CHAPTER VI

IMPACTS OF NICKEL SUPPORTED ON DIFFERENT ZEOLITES ON WASTE TIRE-DERIVED OIL AND FORMATION OF SOME PETROCHEMICALS

6.1 Abstract

Waste tire-derived oils commonly contain the considerable valuable aromatics such as benzene, toluene, ethylbenzene, toluene, xylenes and etc., but they also contain a significantly-high amount of sulfur compounds, which cause a low quality of pyrolytic oil. The strong sulfur odors in tire-derived oil can cause a bad effect on human health since sulfur compounds are carcinogenic substances. Ni is a cheap metal, which exhibits hydrogenation/dehydrogenation and ring-opening like a noble metal, and widely used as promoter in desulfurization of fuels. In this work, Ni was expected to be a catalyst promoter of zeolites for reduction of sulfur content in oil and enhancement of petrochemical formation in oil. Therefore, the effect of 5 wt% nickel loading on different four type zeolites (HZSM-5, HMOR, HY, HBETA) on the sulfur removal and quality of waste-tire derived oil was studied. The results show that the incorporations of nickel on all zeolites significantly reduced sulfur contents in oil. However, the quality of waste tire-derived oil did not only depend on the nickel promoter, but also strongly depended on zeolite supports. The introduction of nickel on HZSM-5 zeolite, which possesses a smaller pore size than HBETA zeolites, provided a lighter oil with higher proportion of gasoline and kerosene than Ni/HBETA catalyst, and produced a higher amounts of valuable aromatic such as ethylbenzene, toluene, cumene, and mixed-xylenes than Ni/HBETA catalyst. Moreover, the addition of nickel on HMOR zeolite, which possesses a 1D zeolite channel structure, also provided a lighter oil with a high proportion of gasoline and kerosene than the Ni-loaded on HBETA (3D zeolite channel structure), and exhibited a better petrochemical production with a higher concentrations of ethylbenzene, toluene, cumene and styrene in maltene. On the other hand, Ni/HBETA provided the lower sulfur content in oil than Ni/HMOR catalyst, but the sulfur removal ability by nickel species on HMOR was higher than nickel species on HBETA zeolite.

Furthermore, the introduction of nickel on HY zeolite provided the heavier oil with higher proportion of gas oil, LVGO and HVGO and lower proportion of petrochemical than Ni/HBETA zeolite whereas the sulfur removal of nickel species on the HBETA support with higher acid strength was better than on the HY support.

6.2 Introduction

In recent decades, pyrolysis of waste tire is the useful process that can recovery valuable chemicals from waste tire and eliminate the environmental impacts from disposal of waste tire. Among the waste tire-derived products, waste tire-derived oils have received more attention since their properties are quite similar to those of commercial diesel and heating oil. Petrochemicals can be classified into olefins and aromatics, and utilized as a raw material in manufacturing of plastics, solvents, detergents, synthetic rubber, cosmetic products and pharmaceuticals. From past to present, petrochemicals such as ethylene, propylene, butadiene and BTEX are mainly produced via cracking of naphtha and ethane derived from crude oil and natural gas (Ren *et al.*, 2009). However, the production of petrochemicals via petroleum and natural gas is not sustainable since the petroleum and natural gas resources continuously decrease. As a result, several alternative processes for production of petrochemical by utilization of methane, coal, biomass and waste tire have attracted a great attention. Among these alternative processes, waste tire pyrolysis is considered as an effective process since it can eliminate waste tire problems by breaking up the tire molecules into valuable chemicals or fuel. Moreover, several studies reported that tire-derived oils contain a considerable concentration of valuable aromatics such as benzene, toluene, ethylbenzene, styrene, xylenes and etc. (Olazar *et al.*, 2008 ; Undri *et al.*, 2014). However, the major drawback is the relatively high concentrations of sulfur and nitrogen, which vary in the range of 0.5-3 wt%, depending on the pyrolysis system and catalysts (Al-Lal *et al.*, 2015). They contain a great amount of sulfur since the sulfur is an additive in vulcanization process. Acidic zeolites such as HBETA, HMOR, HY, HZSM-5 have been proven to be able to reduce sulfur content in oil and enhance the quality of tire-derived oil. Dung *et al.* (2009) stated that HMOR increased the concentration of mono-aromatics in oil, whereas the polycyclic aromatics, especially polar-aromatics significantly decreased. In addition, HMOR also increased the naphtha fraction in oil, whereas the heavy fraction drastically decreased. HBETA and HY zeolites increase naphtha and kerosene fractions, whereas the heavier fraction slightly decreased (Manchantrarat and Jitkarnka, 2012). Thus, these studies indicate that different zeolites provide different product distribution because each zeolite has unique properties. In particular, HZSM-5 zeolite is commonly used as a catalyst in the petrochemical industry due to its pore size, strong acidity and strong resistance to deactivation. Boxiong *et al.*, (2007) found that the HZSM-5 enhanced the production of benzene, toluene and xylenes. The high acid strength of zeolite is favorable for production of valuable aromatics, but the high acid density is favorable for sulfur removal from oil. The pore size of zeolite plays an important role in governing the molecular size of products. The large pore size of HBETA provided better cracking activity and petrochemical formation in oil than the HZSM-5 zeolite with medium pore size. The 3D pore channel structure of HBETA zeolite provided a higher cracking activity and petrochemical productivity than 1D pore channel structure of HMOR due to the longer contact time of molecules in the pore. A zeolite support with a sufficiently pore size (~7 Å) with 3D complex channel structure was suggested for producing a high quality of oil with a high formation of petrochemicals (Muenpol *et al.*, 2015).

Bi-functional catalysts have also been tested in waste tire pyrolysis, and provided the interesting results. Recently, Cu doped on HBETA, HY and HMOR zeolites significantly reduced the sulfur content in oil by 31.0- 37.4 %, respectively and also enhanced the petrochemical formation in oil (Yuwapornpanit and Jitkarnka, 2015). Nickel is favourable to hydrogenation/dehydrogenation reactions, or promotes aromatization and cracking reactions (Botas et al., 2014). For example, Ni over hierarchical ZSM-5 and Beta zeolites enhanced the production of gas and gasoline from hydroreforming of polyethylene-derived thermal cracking oil. In addition Ni/HZSM-5 catalyst can promote the transformation of olefins into aromatics and iso-paraffins (Yin *et al.*, 2005). Another common application of nickel-based catalyst is desulfurization. The sulphur removal efficiency increased with the increase of nickel loading on SBA-15 in adsorptive desulfurization of diesel (Ko *et al.* ,2007).

In addition, Rodrıguez-Castellón *et al.* (2003) revealed that nickel supported on zirconium-doped mesoporous silica promoted the hydrogenation and ring-opening of tetralin. Therefore, the introduction of nickel on zeolites; that are, HBETA, HMOR, HY and HZSM-5 were expected to reduce the sulfur content in tire-derived oil and also enhance formation of valuable petrochemicals in oils. The aim of this work was therefore to investigate the effect of nickel loading on different zeolites (HBETA, HMOR, HY, HZSM-5) on chemical species of waste tire-derived oil and sulfur removing ability of catalysts.

6.3 Experimental

6.3.1 Catalyst Preparation

The commercial zeolites selected in this research were purchased from TOSOH Corporation (Singapore); HBETA (931HOA, Si/Al = 14, H-form), HMOR (640HOA, Si/Al =9, H-form), HY (360HUA, Si/Al=7.5,H-form) and HZSM-5 (840NHA, Si/Al =20, NH_4-form). Prior to activity testing and metal impregnation, HMOR, HY, and HZSM-5 were calcined in standing air at 500 °C for 3 h (Ramping rate of 10 °C/min). HBETA was calcined in standing air at 650 °C for 2 h (Ramping rate of 2 °C/min). Ni-loaded zeolites were prepared using incipient wetness impregnation of $(NiNO_3)_2•6H_2O$ until 5 wt% metal loading based on the mass of catalysts. The catalysts were then dried overnight at 105 °C, and calcined at same conditions. The catalyst powders were pelletized, crushed and sieved to 40-60 mesh of particle sizes. The catalysts were activated by reduction under hydrogen flow (30 ml/min) at 600 °C for 2 h (heating rate 10 °C/min).

6.3.2 Catalyst Characterization

The catalyst samples were characterized by different physicochemical characterization methods. X-Ray diffraction (CuKα radiation), carried out in a Rikagu SmartLab X-Ray Diffractometer, was used to identify the crystallinity of catalysts. XRD patterns were recorded in the 5-65 ° (2θ) range using a scan speed of 10° (2θ)/min. The surface area and pore volume of catalysts were measured using N_2 adsorption-desorption isotherms with Thermo Finnigan Sorptomatic 1990 instrument. The amount of coke deposition on the spent catalysts was measured by thermogravimetric/differential thermal analysis (TG/DTA), carrier out under flowing of nitrogen (10 ml/min) and oxygen (20ml/min) on a Perkin Elmer/Pyris Diamond (Thermogravimetric/Differental Thermal Analysis, TG/DTA). The sample were heated up from room temperature to 900 °C with ramping rate of 10 °C/min. CHNS analyzer was used to determine the sulfur and nitrogen content on spent catalyst using LECO®Elemetal Analyzer.

6.3.3 Waste Tire Pyrolysis

The schematic pyrolysis system is displayed in Figure 6.1. Firstly, 30 g of shredded tire (20-40 mesh) was pyrolyzed in the lower zone of the reactor at 500 °C under atmospheric pressure. The pyrolysis products were carried by 30 ml/min of nitrogen flow to the catalytic bed filled with 7.5 g of catalyst and heated to 350 °C. After the temperatures of lower and upper zones reached to the desired one, the temperature of two zones was kept at desired temperature for 2 h. The resulting products were separated into gas and liquid fraction by condensers (ice-salt condensing system). Gas product was collected in Tedlar PVF bag.

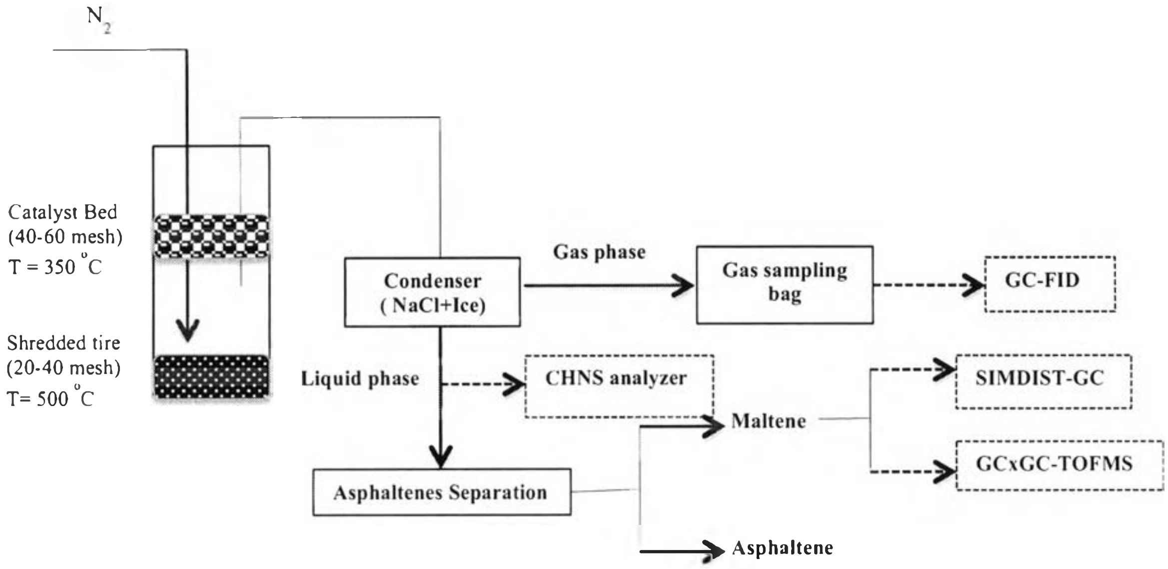

Figure 6.1 Schematic of waste tire pyrolysis system for collection and analysis of products.

6.3.4 Product Analysis

Liquid and solid products were weighed to determine the product yield. The gas yield was determined by mass balance. The gaseous products were analyzed by GC, Agilent Technologies 6890 equipped with HP-PLOT Q column (300 mm x 0.32 mmID and 20 µm film thickness) and FID detector. The liquid products were dissolved in n-pentane (mass ratio of n-pentane/oil =40:1) to precipitate asphaltene. Asphaltene was filtered by using a polyamide membrane (0.45 µm). The maltene solutions were then analyzed by Comprehensive Two-Dimension Gas Chromatography (Agilent Technologies 7890) with Time-of-Flight Mass Spectrometer (LECO, Pegasus® 4D TOF/MS equipped with the 1st GC column was a non-polar Rtx®-5Sil MS (30 m x 0.25mmID x0.25µm) and the 2nd GC column was an Rxi®-17MS(1.790m x 0.1mmID x0.1µm). The primary column was held up at 50 °C for 2 min, and then heated up to 310 °C with a ramping rate of 5 °C/min. After the final temperature was reached, it was held at 310 °C until the analysis was finished. The temperature of secondary column was held at 60 °C for 2 min, and then ramped up to 320 °C with the ramping rate of 5 °C/min. After reached, the final temperature of column was held at 320 °C until the analysis was finished The simulated true boiling point curves were determined by using a Varian GC-3800 simulated distillation gas chromatography equipped with FID detector and a 15m x 0.25 mm x 0.25 µm WCOT fused silica capillary column. The petroleum fractions were cut based on their boiling point ranges according to the ASTM D2887; gasoline (<149 °C), kerosene (149-232 °C), gas oil (232-343 °C), light vacuum gas oil (343-371 °C) and heavy vacuum gas oil (>371 °C). Moreover, sulfur and nitrogen content in tire-derived oil and char were determine by LECO®Elemetal Analyzer (TruSpec®CHNS). Furthermore, sulfur content in the gas products was determined from mass balance.

6.4 Results and Discussion

6.4.1 Catalyst Characterization

The XRD patterns of the HBETA, HMOR, HY, HZSM-5 zeolites and the supported Ni catalysts are displayed in Figure 6.2. Both impregnated catalysts and parent zeolites clearly display the characteristic XRD patterns of BEA, FAU, MOR and MFI structure. Therefore, the introduction of nickel on zeolites seems not to destroy the zeolite structure, but slightly affects the zeolite crystallinity. The characteristic peaks of metallic nickel are present at ~44.5° and ~51.8°.

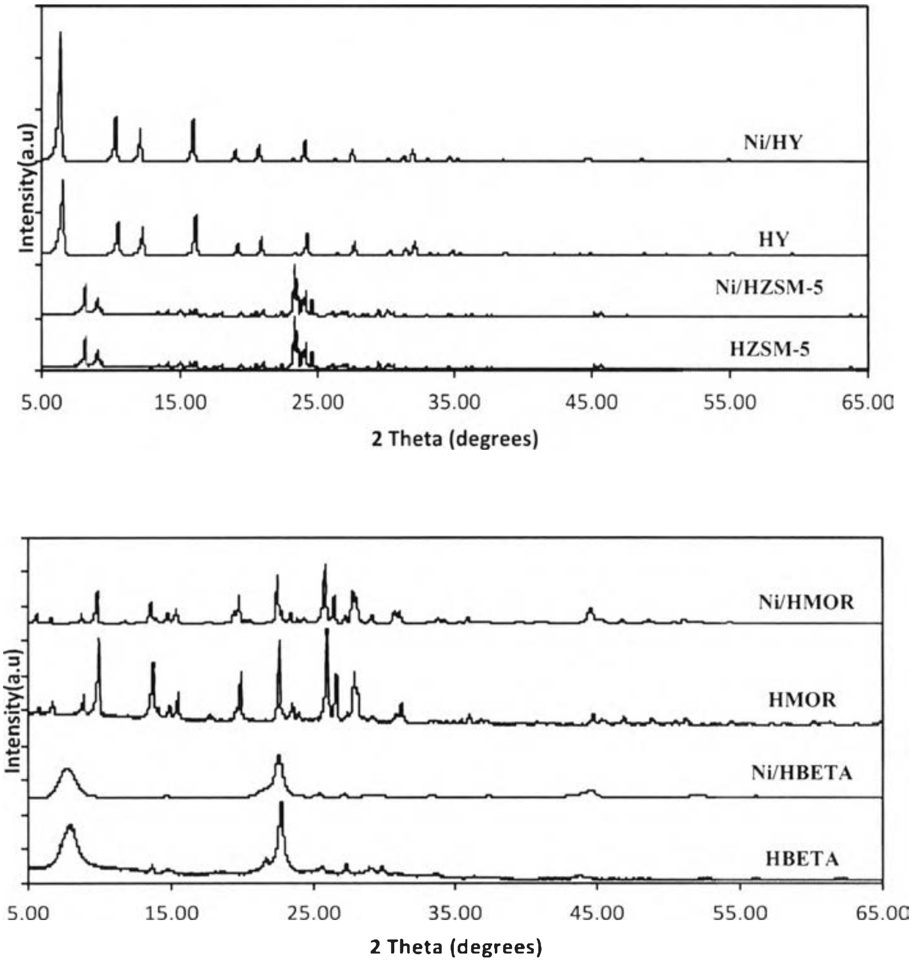

Figure 6.2 XRD patterns of zeolites and impregnated catalysts.

Table 6.1 BET specific area and pore volume of catalysts

Catalyst	Surface Area (m^2/g)	Micropore Volume (cm^3/g)
HBETA	559	0.280
HMOR	395	0.199
HY	546	0.277
HZSM-5	365	0.178
Ni/HBETA	466	0.215
Ni/HMOR	308	0.158
Ni/HY	537	0.264
Ni/HZSM-5	290	0.142

From Table 6.1, the decreases in BET surface area and micropore volume clearly indicate that Ni cluster might be located inside the zeolite pore, and partially block the zeolite channel (Maia et al., 2010). In addition, some metallic nickels may undergo sintering during the reduction of nickel oxide and then move to external surface of catalyst (Botas *et al.*, 2014).

6.4.2 Pyrolysis Yields

The pyrolysis product distribution from using parent zeolites and impregnated catalysts are displayed in Figure 6.3. It can be seen that when catalysts are used, the liquid and gas yields are suppressed while the coke formation over spent catalysts significantly increases. The reduction of liquid yield when catalysts are used in waste tire pyrolysis indicates that catalysts promote cracking activity of pyrolysis liquid. Nickel-modified catalysts are more effective than the parent zeolites since they give higher gas yields and lower liquid yields. Coke formations over spent the nickel modified catalysts is higher than that on parent zeolites since the incorporation of metallic nickel on zeolites increase surface activity and hydrogen transfer, which favors for coke formation.

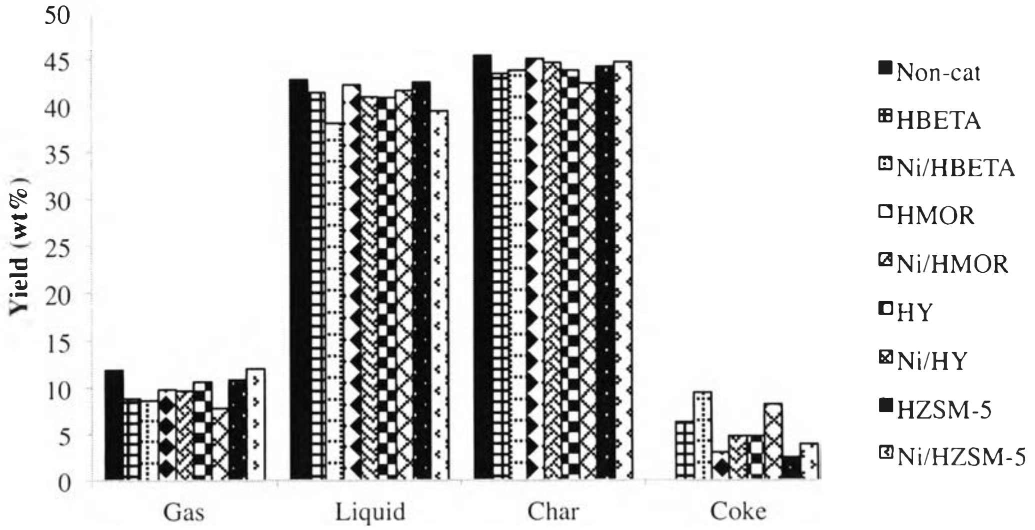

Figure 6.3 Effect of nickel based catalysts on pyrolysis yields

6.4.3. Effect of Ni Loading on Zeolites with Different Pore Sizes

Similarly classified as 3D channel structured possessing zeolites, HBETA has the pore size of 6.4x7.6 Å and HZSM-5 a smaller pore size of 5.3x5.6 Å. The effect of Ni loading was investigated on two supports with different pore sizes, HZSM-5 and HBETA zeolites. Figures 6.4 and 6.5 illustrate the concentration of petroleum fractions in maltenes and maltene compositions, respectively. The results indicate that the incorporation of nickel on HZSM-5 zeolite strongly enhances the gasoline and kerosene, whereas the gas oil, LVGO and HVGO reduce, indicating that the nickel species on HZSM-5 strongly promote cracking activity of HZSM-5 catalyst. Moreover, Ni/HZSM-5 strongly enhances the formation of mono-aromatic, whereas the formation of olefins, naphthenes, di-, poly-, and polar-aromatics reduced. These results indicate that the addition of nickel on HZSM-5 promote the transformation of multi-ring aromatics to mono-aromatics and aromatization of naphthenes and olefins to mono-aromatics. Significant differences are observed on the petroleum fractions and maltene composition with Ni doped on HBETA zeolite. The results show that the gasoline fraction drastically reduces, whereas the kerosene, gas oil, LVGO fractions clearly increase. This result indicates that the incorporation of nickel on HBETA strongly promotes the formation of heavier fraction in maltene. A similar effect of the addition of nickel on the maltene composition is also observed on HBETA. The formations of naphthenes and mono-aromatics significantly decrease, whereas the formations of di-, poly-, and polar-aromatics are drastically increased. It is reasonable to conclude that Ni species on HBETA strongly promote the formation of heavier fractions, especially polycyclic aromatics via the secondary reactions (oligomerization, cyclization, aromatization, etc) of naphthenes and mono-aromatics.

The different catalytic behaviors of Ni species on HZSM-5 and HBETA zeolites associate with different characteristics of the supports. HBETA and HZSM-5 zeolites have 3D pore channel with close Si/Al ratios. Therefore, the major difference of two acidic supports is pore size, the pore size of HZSM-5 is 5.3 Å x 5.6 Å and pore size of HBETA is 6.4 Å x 7.6 Å. Thus, HBETA zeolite has larger pore size than HZSM-5 zeolite, so its pore size provides a higher probability of formation of larger hydrocarbons than the smaller pore size of HZSM-5. Generally, cracking is the main reaction in the catalytic pyrolysis of waste tire. However, the secondary reactions also occur simultanously, depending on the catalyst properties. Hence, the addition of nickel on supports with a large pore size provides a higher probability of undergoing of hydrocarbons via secondary reactions resulting in the high production of multi-ring aromatics. Therefore, the formation of heavy fractions is favorable with the presence of Ni/HBETA catalyst.

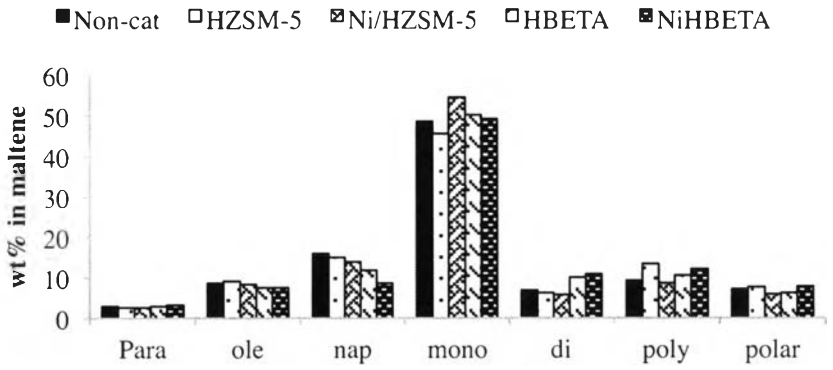

Figure 6.4 Concentration of each group in maltenes using Ni-loaded on HBETA and HZSM-5 zeolites.

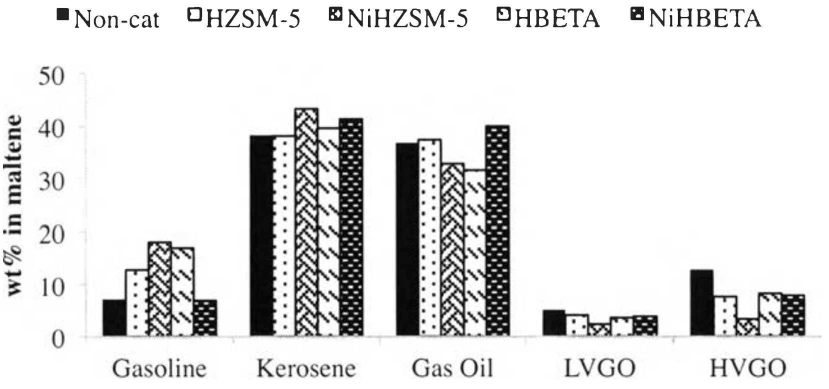

Figure 6.5 Petroluem fractions in tire-derived oils using Ni-loaded on HBETA and HZSM-5 zeolites.

Table 6.2 provides the information about the sulfur contents in oil. In all cases, the sulfur contents in oil significantly decrease by the addition of nickel species to the zeolites. Ni-doped catalysts result in a higher sulfur distribution on the spent catalysts than that obtained from the parent zeolites (see Figure 6.6).

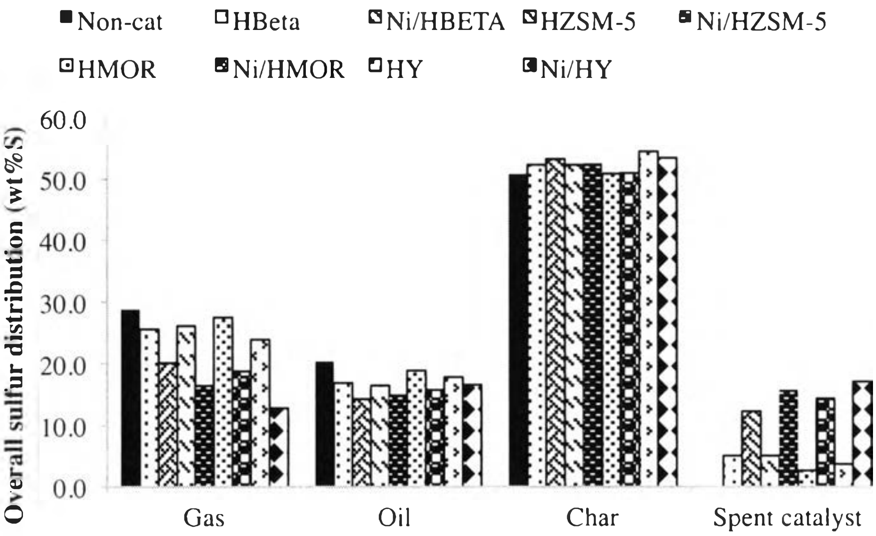

Figure 6.6 Overall sulfur distribution on in waste tire pyrolysis products and spent catalysts obtained from Ni-loaded catalysts.

Table 6.2 Sulfur content in oils obtained from Ni/HBETA and Ni/HZSM-5

Catalyst	Non-catalytic	HBETA	HZSM-5	Ni/HBETA	Ni/HZSM-5
Sulfur content in oil (wt%)	0.96	0.83	0.78	0.75	0.68
Sulfur reduction (%)	Base	14.1	18.8	21.6	29.2

These results indicate that sulfur compounds favorably adsorb on the nickel site. Generally, Ni has strong molecular orbital, which can attract sulfur atom from sulfur compounds. The sulfur compounds can donate the electron density to Ni, and further form a bond with Ni. Once favorably forming a bond with Ni, further desulfurization depends on the interaction of nickel with the support and available hydrogen in pyrolysis system. Desulfurization activity of Ni can be also prohibited by coke formation on the Ni sites of catalyst, which also affects to sulfur removal since the Ni site is less available for adsorption of sulfur compounds, causing the highly- competitive adsorption between hydrocarbons and sulfur compounds. The sites of nickel might be reduced when adsorbed hydrocarbons have undergone hydrogen transfer reaction, leading to coke formation. From the Figure 6.3, it can be clearly seen that the coke formation on Ni/HBETA catalyst is roughly twice as much as that formed on the Ni/HZSM-5. Therefore, sulfur content in oil produced from Ni/HBETA is higher than that produced by Ni/HZSM-5 catalysts since the nickel sites are more highly covered by coke, resulting in the reduction of desulfurization activity.

Moreover, sulfur contents in oil might be affected by different pore size of zeolites as well. It can be clearly seen that the addition of nickel on HBETA slightly results in the higher sulfur content than that obtained from Ni/HZSM-5 catalyst (see Table 6.2). The large pore size of HBETA zeolite allows a higher amount of sulfur-containing compounds to go inside the pore, and then some of sulfur-containing compounds can be desulfurized. Some molecules of sulfur-containing compounds such as thiophene can also be transformed to benzothiophene via undergoing hydrogen transfer reaction with available olefins, followed by cyclization and dehydrogenation. Moreover, some free sulfur molecules, which are formed from cracking of tire, are very active, so they can react with olefins and mono-aromatics to formed thiophenic compounds (Dung *et al.*, 2009). From Figure 6.7, it can be clearly seen that sulfur atoms are more distributed in the forms of benzothiophenes when using Ni/HBETA as a catalyst. This evidence confirms that the higher amount of benzothiophene is preferably formed in large pore size of zeolite, leading to the increment of sulfur content in the oil.

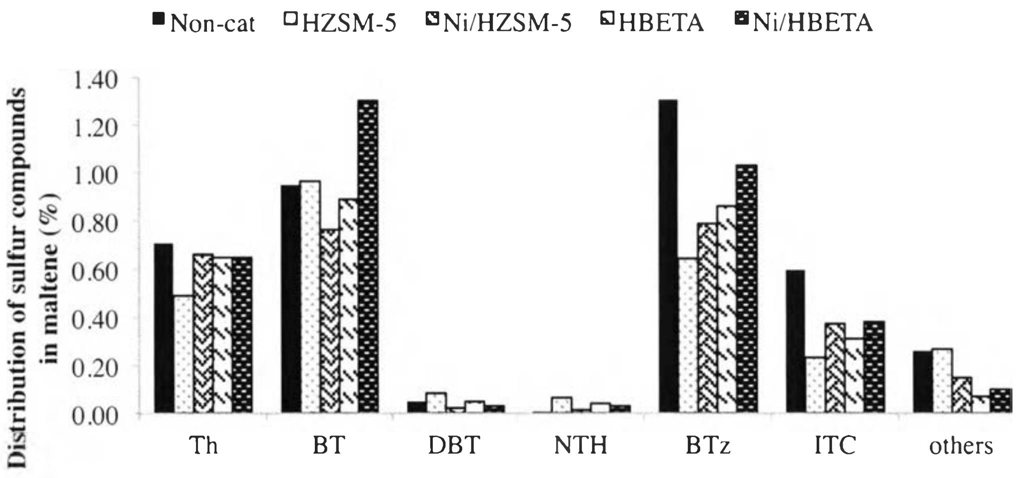

Figure 6.7 Distribution of sulfur compounds in maltenes obtain from Ni/HBETA and HZSM-5.

Regarding the petrochemical contents in oil, the incorporation of nickel on HBETA zeolite significantly suppresses the formation of ethylbenzene, toluene, cumene, styrene and mixed-xylenes (see Figure 6.8), whereas di- and poly-aromatics such as 7-isopropyl-1-methylnaphthalene, 1-ethylnaphthalene and 2-methylbiphenyl significantly increase (see Table 6.3). This can be explained that these di-and poly-aromatics can be formed by combination of valuable small aromatics. It is well known that the pore size of a zeolite governs the molecular size of products, so the molecular size of products cannot be larger than the pore size of a zeolite, unless they are formed at the external surface of a zeolite. Therefore, the addition of nickel on a large pore of HBETA provides a higher possibility of forming of multi-ring aromatics than Ni doped HZSM-5, resulting in the higher amount of di- and poly- and polar- aromatics in maltene.

Table 6.3 Dominant di-and poly-aromatics in maltene obtained from Ni/HBETA and Ni/HZSM-5

Hydrocarbons	wt% in Maltene			
	HBETA	**Ni/HBETA**	**HZSM-5**	**Ni/HZSM-5**
2-Methyl biphenyl	0.00	0.63	0.46	0.00
4,4'-Dimethyl biphenyl	0.45	0.89	0.45	0.05
4-Isopropy lbiphenyl	0.35	0.55	0.40	0.31
Naphthalene	0.36	0.06	0.38	0.28
1-methyl naphthalene	0.99	0.68	0.42	0.03
1,3-dimethyl naphthalene	1.24	0.92	0.71	0.15
1-ethyl naphthalene	1.14	1.93	0.93	0.96
7-isopropyl-1methylnaphthalene	0.51	0.86	0.10	0.15

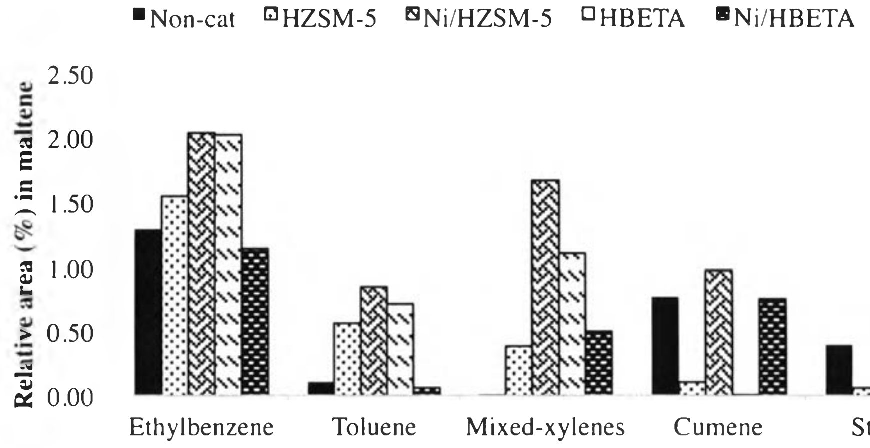

Figure 6.8 Petrochemicals in maltenes obtained from Ni/HBETA and Ni/HZSM-5.

A different behavior is observed with the Ni/HZSM-5 catalyst. In this case, the formation of ethylbenzene, toluene, cumene and mixed-xylenes increase, whereas the concentrations of di-, and poly-aromatics such as 2-methylbiphenyl, 4,4'-dimethylbiphenyl, naphthalene, 1,3-dimethylnaphthalene, and 1-methylnaphthalene decrease. Therefore, the introduction of Ni on HZSM-5 might promote the transformation of these di- and poly-aromatics to valuable aromatics such as ethylbenzene, toluene, mixed-xylene and etc. If the carbon-carbon scission takes place at the position between two benzene rings of 2-methylbiphenyl, the obtained products are benzene and toluene as displayed in **Scheme 1**. However, the concentration of benzene has been not found to increase, so it might possibly convert to other hydrocarbon because the radical benzene ring is very active to react with other hydrocarbons.

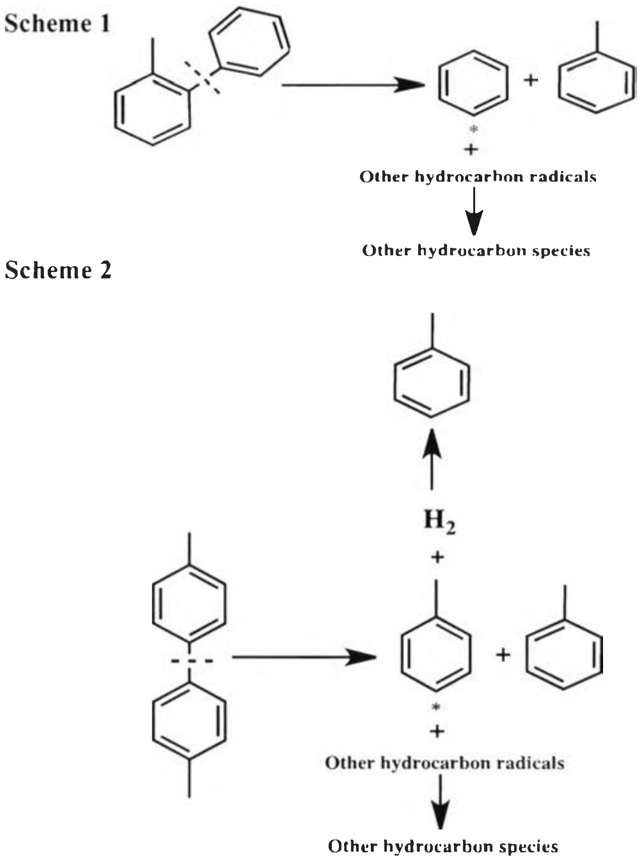

Figure 6.9 Possible reaction pathways for transformation of 2-methylbiphenyl and 4,4'-Dimethylbiphenyl to valuable aromatics by Ni/HZSM-5.

In addition, two molecules of toluene can be formed via these steps as shown in **Scheme 2**. First, the carbon-carbon scission take places at the position between the two benzene rings of 4,4'-dimethylbiphenyl, resulting in toluene and a radical of benzene derivative of toluene. If the toluene radical reacts with hydrogen, toluene can be formed. However, this radical of toluene is very active, it can react with other hydrocarbons to form other hydrocarbon species as well. Furthermore, di-aromatics such as naphthalene, 1,3-dimethylnaphthalene, and 1-methylnaphthalene can be also transformed to valuable aromatics via two steps. One rings of naphthalene, 1,3-dimethylnaphthalene and 1-methylnaphthalene are firstly hydrogenated at a nickel site to form tetralinic species (Kim *et al.*, 2014; Park *et al.*, 2013). Second, the naphthenic ring of tetralinic species are cracked to formed valuable petrochemicals as displayed in Figure 6.10 (Kim *et al.*, 2014; Park *et al.*, 2013; Bredael and Vinh, 1978).

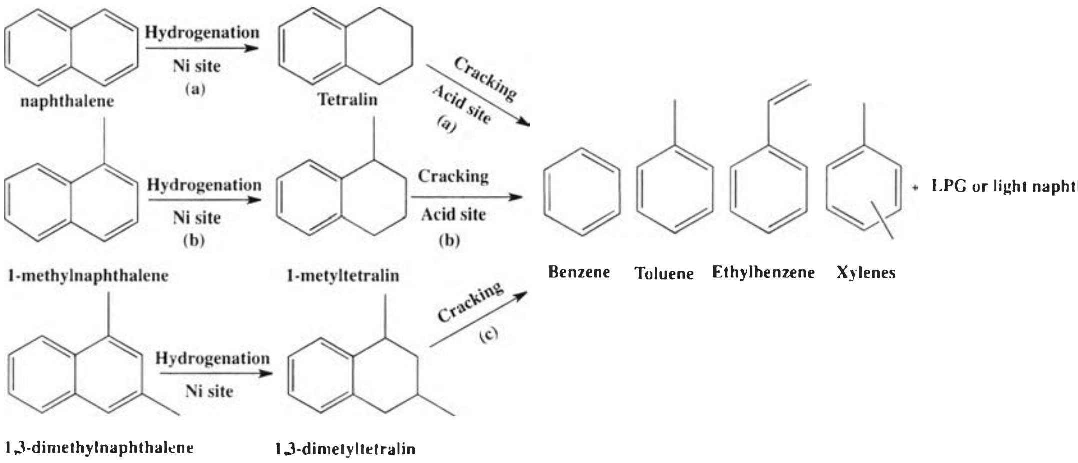

Figure 6.10 Possible reaction pathways of naphthalene, 1-methylnaphthalene and 1,3-dimethylnaphthalene by Ni/HZSM-5 adapted from Kim et al., 2014(a), Park et al., 2013(b), and Bredael and Vinh, 1978 (c).

6.4.4. Effect Nickel Loading on Zeolites with Different Channel Structures

With an almost equal pore size, HBETA with 3D pore channel structure and HMOR with 1D pore channel structure were used as the supports for investigating the effect of Ni loading on different pore channel structures. The oil produced by Ni/HMOR is lighter than that produced by Ni/HBETA since the composition of oil contains a higher amount of gasoline and kerosene and a lower amount of gas oil, LVGO and HVGO (see Figure 6.11). In addition, the introduction of nickel on HMOR strongly enhances the formation of mono-aromatics and olefins, whereas the formation of di-, poly-, polar-aromatics and naphthenes reduces. These results clearly indicate that nickel species on HMOR zeolite promote the formation of mono-aromatics and olefins together with suppression of di-, poly-, and polar-aromatics and aromatization of naphthenes. In the opposite, the Ni/HBETA catalyst enhances the formation of heavy components, with a significant increment of di-, poly- and polar-aromatics. Ni doping on HMOR and HBETA zeolites promotes aromatization activity of catalysts; Ni doped on HMOR favors the aromatization of napthenes, forming mono-aromatics, whereas Ni doped on HBETA favor the aromatization of naphthenes and olefins, forming multi-ring aromatics. This is probably a result of the different pore channel structures of zeolites. HMOR zeolite possesses a 1D channel structure, which allows a hydrocarbon molecule can further react with other hydrocarbons at a shorter time than the 3D channel structure of HBETA zeolite. In a 3D channel structure, intermediate hydrocarbons formed from previously-cracked molecules diffuse along the zeolite channel, and then might be combined with other hydrocarbons at nickel sites at a longer contact time, leading to the high formation of multi-ring aromatics. Therefore, the long residence time in a zeolite channel provides a higher possibility of multi-ring aromatics formation.

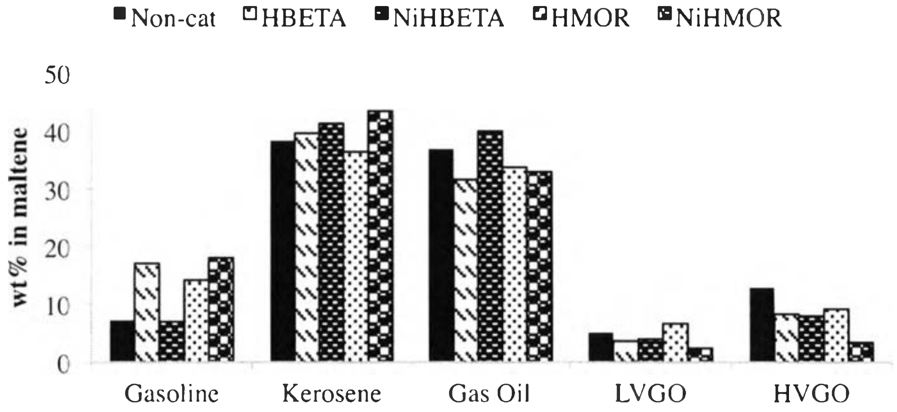

Figure 6.11 Petroluem fractions in tire-derived oils using Ni-loaded on HMOR and HBETA zeolites.

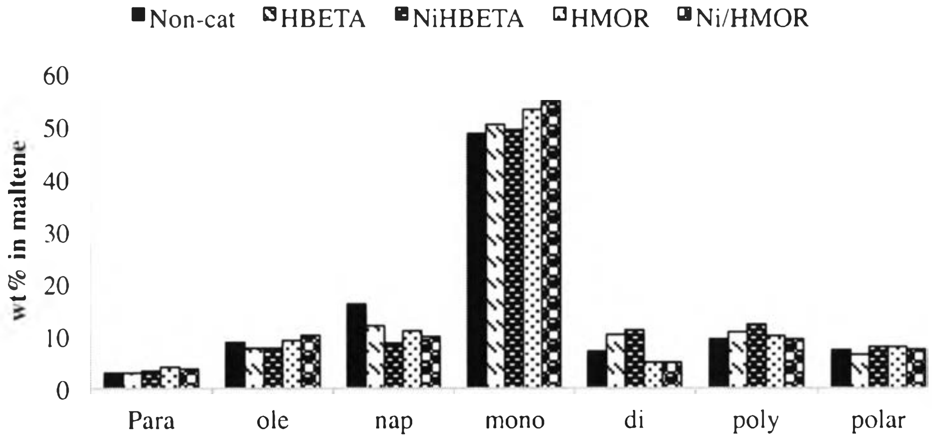

Figure 6.12 Concentration of each group in maltenes using Ni-loaded on HMOR and HBETA zeolite.

Table 6.4 Sulfur content in oil obtained from Ni/HBETA and Ni/HMOR catalysts

Catalyst	Non-catalytic	HBETA	HMOR	Ni/HBETA	Ni/HMOR
Sulfur content in oil (wt%)	0.96	0.83	0.9	0.75	0.78
Sulfur reduction (%)	Base	14.1	5.8	21.6	19.1
Sulfur reduction by Ni (%)	-	Base	Base	9.64	13.3

Table 6.4 illustrates the sulfur content in oils obtained from Ni/HBETA, Ni/HMOR catalysts and parent zeolites. HBETA zeolite with a 3D channel structure provides a lower amount of sulfur content in oil than that produced by HMOR zeolite since the complex channel structure of HBETA allows the sulfur compounds to stay inside the zeolite channel for a longer residence time, resulting in the higher possibility of desulfurization of sulfur compounds. In addition, the introduction of Ni on both zeolites clearly reduced the sulfur content in oil. The sulfur content in oil obtained from Ni/HBETA is slightly lower than that obtained from Ni/HMOR catalysts. This clearly indicates that the nickel located on 3D zeolite channel provides better desulfurization activity since the sulfur compounds can stay longer in zeolite channel, and then are desulfurized at nickel site more effectively than 1D zeolite channel. Regarding the sulfur reduction by Ni species, the addition of Ni on HMOR zeolite give a better sulfur reduction than that obtained from the Ni/HBETA catalyst. This can be explained that the coke formation on the spent Ni/HBETA is higher than on Ni/HMOR, resulting in the reduction of available Ni

sites, which directly affects the desulfurization activity of catalysts since the desulfurization of sulfur compounds mainly take places on the Ni site.

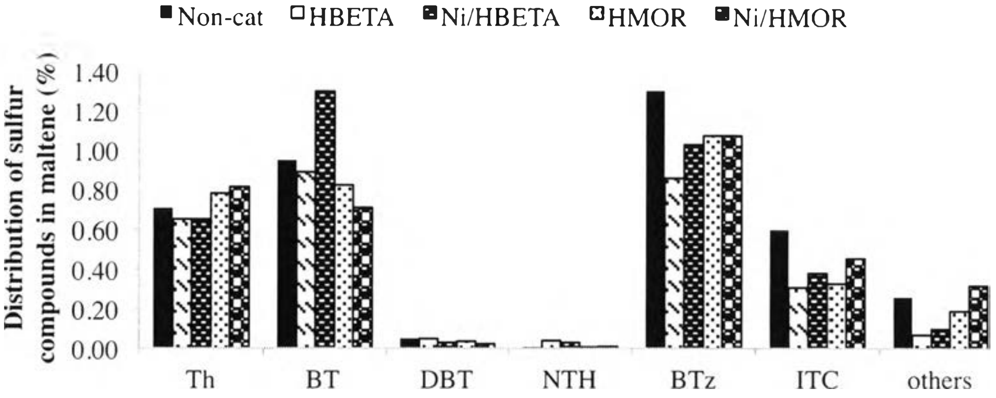

Figure 6.13 Distribution of sulfur compounds in maltenes using Ni-loaded on HMOR and HBETA zeolites.

Figure 6.13 displays that benzothiophene (BT) significantly reduces when Ni is doped on HMOR, but sharply increases for Ni/HBETA zeolite. This clearly indicates that the incorporation of Ni on 3D zeolite channel does not only promote sulfur removal from sulfur –containing compounds, but also the interaction of sulfur compounds with other hydrocarbons. The longer residence time of hydrocarbons or sulfur-containing compounds in the channel can provide a higher interaction of hydrocarbons and free sulfur atom, which are directly evolved from cracking of tire molecules.

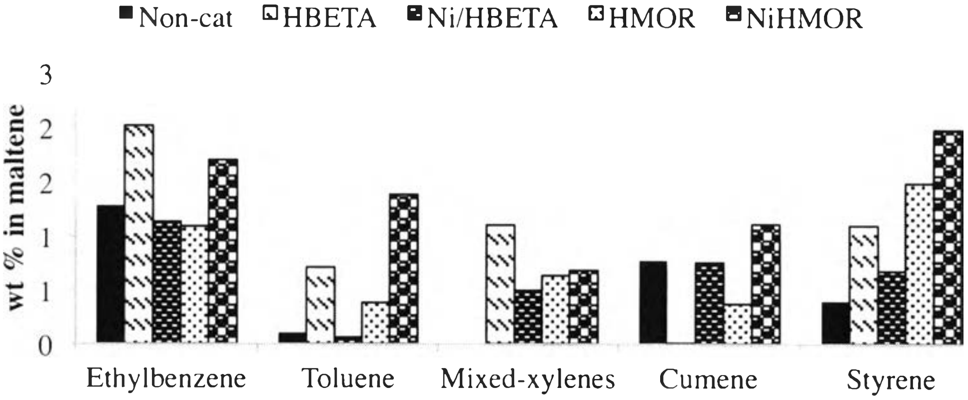

Figure 6.14 Petrochemicals in maltenes using Ni-loaded on HMOR and HBETA zeolites.

Regarding the petrochemical species in maltene, nickel doping on HBETA zeolite significantly decreases the formation of ethylbenzene, toluene, styrene and mixed-xylenes (see Figure 6.14). On the other hand, it was found that the concentrations of 2-methyl biphenyl and fluorene in oil clearly increase with using Ni/HBETA catalyst (see Table 6.5). Therefore, the Ni loading in 3D zeolite channel might promote the interaction of any valuable aromatics as mentioned above to multi-ring aromatics such as 2-methylbiphenyl, fluorene and etc.

Table 6.5 Dominant poly-aromatics species in maltenes obtained from Ni/HBETA and Ni/HMOR catalysts

Hydrocarbons	wt% in Maltene			
	HBETA	Ni/HBETA	HMOR	Ni/HMOR
2-methylbiphenyl	1.18	1.49	1.38	1.24
2-ethylbiphenyl	1.32	1.12	1.15	0.65
Fluorene	0.14	0.26	0.12	0.10

On the other hand, using Ni/HMOR, the formation of ethylbenzene, toluene, cumene and styrene significantly increases, whereas the concentration of poly-aromatics in maltene decreases. Simultaneously, it is also found that the concentration of 2-ethylbiphenyl and 4-methylbiphenyl slightly decreases (see Table 6.5), and these two poly-aromatics can be transformed to ethylbenzene and toluene as illustrated in Figure 6.15. Therefore, the introduction of nickel on HMOR zeolite might promote cleavage of biphenyl compounds. Ethylbenzene and benzene can be directly formed via carbon-carbon scission at the position between two benzene rings of 2-ethylbiphenyl. However, it was found that the concentration of benzene in maltene is extremely lower than that of ethylbenzene, so the benzene radical might react with other hydrocarbon radicals to form other hydrocarbon species as displayed in **Scheme 1**. Toluene and benzene can be directly formed via carbon-carbon scission at the position between two benzene rings of 4-methylbiphenyl as displayed in **Scheme 2**, but benzene might also be converted to other hydrocarbons because benzene with radical is very active to react with other hydrocarbons molecules (see Figure 6.14).

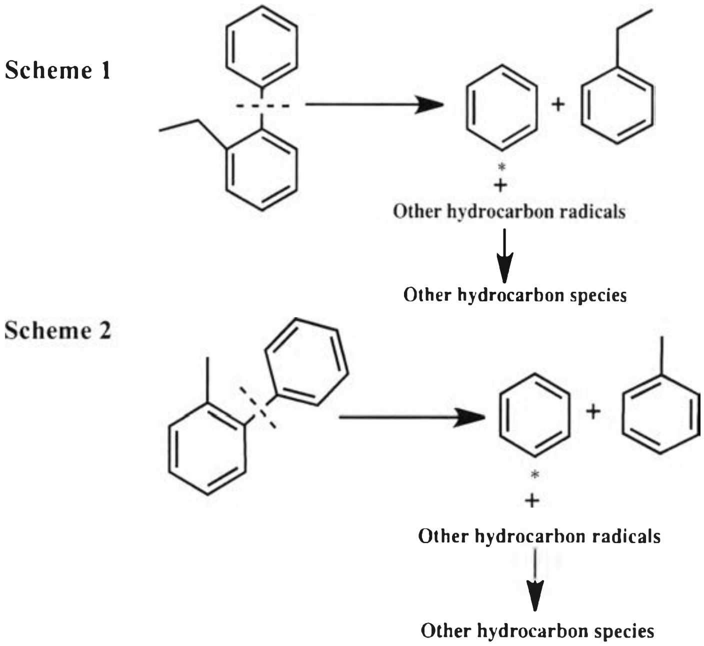

Figure 6.15 Possible reaction pathways for transformation of 2-ethylbiphenyl, 4-methylbiphenyl to valuable aromatics promoted by Ni/HMOR.

In summary, the effect of zeolite channel structure is one of important factors, which should be considered in selecting a catalyst for enhancement of oil quality and petrochemical production from pyrolysis of waste tire. The introduction of nickel on a zeolite with 1D channel structure is better than on a zeolite with a 3D channel structure in terms of petrochemical formation and quality of oil. Therefore, it can be suggested that for the enhancement of oil quality and petrochemical production by using Ni is not recommended as a promoter, a zeolite that has a complex channel structure since the combination of complex 3D zeolite channel and Ni species do not only promote cracking activity of catalyst, but also promote the secondary reactions (oligomerization, cyclization, aromatization and etc.), leading to the high formation of heavy hydrocarbons. Moreover, Ni catalysts normally promote the high formation of coke on the nickel sites, so the combination of nickel with 3D channel structure promoted the higher coke formation than the nickel supported on a zeolite with 1D channel structure since the hydrocarbons, which can stay inside in the 3D channel with a long residence time, easily undergo aromatization and combination reactions, forming coke on the catalyst. The high formation of coke on catalyst strongly decreases the catalytic activity, leading the rapid deactivation of catalyst.

6.4.5. Effect of Nickel Loading on Zeolites with Different Acid Densities

The effect of Ni loading was investigated on two zeolites with different acid densities. With a similar pore size, HBETA (6.4 x 7.6 Å) with the Si/Al ratio of 14 was used in comparison with HY (7.4 Å) with the Si/Al ratio of 7.5. Similarly, the introduction of nickel on HBETA and HY zeolites favorably produces the heavier oils with a high proportion of di-, poly-, and polar-aromatics as compared to the parent zeolites. However, the oil produced from Ni/HY catalyst slightly is heavier that the one produced from Ni/HBETA catalyst. Moreover, it is clearly seen that the amounts of di-, poly- and polar-aromatics in the oil obtained from Ni/HY catalyst are higher than those produced by Ni/HBETA catalyst. This can be suggested that nickel species on these two acidic zeolites might promote the combination of lighter hydrocarbons (naphthene, olefins, mono-aromatics) to form multi-ring aromatics. The increment of heavy hydrocarbons might associate with the acidity of catalyst and coke formation on the catalyst. Generally, nickel promotes the hydrogen transfer reactions, leading to the formation of hydrocarbons with various C/H ratios, which can act as a coke precursor. Moreover, the introduction of nickel on a zeolite with a higher acid density (lower Si/Al ratio), for this case, can drive a higher formation of heavy hydrocarbon, especially multi-ring aromatics than the parent zeolite since the high acid density of zeolite promotes cyclization and aromatization activity of catalyst, resulting in reduction of olefins and naphthenes in the maltene (see Figure 6.16). Furthermore, the high coke formation on the spent catalysts is a clear indicator that the introduction of nickel with HBETA and HY zeolites provides a higher cracking activity than the parent zeolites. However, the higher cracking activity obtained with nickel promoter does not result in the formation of lighter hydrocarbons, but the higher amount of heavier hydrocarbons was formed. Therefore, the high catalytic activity usually associates with coke formation on the catalyst. The high coke formation over nickel-based catalysts might reduce the active sites, which is favorable for cracking of hydrocarbons. Therefore, it can be concluded that the introduction of nickel on HY zeolite with a higher acid density promotes the higher formation of di-, poly-, and polar-aromatics than those obtained from the Ni/HBETA catalyst, resulting in the higher proportions of gas oil, LVGO and HVGO (see Figure 6.17).

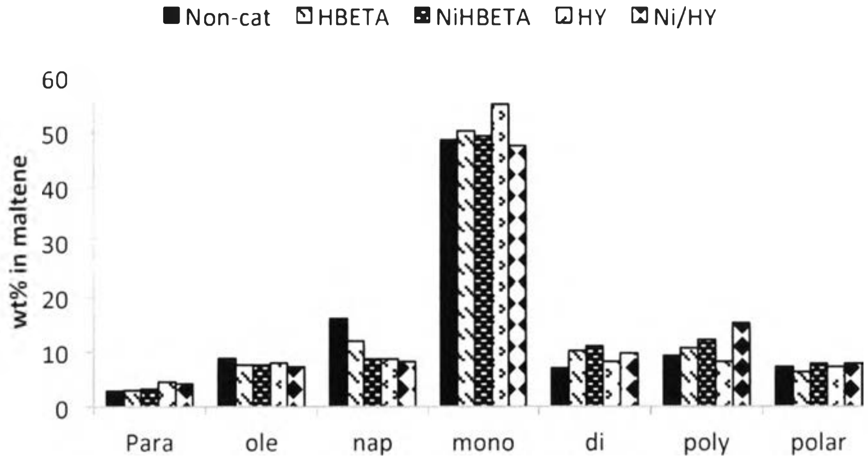

Figure 6.16 Concentration of each group in maltene using Ni-loaded on HBETA and HY zeolites.

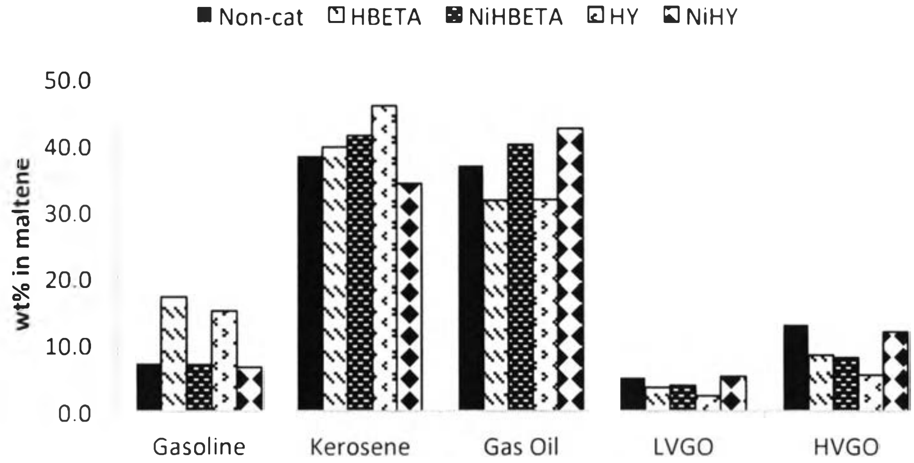

Figure 6.17 Petroluem fractions in tire-derived oil using Ni-loaded on HBETA and HY zeolites.

Furthermore, the introduction of nickel on HBETA and HY zeolites causes a higher reduction of sulfur content in oil than those obtained from the parent zeolites (see Table 6.6). Apparently, the Ni/HBETA catalyst produces the oil with a lower sulfur contents than the Ni/HY catalyst.

Table 6.6 Sulfur content in oils obtained from Ni/HBETA and Ni/HY catalysts

Catalyst	Non-catalytic	HBETA	HY	Ni/HBETA	Ni/HY
Sulfur content in oil (wt%)	0.96	0.83	0.88	0.75	0.8
Sulfur reduction (%)	Base	14.1	8.4	21.6	16.5

These results indicate that the introduction of nickel on a zeolite with higher acid strength (higher Si/Al ratio) slightly results in a lower sulfur content in oil since the competition adsorption between other hydrocarbons and sulfur compounds occurs on nickel sites. Moreover, the high content of total aromatics are produced from Ni/HY than from Ni/HBETA. Therefore, the higher amount of aromatics might be adsorbed on the nickel sites of HY zeolite, resulting in the reduction of desulfurization activity of nickel species on HY zeolite. Moreover, the aromatic adsorptions have less influence on the desulfurization activity of catalysts with higher acidity (Ding *et al.*, 2007). Figure 6.18 displays that thiophenes decrease with using Ni/HY as a catalyst, but not Ni/HBETA. These results indicate that high acid density of HY zeolite favorably breaks the C-S bond of thiophene. Moreover, the other sulfur species slightly increase with the presence of nickel on HBETA and HY zeolite. It can be explained that the introduction of nickel on these two zeolites might reduce the active sites of HBETA and HY zeolites, which favorably breaks C-S and C-N bonds of sulfur-containing compounds. Generally, the first step of the sulfur removal from of sulfur-containing compounds is adsorption of sulfur atom on nickel sites. The Ni/HBETA and Ni/HY catalysts generate a high amount of coke on the catalyst, especially on the nickel sites, so the available nickel sites, which is favorable for removal of sulfur-containing compounds, are reduced when the coke formation and competitive adsorption of aromatics hydrocarbons take place on the nickel sites.

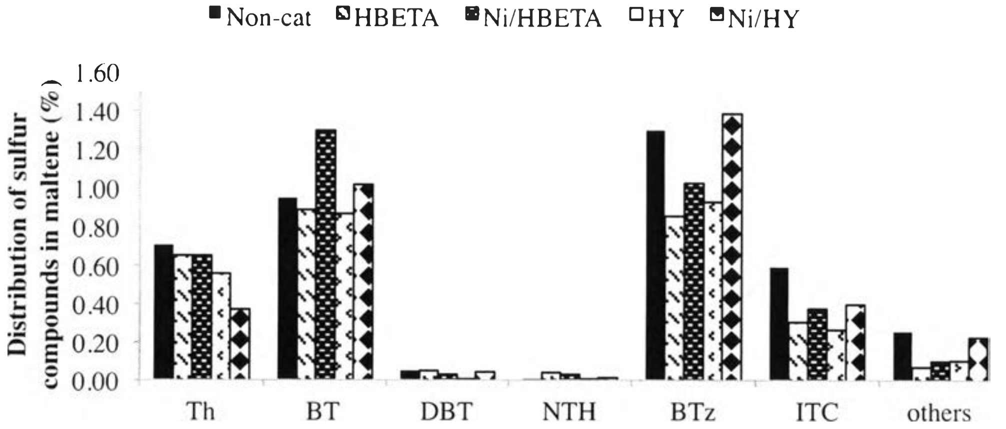

Figure 6.18 Distribution of sulfur-containing compounds in maltenes obtained from Ni/HBETA and Ni/HY catalysts.

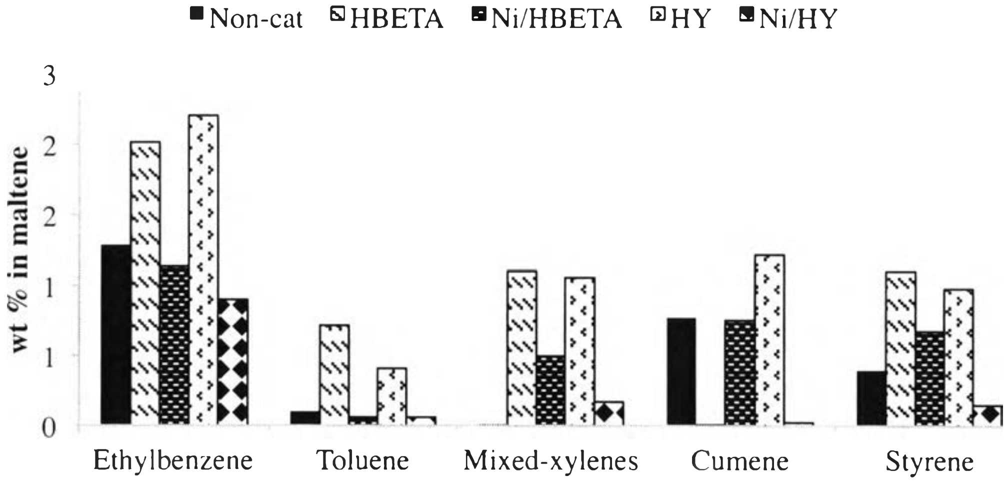

Figure 6.19 Petrochemicals in maltenes obtained from Ni/HBETA and Ni/HY catalysts.

Regarding the petrochemical species in maltenes, nickel species on HBETA and HY zeolites significantly decrease the formation of ethylbenzene, toluene, styrene and mixed-xylenes (see Figure 6.19). On the other hand, it is also found that the concentrations of 2-methylbiphenyl, 2-ethylbiphenyl and 4-isopropylbiphenyl significantly increase with the addition of nickel on the HY zeolite, and the concentrations of 7-Isopropyl-1-methylnaphthalene, 2-methylbiphenyl and 2-ethylbiphenyl also increase with using the Ni/HBETA catalyst (see Table 6.8).

Table 6.8 Dominant di- and poly-aromatics in maltenes obtained from Ni/HBETA and Ni/HY catalysts.

Hydrocarbons	wt % in Maltene			
	HBETA	Ni/HBETA	HY	Ni/HY
2-methyl biphenyl	1.18	1.49	1.13	1.92
4-Isopropyl biphenyl	0.35	0.55	0.20	0.49
2-ethylbiphenyl	1.32	1.12	1.05	1.56
7-isopropyl-1methylnaphthalene	0.51	0.86	0.34	0.35

This can be explained that some of petrochemicals and other mono-aromatics, naphthenes and olefins might be converted to these poly-aromatics. The amounts of these poly-aromatics depend on the acid density and acid strength of the two zeolites since the two supports have quite similar pore size and 3D pore channel structure. Therefore, it can be concluded that the introduction of nickel on a zeolite with high acid density such as HY, promotes the higher formation of poly-aromatic such as methylbiphenyl, ethylbiphenyl, isopropylbiphenyl and etc. The introduction of nickel on HBETA zeolite, which exhibits a higher acid strength promote the formation of the poly-aromatics as well, but the high acid density is more effective for enhancement of multi-ring aromatic formation.

6.5 Conclusions

The effect of nickel promoter loaded on different zeolites; that are HBETA, HZSM-5, HMOR, and HY, were studied. The result showed that all Ni doped catalysts enhanced the aromatic formation and sulfur removal from oil. However, the catalytic behaviors of nickel promotion strongly depended on zeolite properties. The pore size of zeolite supports was found to govern the size of hydrocarbons products and sulfur removing ability of Ni catalysts. The incorporation of Ni on a HZSM-5 with a smaller pore size produced the lighter oil with higher proportion of gasoline, kerosene and valuable petrochemicals than the Ni/HBETA. Moreover, Ni/HZSM-5 provide the oil with a lower sulfur content than the Ni/HBETA due to lower coke formation and a lower possibility of forming of large hydrocarbons and sulfur-containing compounds. The channel structure of zeolite supports was found to govern the hydrocarbon products and sulfur removing ability of Ni catalyst due to the effect of residence time of hydrocarbons in the pore. The introduction of Ni on HMOR zeolite with 1D channel structure produced the slightly higher sulfur oil with a higher proportion of gasoline, kerosene and valuable petrochemicals than Ni loaded on HBETA zeolite (3D channel structure) due to lower coke formation and a shorter contact time of hydrocarbons. The acid density of zeolite supports was found to promote the formation of heavy aromatics and control the sulfur removing ability of Ni catalysts. The incorporation of nickel on HY zeolite with a higher acid density (lower Si/Al ratio) produced the higher sulfur oil the with a higher proportion of gas oil, LVGO and HVGO, but a lower amount of valuable petrochemicals due to higher competition adsorption of hydrocarbons and sulfur-containing compounds on Ni sites. In conclusion, for the enhancement of oil quality and petrochemical production, Ni is not recommended as a promoter on a zeolite that has a complex channel structure and a large pore size since the introduction of Ni on this kind of supports promoted the formation of heavy hydrocarbons and reduced the sulfur removing ability of Ni catalyst. Therefore, for the production of the waste tire-derived oil with high petrochemicals and low sulfur contents by using Ni promoter, the zeolite supports must have a suitable pore size of around 5.5-7 Å and 1D channel structure that allows hydrocarbons and sulfur compounds can stay inside at enough contact time to form valuable petrochemical and to remove sulfur compounds.

6.6 Acknowledgements

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