CHAPTER VI

EFFECT OF BRÖNSTED ACID DENSITY OF MESOPOROUS MCM-48 ON TIRE-DERIVED OIL, PETROCHEMICALS, AND SULFUR REMOVAL

6.1 Abstract

MCM-48 (Mobil Composition of Matter number 48) is a cubic-structured mesoporous silica material widely used in many applications such as separation and catalysis. The addition of alumina atoms into the framework of Si-MCM-48 can generate the Brönsted acid sites whose density is increased with the increasing number of Al atoms. This work investigated the waste tire pyrolysis by using Si-MCM-48 and Al-MCM-48 synthesized via a hydrothermal method as catalysts. The pyrolysis of waste tire was conducted in a bench-scale reactor. The catalyst was characterized by using small-angle XRD, BET, XRF, TPD-NH₃, ^{27}Al solid-state NMR, and TGA. In addition, the products were analyzed by using SIMDIST-GC and S analyzer, while a GC×GC-TOF/MS was used to analyze the species in oils. The results from GCxGC-TOF/MS showed that Si-MCM-48 can help to remove the large molecules, di- and poly-aromatic hydrocarbons, more greatly than the Al-MCM-48 catalysts. Moreover, all catalysts increased the concentration of petrochemicals in maltenes, except Al-MCM-48 (25) that has the highest Brönsted acid density and strength. The production of petrochemicals can be ranked in the order: Al-MCM-48 (42) > Si-MCM-48 > Al-MCM-48 (82) > no catalyst > Al-MCM-48 (25). Additionally, the Si-MCM-48 catalyst gave the highest ability to remove sulfur, which is 33.9 % of sulfur removal from tire-derived oil. In addition, the desulfurization of tire-derived oils by using Al-MCM-48 catalysts can be enhanced with decreasing Si/Al ratio or increasing Brönsted acid density. It can be concluded that a large pore size affects more pronouncly than the acid density to the ability of a catalyst on removal of large molecules from tire-derived oil; however, Brönsted acid sites are still essential for removal of sulfur- and heteroatom-containing compounds.

6.2 Introduction

Tire-derived oil is an aromatic-based hydrocarbon mixture comprised of 73 % aromatic hydrocarbons, including some large aromatic hydrocarbons. The group of mono-aromatic hydrocarbons is the main compounds that consist of 34.9 wt.% in maltenes (Yuwapornpanit and Jitkarnka, 2015). Some mono-aromatics in tire-derived oil are valuable products such as benzene (C_6H_6), toluene (C_7H_8), xylenes (C_8H_{10}), ethylbenzene (C_8H_{10}), and cumene (C_9H_{12}) that are widely used in petrochemical industry. For examples, benzene is used for coating, printing and extracting. Furthermore, it is used as a raw material for production of plastics. Toluene is used as an octane booster to improve the performance of machines. Some applications of xylenes are similar to benzene, which are used for printing and painting. Ethylbenzene is primarily used in the manufacture of styrene. Cumene is mainly used as a raw material in the manufacture of phenol and acetone. Moreover, large aromatic hydrocarbons (di- and poly-aromatic hydrocarbons) were found about 25 wt.% in maltenes (Yuwapornpanit and Jitkarnka, 2015). Moreover, Laresgoiti *et al.* (2004) found polycyclic aromatic hydrocarbons such as naphthalene, fluorene, phenanthrene and biphenyl in tire-derived oil by using fluidized-bed pyrolysis units. Furthermore, the amount of polycyclic aromatic hydrocarbons also increased with increasing pyrolysis temperature (Cunliffe and Williams, 1998). The presence of large aromatic hydrocarbons in fuels does not only damage the engines, but also increases the high amount of toxicity in the environment due to the incomplete combustion. It is therefore essential to decrease large aromatic molecules in tire-derived oil, which a catalyst with a large pore size may be needed.

Mesoporous materials have large pore sizes with the diameter range of 2-50 nm. They are widely used in many applications such as separation and catalysis. Normally, MCM-41 and MCM-48 are popular mesoporous materials due to high surface area, pore volumn, and uniform structure. Mesoporous molecular sieves, MCM-41 and MCM-48, were successfully synthesized during 1990s by the researchers at Mobil Oil Corporation. Moreover, the pore diameter was controlled by surfactant as a pore directing agent. The structure of MCM-41 is a one-dimension material that consists of an array of hexagonal channel, and MCM-48 has three-

dimension cubic structure (Van *et al.*, 2008). Previously, researchers studied the performance of mesoporous molecular sieves, MCM-48 and MCM-41, as a catalyst in waste tire pyrolysis. Dũng *et al.* (2009a) observed that MCM-41 catalyst decreased the carbon number distribution in tire-derived oil from C5-C50 for the non-catalytic case to C10-C20. The result from liquid column chromatography showed that MCM-41 can reduce the contents of poly- and polar-aromatics with the increasing mono-aromatic hydrocarbons in the oil. In addition, the activity of mesoporous MCM-48 catalyst in waste tire pyrolysis was studied by Witpathomwong *et al.* (2011). Similarly, it was found that the concentration of poly- and polar-aromatic hydrocarbons slightly decreased, indicating that the elimination of large molecules in tire-derived oil was successful using mesoporous catalysts because of their large pore sizes that can handle the large molecules.

Moreover, several researchers studied mesoporous aluminosilicate materials, which alumina atoms are incorporated into the ordered mesoporous silica. They have potential in the applications of adsorption and acid catalyst. Park *et al.* (2008) studied the catalytic performance of Si-MCM-48 and Al-MCM-48 in the degradation of polypropylene. The authors found that Al-MCM-48 catalyst provided a higher conversion than Si-MCM-48 catalyst. Additionally, in the oil products, the introduction of alumina atoms in Si-MCM-48 can reduce the carbon number distribution in oil from C7-C14 to C7-C10 since alumina atoms incorporated in the silica framework are the acid sites, and provided better cracking activity. Similarly, Jeon *et al.* (2007) used mesoporous MCM-48 as a catalyst for degradation of linear low density polyethylene (LLDPE). In oil products, Al-MCM-48 generated C_7-C_{10} hydrocarbons while Si-MCM-48 generated broader distribution of oil products in the range of C_8-C_{14} hydrocarbons. Therefore, higher acid sites showed the good performance for degradation of large molecules of polymers. On the other hand, mesoporous MCM-48 was used as a catalyst for hydrocracking process (Alsobaai *et al.* 2007). They found that Al-MCM-48 (Si/Al = 25) that has the highest total acidity provided the highest conversion of gas oil to diesel production. Furthermore, aluminosilicate mesoporous materials with various Si/Al ratios have been used as absorbents to remove sulfur in the diesel fuel (Liu *et al.*, 2007). The authors observed that sulfur removal can be ranked in the order: Al-MCM-41 (50) > Al-MCM-41 (30)

> Al-MCM-41 (100), indicating that the adsorption capacity of sulfur-containing compounds depended on the amount of Lewis acidic sites. A strong interaction between sulfur-containing compounds with Lewis acidic sites helped to increase the adsorption capacity over Al-MCM-41.

According to the literature review, mesoporouse can handle large molecules due to its large pore size. In order to improve the quality of tire-derived oil in terms of large aromatic hydrocarbons reductions, mesoporous MCM-48 are necessarily used as a catalyst. Moreover, Al-MCM-48 catalyst that was introduced alumina atoms into silica framework, generating acid sites, was expected to enhance desulfurization in oils. Furthermore, the components such as in tire-derived oil by using mesoporous MCM-48 have not been identified in the previous work. The purpose of this work was therefore to investigate the potential effect of acid density of mesoporous MCM-48 catalysts on removal of large aromatic and sulfur compounds and the production of petrochemicals in tire-derived oil from waste-tire pyrolysis.

6.3 Methodology

6.3.1 Catalyst Preparation

Tetraethoxysilane (TEOS) (Merck) and aluminum isoproproxide ($\geq$ 98+%, Acros) were used as the silicon and aluminium sources, respectively. Cetyltrimethyl-ammonium bromide (CTAB) ($\geq$ 99+%, Acros) was used as the template. Other chemicals are sodium hydroxide, aqueous ammonia (aq. NH_3), and ethanol. The Si-MCM-48 catalyst was synthesized at room temperature following the 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 heating rate 2 °C/min.

The Al-MCM-48 catalysts (starting Si/Al of precursors = 50, 75, and 200) were synthesized via hydrothermal synthesis method (Huang *et al.*, 2008) using tetraethoxysilane (TEOS), aluminum isopropoxide, and cetyltrimethylammonium bromide (CTAB) as the silica source, alumina source, and templating agent, respectively. 9.56 g of CTAB was dissolved in 170 ml of deionized water at 35 °C. Then, 3.15 g of NaOH was added into the resulted solution, and stirred for 10 min. After that, 29.07 ml of TEOS and 0.13-0.55 g of alumina precursor were added and stirred for 2 h at 35 °C. Then, the gel was transferred to a Teflon-lined autoclave and heated at 120 °C for 40 h. The solid product was filtrated and washed with deionized water. Next, the catalyst was dried at 80 °C overnight and calcined at 540 °C with 2 °C/min heating rate for 6 h. Finally, the catalyst powder was pelletized, crushed, and sieved into the particle size range of 40-60 mesh.

6.3.2 Catalyst Characterization

The X-ray diffraction patterns of samples were 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. 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. The Si/Al ratios of catalyst were determined by the X-ray fluorescence (XRF) instrument combined with AXIOS&SUPERQ version 4.0 systems. The IQ+ program was used to analyze the elemental composition of catalysts. 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. The ^{27}Al MAS NMR spectra were analyzed by a Bruker DPX-300 NMR spectrometer. The spectra were recorded at a frequency of 78 MHz. The experimental conditions were set as follows: 800 numbers of scan (NS), a relaxation delay of 4 second, spin rate of 5 kHz and spectral size 4 K with 2 K time domain size. 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 sulphur content in spent catalysts.

6.3.3 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 7.5 g of catalyst was loaded into the catalytic zone. 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.

6.3.4 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 obtained maltene solution. 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 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).

6.4 Results and Discussion

6.4.1 Catalyst Characterization

The small-angle X-ray scattering (SAXS) patterns of Si-MCM-48 and Al-MCM-48 (starting Si/Al of precursors = 50, 75, and 200) are shown in Figure 6.1. The small angle X-ray scattering (SAXS) patterns of all catalysts present the diffraction peaks at approximately $2\theta = 2.5°$ and $2\theta = 3.0°$, corresponding to the d-spacing of d_{211} and d_{220} planes, respectively, which are the characteristics of the parent MCM-48, and correspond to the Ia3d group (Kosslick *et al.*, 1998). Figure 6.1b illustrates the intensities of diffraction peaks decrease with decreasing Si/Al ratios. It can be suggested that the amount of alumina atoms incorporated into Si-MCM-48 framework, resulting in the decreasing degree of crystallinity of a cubic structure. Additionally, the ratio of d_{211}/d_{220} in the range of 0.86-0.87 also confirms the characteristics of a cubic symmetry (Danumah *et al.*, 2001). The Si/Al ratios and textural properties of Si-MCM-48 and Al-MCM-48 catalysts are reported in Table 6.1. The lattice parameters (a_0) were calculated from the d-spacing value of d_{211} plane. In addition, the specific surface areas, pore volumes and pore diameters are reported in Table 6.2.
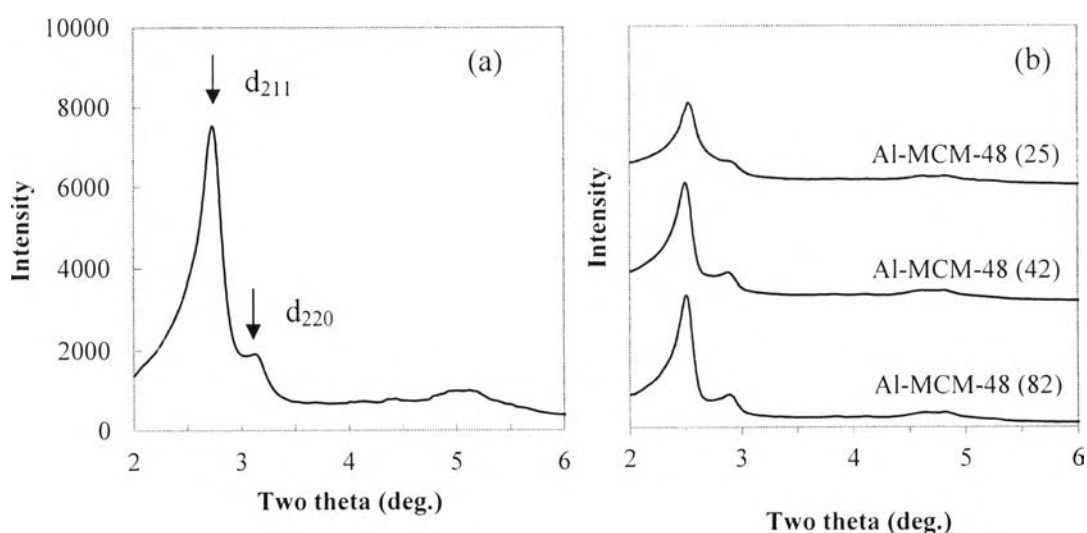

Figure 6.1 (a) SAXS patterns of Si-MCM-48, and (b) XRD patterns of Al-MCM-48 with various Si/Al ratios.

Table 6.1 Si/Al ratios and textural properties of Si-MCM-48 and Al-MCM-48 catalysts

Catalyst	Si/Al ratio		XRD		
	Synthesis Gel	Calcined Catalyst[a]	d211 (Å)	Lattice Parameter, a_0 (Å)[b]	Wall Thickness (Å)[c]
Si-MCM-48	-	-	33.2	81.3	12.4
Al-MCM-48	200	82	34.3	84.1	14.1
Al-MCM-48	75	42	35.3	86.5	14.5
Al-MCM-48	50	25	34.9	85.5	14.6

[a] XRF results

[b] Lattice parameter $(a_0) \approx d_{211}\sqrt{6}$

[c] Wall thickness $= a_0/3.092 - (D_{BJH}/2)$

Table 6.2 Physical properties of Si-MCM-48 and Al-MCM-48 catalysts

Catalyst	N₂ Sorption		
	Specific Surface Area (m²/g)	Pore Volume (cm³/g)	Pore Diameter D_{BJH} (Å)
Si-MCM-48	939.8	0.7	27.8
Al-MCM-48 (82)	1,229.6	1.0	26.2
Al-MCM-48 (42)	1,468.4	1.1	26.9
Al-MCM-48 (25)	782.1	0.9	26.1

The TPD-NH₃ profiles of Si-MCM-48 and Al-MCM-48 are shown in Figure 6.2a. Only one peak was observed in the TPD-NH₃ profiles of all catalysts, indicating that there is one similar group of acid sites that have similar acid strength. The acid density on catalysts was determined by integration of the desorption peak of ammonia. Thus, the acidity of catalysts is in the trend of Al-MCM-48 (25) > Al-MCM-48 (42) > Al-MCM-48 (82) > Si-MCM-48, indicating that the increasing

alumina atoms can generate the acid sites on the catalysts. The number in a parenthesis represents the Si/Al ratio of the catalyst obtained from XRF. Moreover, the acid density of pure silica MCM-48 is present, which is associated with the silanol groups (Seddegi et al., 2002). Additionally, the acid strength can be described by the ammonia desorption temperature (Table 6.3). It can be concluded that the acid strength of catalysts is in the order of Al-MCM-48 (25) ≈ Al-MCM-48 (42) > Si-MCM-48 > Al-MCM-48 (82). The ^{27}Al MAS NMR spectra of Si-MCM-48 and Al-MCM-48 with the Si/Al ratios of 25, 42, and 82 are shown in Figure 6.2b. The signal intensities of peak in the case of Al-MCM-48 (Si/Al = 25 and 42) present the unique resonance at approximately 51 ppm, which is assigned to a tetrahedrally-coordinated aluminum, whereas the signal does not appear in the cases of Al-MCM-48 (82) and Si-MCM-48. However, the octahedrally-coordinated aluminum, which may have given a resonance around 0 ppm, is absent in the ^{27}Al MAS NMR spectra of all catalysts (Tsomaia et al., 2003). It is explained that the aluminum atoms have been completely incorporated into the silica framework in the cases of Al-MCM-48 with the Si/Al ratios of 25 and 42. In addition, there is no peak of ^{27}Al MAS NMR spectrum in the case of Al-MCM-48 (82), causing the introduction of a very small amount of alumina atom during the synthesis with the Si/Al of precursors of 200. Moreover, Al-MCM-48 (82) catalyst might generate the formation of extraframework alumina oxide, observing from the low acid strength in its TPD-NH_3 profile.

Table 6.3 Ammonia desorption temperature of catalysts

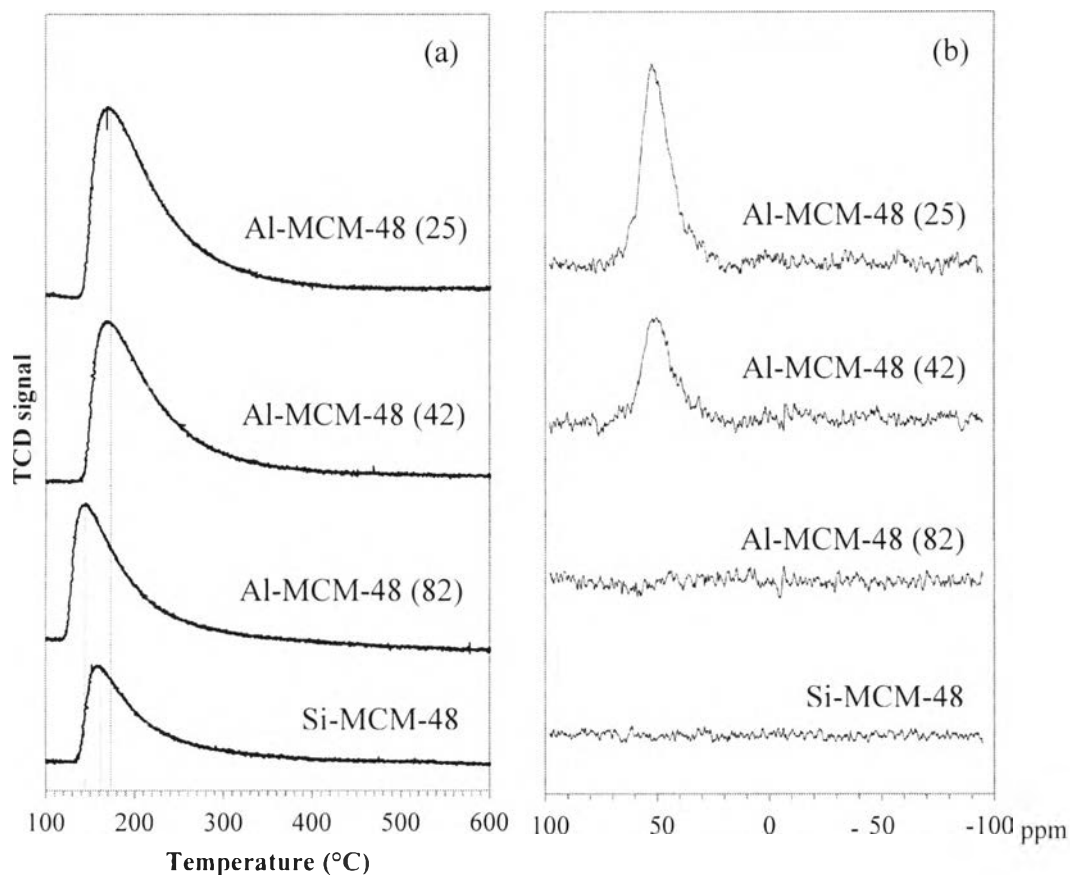| Catalyst	NH_3 Desorption Temperature (°C)
Si-MCM-48	160
Al-MCM-48 (82)	140
Al-MCM-48 (42)	170
Al-MCM-48 (25)	170

Figure 6.2 (a) TPD-NH$_3$ profiles, and (b) ^{27}Al MAS NMR spectra of Si-MCM-48 and Al-MCM-48 catalysts (Si/Al ratio = 25, 42 and 82).

6.4.2 Tire-derived Oils

The liquid products were analyzed by using a GC×GC-TOF/MS, which is a powerful instrument to separate the complex mixtures. More than 1,000 compounds were found in the maltene solutions. Thus, they were categorized into 7 groups; that are, paraffins (p), olefins (ole), naphthenes (nap), mono-aromatics (mono), di-aromatics (di), poly-aromatics (poly) and polar-aromatic hydrocarbons (polar). Figure 6.3 shows the concentration of each group of components in maltenes using Si-MCM-48 and Al-MCM-48 with various Si/Al ratios. The use of mesoporous Si-MCM-48 catalysts with a large pore size and Al-MCM-48 with high acid density were aimed to handle large molecules such as di- and poly-aromatic hydrocarbons and remove sulfur in tire-derived oil. From the results, the amounts of di- and poly-aromatic hydrocarbons are 7.6 wt.% and 9.1 wt.%, respectively, for the

non-catalytic case, and reduce to 4.1 wt.% and 6.4 wt.%, respectively by using the Si-MCM-48 catalyst. It can be explained that mesoporous Si-MCM-48 allows bulky molecules to pass through inside the pores and promotes the activity of cracking di- and poly-aromatics, forming mono-aromatic hydrocarbons. Furthermore, it has a 3D complex pore structure that gave a high contact time of molecules in pores. It illustrates that the amount of mono-aromatic hydrocarbons is increased from 47.7 wt.% for non-catalytic case to 51.7 wt.% by using Si-MCM-48 catalyst.

In addition, the introduction of Al atoms into silica framework that creates Brönsted acid sites increased the amount of di- and poly-aromatic hydrocarbons in oils is in the trend of Al-MCM-48 (25) > Al-MCM-48 (42) > Al-MCM-48 (82), indicating that the increase of acidity on Al-MCM-48 promotes the formation of aromatics via carbenium ions. Moreover, the concentrations of olefins and naphthenes decrease by using Al-MCM-48. It can be suggested that olefins and naphthenes are converted to the bigger molecules, such as mono-, di-, and poly-aromatic hydrocarbons via aromatization inside the pores. It can be concluded that the large pore size of Si-MCM-48 catalyst with no Brönsted acid sites can remove the large hydrocarbons (di- and poly-aromatics) better than the aluminosilicate mesoporous MCM-48.
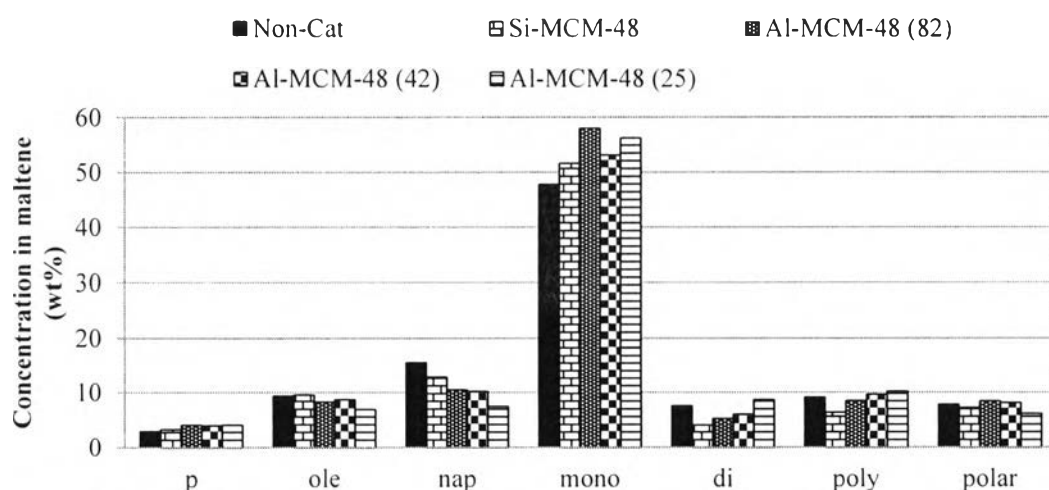

Figure 6.3 Concentration of each group of components in maltenes.

6.4.3 Petroleum Fractions

Figure 6.4 shows the petroleum fractions of maltenes, which were cut according to the true boiling points curves, into five fractions; that are, full range naphtha (<200 °C), kerosene (200-250 °C), gas oil (250-370 °C), and long residues (>370 °C). The result shows that the mesoporous Si-MCM-48 catalyst gave the highest naphtha fraction and low amounts of heavier fractions, including gas oils and long residue. It can be suggested that Si-MCM-48 has the highest activity on cracking of large molecules in heavy gas oil and long residue. When compared to the Si-MCM-48 catalyst, Al-MCM-48 catalysts provide a lower amount of naphtha fraction and a higher amount of heavy gas oil and long residue fractions, especially Al-MCM-48 with the Si/Al ratios of 25 and 42. Supported from the GCxGC-TOF results, the Al-MCM-48 catalysts have less ability on cracking of large molecules than Si-MCM-48 even though they possess Brönsted acid sites. It can be explained that the Brönsted acid sites simultaneously promoted the aromatization, and together with a larger enough mesopore, larger molecules can also be formed.
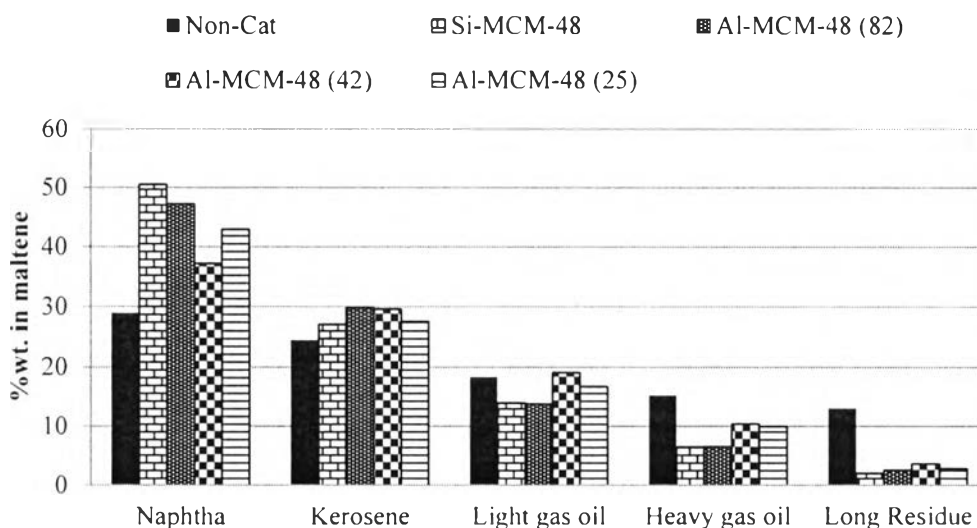

Figure 6.4 Petroleum fraction in maltenes.

6.4.4 Petrochemicals

Previously, Figure 6.3 has shown that the tire-derived oils are aromatic-based hydrocarbon mixtures, so they are not suitable for uses directly as vehicle fuels. However, they can be used as chemical feedstocks since they contain petrochemicals that are remarkable products, such as benzene, toluene, xylenes, ethylbenzene, and cumene, which are widely used as raw materials in petrochemical industry. Figure 6.5 shows the concentrations of petrochemical productions in tire-derived oils. The use of catalysts increases the concentration of petrochemicals in maltenes, except Al-MCM-48 (25). Moreover, the production of petrochemicals can be ranked in the order: Al-MCM-48 (42) > Si-MCM-48 > Al-MCM-48 (82) > no catalyst > Al-MCM-48 (25). As a result, Al-MCM-48 (42) produces the highest amount of benzene whereas the other catalysts did not produce. The concentrations of toluene and ethylbenzene highly increased with using the Si-MCM-48 and Al-MCM-48 (42) catalysts. Toluene was increased 1.8 wt.% and 2.0 wt.% while ethylbenzene was increased to 3.0 wt.% and 2.6 wt.% for the Si-MCM-48 and Al-MCM-48 (42) catalysts, respectively. Moreover, p-xylene did not increase with using the catalysts. and the concentration of cumene is suppressed by using Si-MCM-48 whereas Al-MCM-48 (42) enhances cumene production significantly. Al-MCM-48 (25) gives the lowest petrochemicals production. It is possible that Al-MCM-48 (25), which has the highest Brönsted acid density (the highest Al incorporated atoms in the framework) and high strength. promotes the aromatization of naphthenes and olefins in its mesopores, forming larger aromatic molecules.
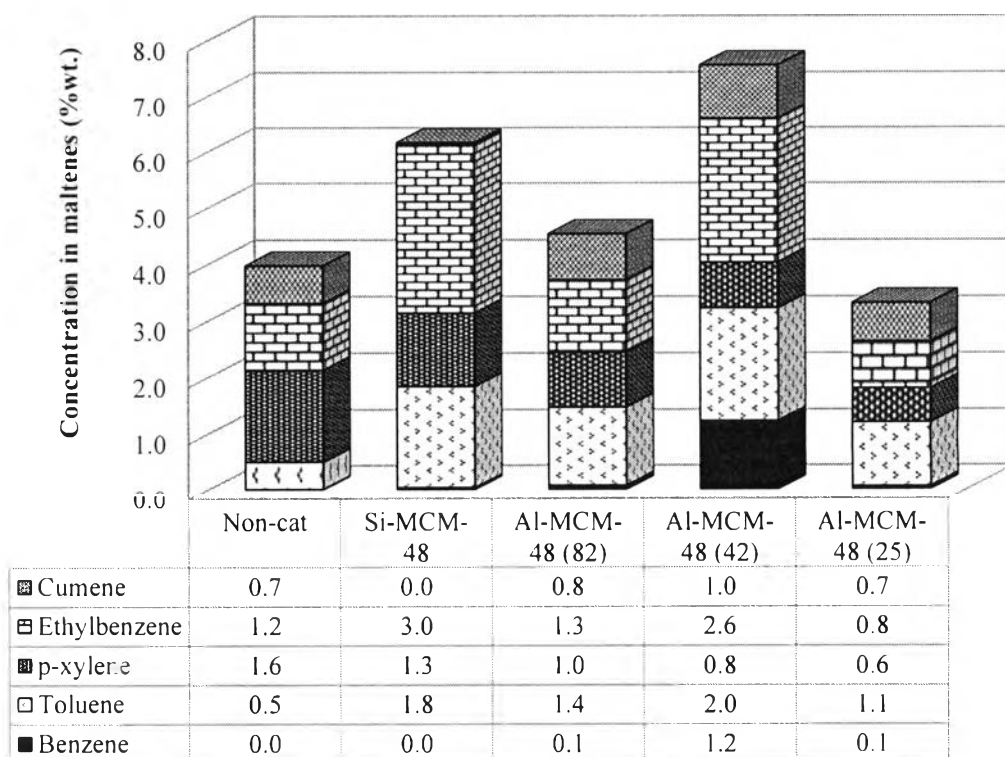
	Non-cat	Si-MCM-48	Al-MCM-48 (82)	Al-MCM-48 (42)	Al-MCM-48 (25)
▣ Cumene	0.7	0.0	0.8	1.0	0.7
⊟ Ethylbenzene	1.2	3.0	1.3	2.6	0.8
▣ p-xylene	1.6	1.3	1.0	0.8	0.6
☐ Toluene	0.5	1.8	1.4	2.0	1.1
■ Benzene	0.0	0.0	0.1	1.2	0.1

**Figure 6.5** Concentration of petrochemicals in maltenes.

6.4.5 Desulfurization Activity

Table 6.4 exhibits the ability of sulfur removal from tire-derived oil by using Si-MCM-48 and Al-MCM-48 catalysts. It can be observed that all catalysts can reduce sulfur in oil. Moreover, the Si-MCM-48 catalyst has the highest ability to remove sulfur, which is 33.9 % of sulfur removal from tire-derived oil. Among the Al-MCM-48 catalysts, the percentage of sulfur removal increases with the increasing acid density in the order of Al-MCM-48 (25) > Al-MCM-48 (42) > Al-MCM-48 (82). It can be suggested that Si-MCM-48 can help C-S bond to break better than Al-MCM-48 catalyst because Si-MCM-48 catalyst was found to more greatly promote the cracking activity than Al-MCM-48 catalysts as shown in Figure 6.4. Moreover, the ability on desulfurization by using Al-MCM-48 catalysts depends on the amount of acid sites, indicating that sulfur-containing compounds strongly interact with the Brönsted acid sites, which are usually needed in desulfurization; so enhancing the interaction of sulfur compounds on the catalyst surfaces (Liu et al., 2007).

Table 6.4 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
Al-MCM-48 (82)	1.21 ± 0.01	5.12
Al-MCM-48 (42)	1.12 ± 0.03	11.8
Al-MCM-48 (25)	1.02 ± 0.02	19.7
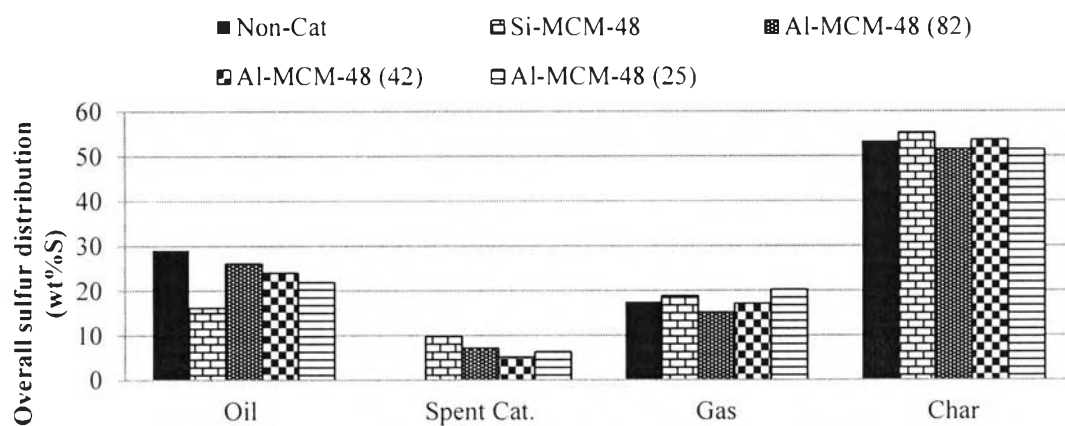
Figure 6.6 Overall sulfur distributions (wt%S).
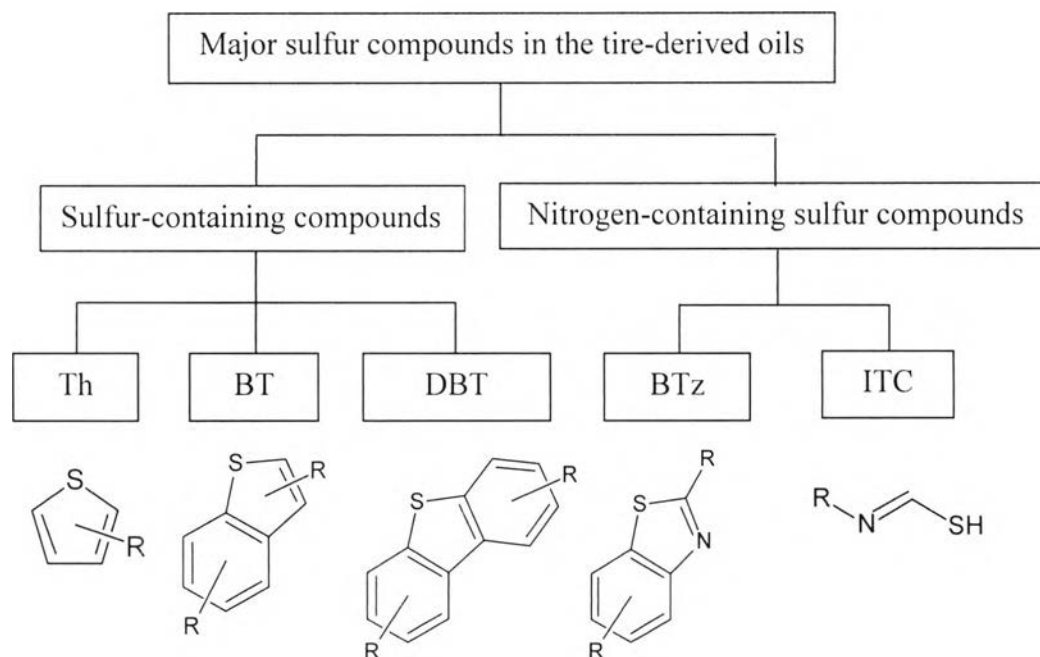
R = alkyl or phenyl group

Figure 6.7 Major groups of sulfur compounds in the tire-derived oils.

Around 20-26 % of S is distributed in the oil fractions from using Al-MCM-48 catalysts (Figure 6.6). The sulfur species in the tire-derived oils are classified into two major groups: (1) sulfur-containing compounds, which consist of thiophenes (Ths), benzothiophenes (BTs), and dibenzothiophenes (DBTs), and (2) nitrogen-containing sulfur compounds, which consist of benzothiazoles (BTz) and isothiocyanates (ITC). The structures of sulfur species are shown in Figure 6.7. The sulfur–containing compounds in maltenes by using Si-MCM-48 and Al-MCM-48 catalysts are shown in Figure 6.8. The results show that Si-MCM-48 catalyst sharply decreases benzothiophenes and isothiocyanates, whereas Al-MCM-48 decreases thiophenes and benzothiazoles. The amounts of thiophenes and benzothiazoles that are removed depend on the acid density of Al-MCM-48. It has been known that the increase of acidity of catalysts can help thiophenes and benzothiazoles compounds to interact with the surface of catalysts. Moreover, the GCxGC-TOF/MS results reveal that benzothiazole and isothiocyanato-benzene are the main sulfur compounds in the tire-derived oils, which is similar to Choi *et al.* (2014). The presence of sulfur

compounds in tire-derived oil is caused by sulfur compounds used in the vulcanization process in the manufacture of tires. In addition, the presence of nitrogen compounds in the oil is resulted from the degradation of accelerators, such as N,N-diisopropyl-2-benzothiazole-sulfenamide (Quek *et al.*, 2013), during pyrolysis of waste tire.
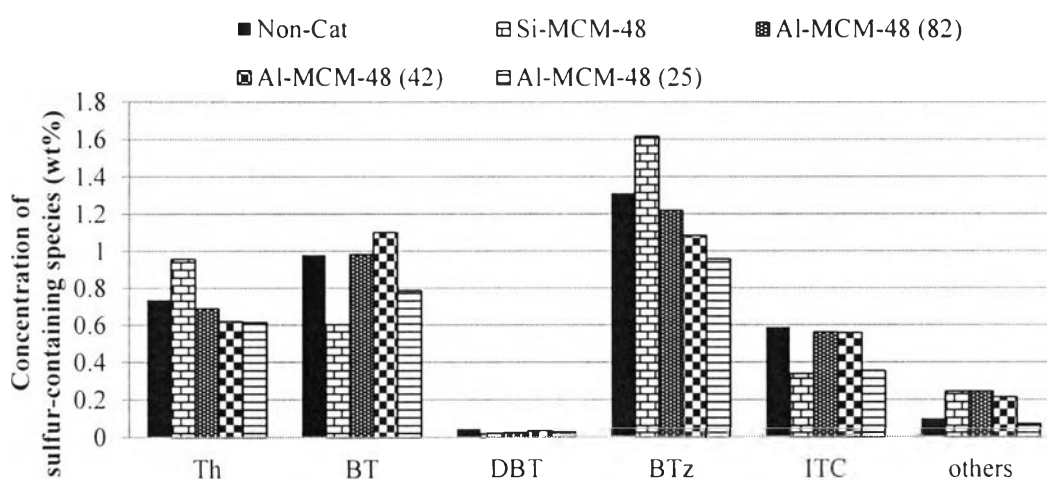

Figure 6.8 Sulfur–containing compounds in maltenes.

6.5 Conclusions

The Si-MCM-48 catalyst decreased large molecules in tire-derived oil more greatly than the Al-MCM-48 catalysts, indicating that the effect of large pore size is more pronounced than the effect of acid density on removal of large molecules from the oil. Moreover, all catalysts increased the production of petrochemicals in maltenes, except Al-MCM-48 (25) due to its high Brönsted acid density that caused acid-catalyzed reactions to occur rather than cracking of large molecules. The Si-MCM-48 and Al-MCM-48 (42) catalysts sharply enhanced the selectivity of toluene and ethylbenzene. In addition, the Si-MCM-48 catalyst gave the highest ability to remove sulfur in oil whereas the decreasing Si/Al ratio of Al-MCM-48 catalysts enhanced the sulfur removal in oils, indicating that the Brönsted acid sites are necessary for sulfur removal ability of catalysts although a large amount of Brönsted acid sites may result in the production of large molecules.

6.6 Acknowledgements

6.7 References

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