	190	525	204351	68491
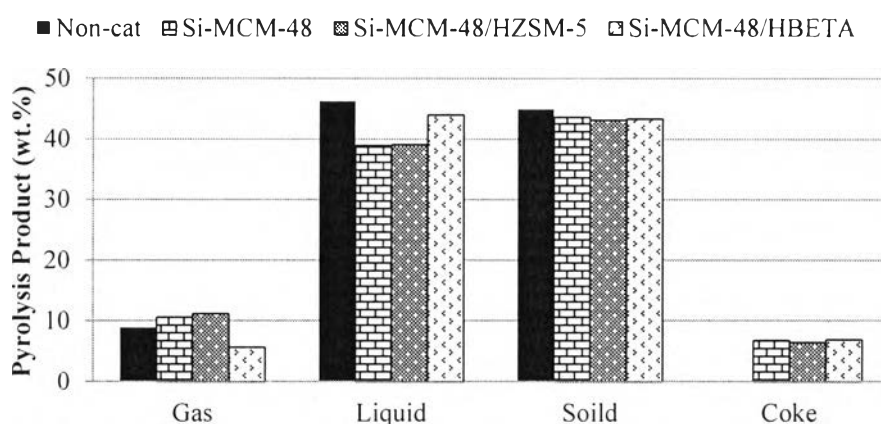
Figure 7.13 Product distributions in the Si-MCM-48/HZSM-5and Si-MCM-48/HBETA cases.

The product distribution of single bed of Si-MCM-48 and the double bed of Si-MCM-48/HZSM-5 and Si-MCM-48/HBETA as shown in Figure 7.13. It illustrates that HZSM-5 as the catalyst in the upper bed that has a medium pore size provides the same product distribution as compared to Si-MCM-48 whereas the double bed of Si-MCM-48/HBETA decreases the gas yield with the increasing liquid yield, indicating that the large pore size of HBETA promote the combination of gas molecules in pores, and then larger molecules are formed, so the liquid yield increases.
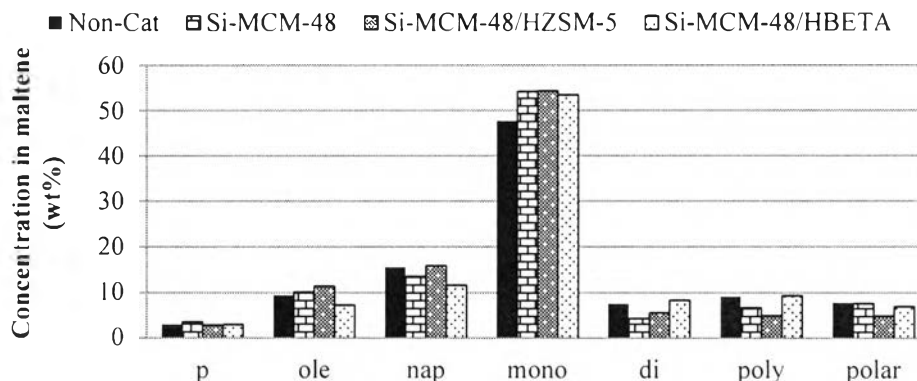
Figure 7.14 Concentration of each group of components in maltenes in the Si-MCM-48/HZSM-5and Si-MCM-48/HBETA cases.

Figure 7.14 shows the concentration of each group of components in maltenes. It observes that the use of HBETA as the upper bed catalyst that has a larger pore size than HZSM-5, gives a high amount of di- and poly- aromatic hydrocarbons while the amount of olefins and naphthenes decreases. Moreover, the other groups do not change significantly as compared to the single bed Si-MCM-48, indicating that the large pore size of HBETA promote the aromatization of olefins and naphthalenes in pores to form large aromatic hydrocarbons. On the other hand, double bed of Si-MCM-48/HZSM-5 decreases the amount of poly- and polar-aromatic hydrocarbons whereas olefins, naphthenes, and di-aromatic hydrocarbons slightly increased, indicating that HZSM-5 promotes the activity of cracking poly- and polar-aromatic hydrocarbons due to the large number of strong acid sites as seen in Table 7.2. The number of strong acid sites highly affects the cracking reaction. (Li *et al.*, 2014; Jung *et al.*, 2004). Moreover, the activity of cracking poly- and polar-aromatic hydrocarbons may have occured on the external surface of HZSM-5 since HZSM-5 has medium pore size that cannot allow large molecules into the pores.

Figure 7.15 shows the production of petrochemicals such as benzene, toluene, xylenes, ethylbenzene, and cumene in tire-derived oils. It illustrates that the concentration of petrochemicals in maltenes can be ranked in the order: Si-MCM-48/HZSM-5 (10.1 wt.%) > Si-MCM-48/ HBETA (7.2 wt.%) > Si-MCM-48 (6.2 wt.%). For the double bed of Si-MCM-48/HBETA catalyst, the increase of

petrochemical production might occur from the condensation of gas molecules in pore due to the decrease of gas yield (Figure 7.13), whereas the high concentration of petrochemicals in tire-derived oil in the case of double bed of Si-MCM-48/HZSM-5 might occur from the cracking of mono-aromatic hydrocarbon as seen in Figure 7.14 that shows the same amount of mono-aromatic hydrocarbons.

From the GCxGC-TOF/MS results, (3E)-3,5-Hexadien-2-ylbenzene (m/z = 158) and 3-Cyclohexen-1-ylbenzene (m/z = 158) (Figure 7.16) that are mono-aromatic hydrocarbons decrease significantly in tire-derived oil by using the double bed of Si-MCM-48/HZSM-5 as compared to Si-MCM-48. It is possible that the medium pore size and the large number of strong acid sites help to crack alkyl and phenyl groups of these mono-aromatic hydrocarbons, that are the derivative of benzene ring, and gives a smaller mono-aromatic hydrocarbons such as petrochemicals.
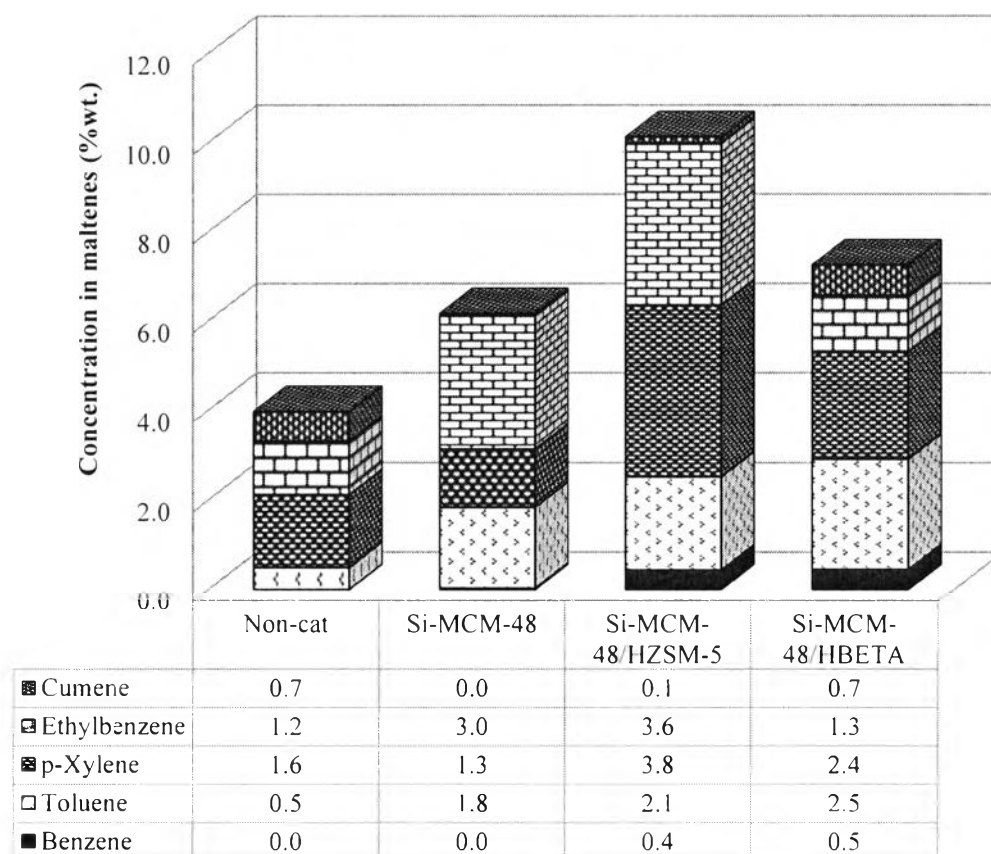

	Non-cat	Si-MCM-48	Si-MCM-48/HZSM-5	Si-MCM-48/HBETA
Cumene	0.7	0.0	0.1	0.7
Ethylbenzene	1.2	3.0	3.6	1.3
p-Xylene	1.6	1.3	3.8	2.4
Toluene	0.5	1.8	2.1	2.5
Benzene	0.0	0.0	0.4	0.5

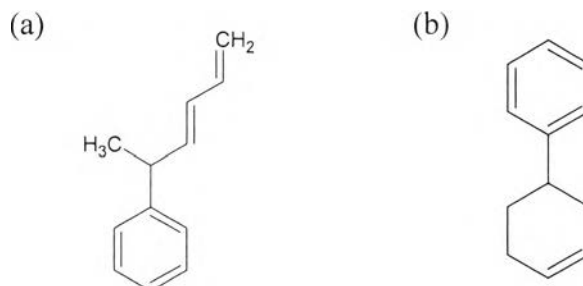Figure 7.15 Concentration of petrochemicals in maltenes in the Si-MCM-48/HZSM-5 and Si-MCM-48/HBETA cases.

Figure 7.16 (a) (3E)-3,5-Hexadien-2-ylbenzene (m/z =158), and (b) 3-Cyclohexen-1-ylbenzene (m/z = 158) in the Si-MCM-48/HZSM-5and Si-MCM-48/HBETA cases.
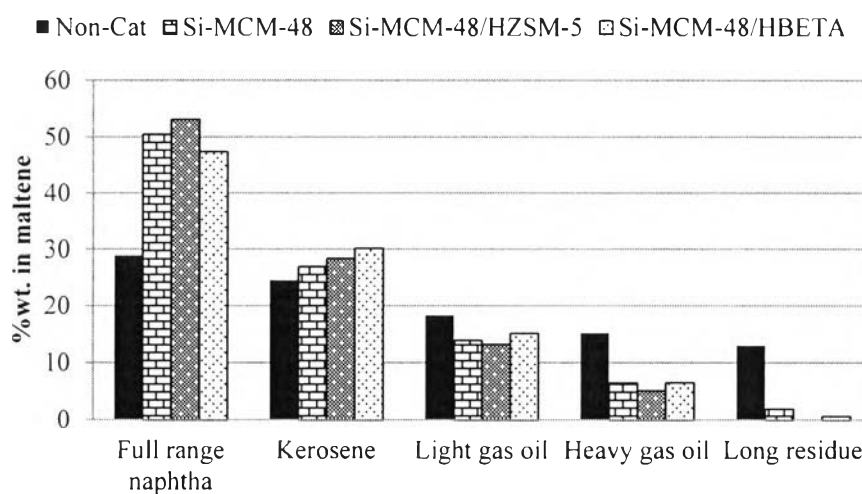

Figure 7.17 Petroleum fraction in maltenes in the Si-MCM-48/HZSM-5and Si-MCM-48/HBETA cases.

The double bed of Si-MCM-48/HZSM-5. which has a medium pore size and large number of strong acid sites increases full range naphtha fraction by 2 %, and also slightly decreases the amount of light gas oil, heavy gas oil, and long residue as compared to the single bed of Si-MCM-48. On the other hand, a large pore HBETA as the upper bed decreases the amount of full range naphtha while the other fractions slightly increase (Figure 7.17). From the results. it can be concluded that the double bed of Si-MCM-48/HZSM-5 gives a cracking activity whereas the double

bed of Si-MCM-48/HBETA gives a combination of small to larger molecules. Therefore, tire-derive oil from the double bed of Si-MCM-48/HZSM-5 is lighter than that the double bed of Si-MCM-48/HBETA.
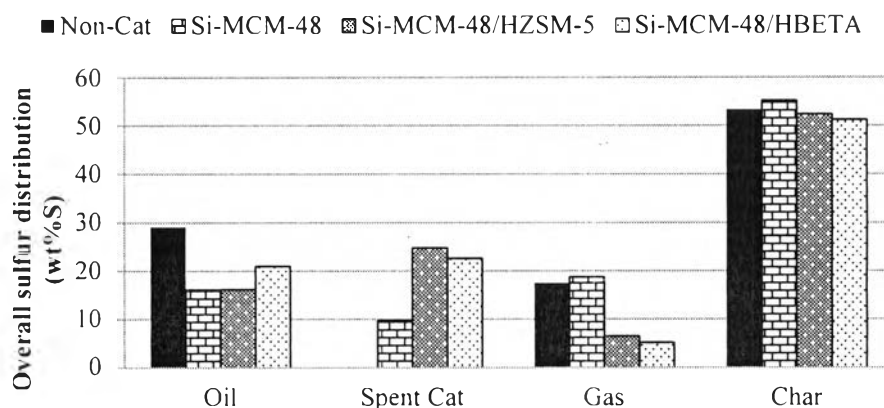

Figure 7.18 Overall sulfur distributions (wt%S) in the Si-MCM-48/HZSM-5 and Si-MCM-48/HBETA cases.

In terms of sulfur removal, Figure 7.18 shows the sulfur distribution in pyrolytic products, and Table 7.5 reports the sulfur content in oil. It can be seen that the double bed of Si-MCM-48/HBETA gives a lower amount of sulfur distributed on the spent catalysts than the double bed of Si-MCM-48/HZSM-5 catalyst due to a lower amount of strong acid sites. Moreover, the double bed of Si-MCM-48/HBETA catalyst also decreases the sulfur distributed in gas with increasing sulfur distributed in oil more greatly than the double bed of Si-MCM-48/HZSM-5. It can be suggested that the large pore size of HBETA has capacity to form large sulfur compounds. Similarly, Figure 7.19 shows the large sulfur compounds such as benzothiophenes and dibenzothiophenes sharply increase in the case of double bed of Si-MCM-48/HBETA, resulting from the large pore of HBETA that has capacity to promote the interaction of olefins and thiophene. On the other hand, benzothiazoles and isothiocyanates, that are N-containing sulfur compounds, sharply decrease in the case of double bed of Si-MCM-48/HZSM-5, indicating that the large number of strong acid sites helps the C-N bond to break easily.

Table 7.5 Sulfur content in oils (wt.%)

Catalyst	wt% Sulfur in Oil	Sulfur Removal (%)
No Catalyst	1.27 ± 0.04	-
Si-MCM-48	0.84 ± 0.01	33.9
Si-MCM-48/HZSM-5	0.84 ± 0.01	33.9
Si-MCM-48/HBETA	0.96 ± 0.03	24.4
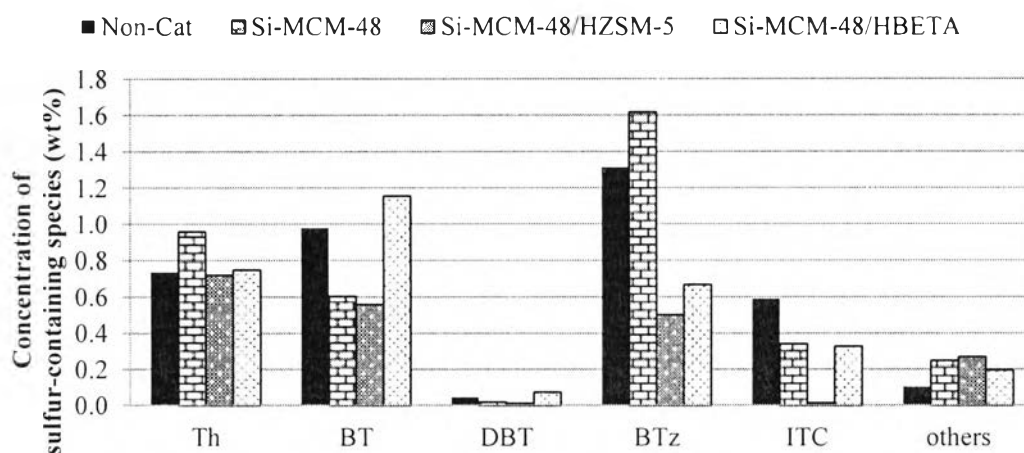
Figure 7.19 Sulfur–containing compounds in maltenes in the Si-MCM-48/HZSM-5 and Si-MCM-48/HBETA cases.
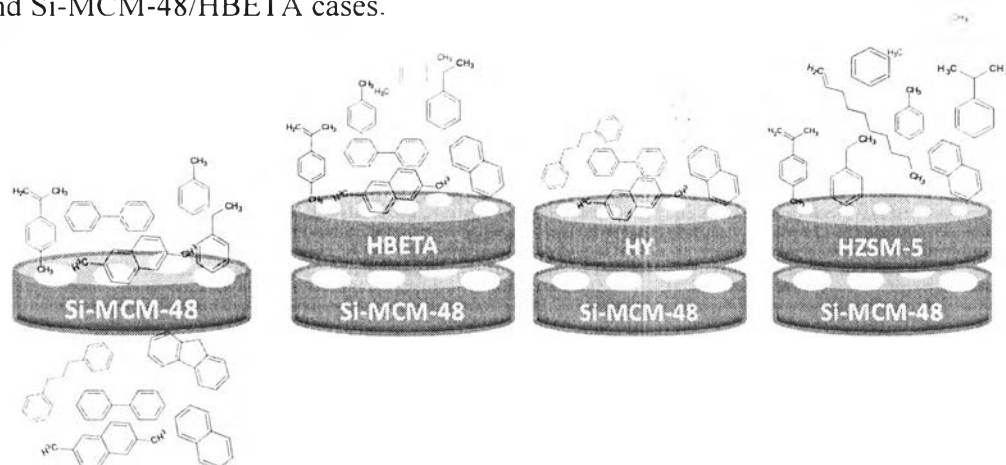
Figure 7.20 Example of major molecules in maltene in Si-MCM-48, Si-MCM-48/HBETA, Si-MCM-48/HY, and Si-MCM-48/HZSM-5.

In summary, the single bed of Si-MCM-48 decreased large molecules such as di- and poly-aromatic hydrocarbons in tire-derived oil because the large pore size of Si-MCM-48 allows bulky molecules diffuse through inside the pores and promotes the activity of cracking large hydrocarbons. For the double bed catalysts (Figure 7.20), Si-MCM-48/HBETA resulted in a high formation of large molecules and a slight increase in petrochemicals, especially toluene, p-xylenes, and cumene. Si-MCM-48/HY highly increased the formation of large molecules whereas the production of petrochemical decreased, indicating that some petrochemicals were converted to larger aromatic hydrocarbons. It can be concluded that the second bed catalyst (pore size = 7Å) has a high capacity to form large molecules. Moreover, Si-MCM-48/HZSM-5 resulted in a high production of petrochemicals but a low concentration of large aromatic hydrocarbons.

As a result, Si-MCM-48/HZSM-5 is the best catalyst because it does not only decrease large aromatic hydrocarbons, but also highly increased petrochemicals production in tire-derived oil. It can be concluded that the upper bed catalyst should have a pore size about 5Å to limit the formation of large molecules in pores. Additionally, the upper bed catalyst should be a acid catalyst because it helped to promote cracking activity.

7.5 Conclusions

HY used as the catalyst in the upper bed gave a heavier liquid product than Si-MCM-48/HBETA due to higher acid density that caused formation of small molecules to large molecules via carbenium ion; thus, petrochemical production in the Si-MCM-48/HY case also decreased. Additionally, the HZSM-5 used as the catalyst in the upper bed showed a cracking ability and a high selectivity of petrochemicals production than the HBTEA due to its medium pore size that has a less capacity to form large molecules, and a large number of strong acid sites that help to promote cracking activity. Moreover, used in the upper bed, HZSM-5 can remove the sulfur in oil better than HBETA.

7.6 Acknowledgements

7.7 References

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