

CHAPTER VII

CATALYTIC PYROLYSIS OF WASTE TIRE USING HBETA/MCM-41 CORE-SHELL COMPOSITE

7.1 Abstract

The catalytic pyrolysis of waste tire was investigated using core-shell composite of HBETA and MCM-41 as a catalyst in a bench-scale pyrolysis reactor, aiming to enhance the formation of petrochemicals and reduce the heavy aromatics in waste tire-derived oil. The core-shell composite of HBETA and MCM-41 was synthesized by growing of MCM-41 over HY zeolite seeds. The MCM-41 shell thickness was in the range of 50-100 nm. Gaseous products were analyzed by GC-FID, whereas the GCxGC-TOF/MS and SIMDIST-GC were used for analysis of waste tire-derived oil. Moreover, the sulfur content in oils was determined by S-analyzer. As a result, the core-shell composite catalyst exhibited a great catalytic behavior in the enhancement of quality of waste tire-derived oil. The oil produced from the composite catalyst contained a higher amount of gasoline and valuable aromatics (BTEX) than the pure HBETA and MCM-41 catalysts, indicating the existence of core-shell composite exhibited a higher cracking activity and better petrochemical selectivity than pure HBETA and MCM-41 catalyst. Furthermore, the core-shell catalysts also provided a lower sulfur content in oil than the both HBETA and MCM-41 catalysts. Therefore, the core-shell composite of HBETA and MCM-41 present a great potential in waste tire pyrolysis application. In conclusion, it is evident that the quality enhancement of the tire-derived oil is contributed from the synergy of the interaction between MCM-41 shell and HBETA core.

7.2 Introduction

Valuable aromatics (BTEX) are important chemicals, which commonly utilized as a raw material in the production of plastics, solvents, detergents, synthetic rubber, cosmetic products and pharmaceuticals. As the petroleum resources on the

earth decrease with a considerable rate, the production of fuels and petrochemicals from waste tire-derived oil has attracted a great attention. However, the relatively-high concentrations of bulky aromatics and sulfur-containing compounds are main drawbacks since the high content of bulky aromatics and sulfur-containing compounds in oil cannot be directly used as a vehicle fuel or petrochemical feedstock (Yuwapornpanit and Jitkarnka, 2015). Several zeolites such as HMOR, HBETA, HY, and HZSM-5 have been used as catalysts, but they still cannot effectively reduce the formation of bulky aromatics in oils (Boxiong *et al.*, 2007; Muenpol *et al.*, 2015). There are two possible reasons that can explain the high formation of bulky aromatics in tire-derived oil. The first reason is that the formation of aromatics increases with the increase of acidity. The second reason is that the sizes of aromatics molecules are larger than the micropore of zeolites; then, large aromatic compounds are not cracked into smaller aromatics or light hydrocarbon products. Hence, mesoporous materials, which have a large pore size and low acidity, are attractive for use as a catalyst in the pyrolysis of waste tire. Dũng *et al.* (2009) reported that using MCM-41 as a catalyst caused a reduction in the concentration of poly- and polar- aromatics in the pyrolytic oil. A year later, Dũng *et al.* (2010) informed that using SBA-1 did not alter the concentration of saturated hydrocarbon, mono-, di-, poly- and polar- aromatics in tire-derived oil. As a result, composite materials have been developed and used to overcome the drawbacks of zeolites and mesoporous materials.

The so-called “core-shell” composites provided higher diffusion efficiency and more surface acidity distribution due to the good connection of their mesopores and micropores (Jia *et al.*, 2013). For example, MCM-41/FAU composite materials displayed higher conversion of vacuum gas oil than USY zeolite in cracking of vacuum gas oil (Kloestra *et al.*, 1996). MCM-41/ZSM-5 composite materials also showed the high catalytic performance in n- C₁₂ cracking (Haug *et al.*, 2000). Similarly, MCM-41/ZSM-5 showed the higher catalytic performance in n-C₁₂ cracking than fresh ZSM-5 and NaOH-treated ZSM-5 zeolites (Na *et al.*, 2013). MCM-41/BETA enhanced the selectivity of gasoline in the catalytic cracking of used palm oil (Ooi *et al.*, 2004). Therefore, it is evident that the composite of HBETA

core and MCM-41 shell has high potential to reduce large polycyclic aromatics, and increase valuable mono- aromatic production since the MCM-41 shell with a mesopore was expected to pre-crack large molecules from the thermal pyrolysis of waste tire, and then the product can diffuse through the HBETA core much easily for subsequent cracking. The aim of this work was therefore to investigate the effect of core-shell composite of HBETA and MCM-41 catalyst on the waste tire pyrolysis products in terms of oil quality improvement and enhancement of valuable petrochemical formation.

7.3 Experimental

7.3.1 Synthesis of Core-shell Composite

The core-shell structure composite of HBETA zeolite and MCM-41 was synthesized by the method in Li *et al.*, (2009). 4.25 g of CTABr was dissolved in 40 mL of deionized water, and 1.2 g of HBETA was added to the solution at 25 °C with stirring for 24 h to form Slurry A. Solution B was prepared by dissolving 9.79 g of sodium metasilicate in 100 mL of deionized water, and the pH was adjusted to 11 by adding 6 M H₂SO₄. After stirring for 10 min, Slurry A was added drop by drop to Solution B. After that, the mixture was stirred at room temperature for 2 h and kept into an autoclave at 120 °C for 72 h. Then, the solid product was filtered, washed, dried, and calcined at 540 °C for 6 h. In the synthesis of MCM-41, the 4.25 g of CTABr was dissolved in 40 mL of deionized water, followed by the addition of the solution containing 9.79 g sodium silicate and 100 mL of deionized water. The solution of sodium silicate was priorly stirred until the solution was clear before addition to the CTABr solution. After stirring at 25 °C for 2 h, the mixture of CTABr, sodium silicate and DI water was transfer into an Teflon line autoclave at temperature 120 °C for 3 days. Then, the solid product was filtered, washed, dried, and calcined at 540 °C for 6 h. The catalyst power were pelletized, crushed and sieved to 40-60 mesh of particle size.

7.3.2 Catalyst Characterization

The catalyst samples were characterized by different physicochemical characterization methods. X-Ray diffraction ($\text{CuK}\alpha$ radiation), carried out in a Rigaku TTRAXIII Diffractometer and Rikagu SmartLab X-Ray Diffractometer and, were used to collecting of small-angled X-ray scattering pattern (SAXS) and wide-angle XRD pattern, respectively. Wide-angle XRD patterns were recorded in the $5\text{--}65^\circ$ (2θ) range using a scan speed of 10° (2θ)/min, and the SAXS patterns were record in the $2.0\text{--}6.0^\circ$ (2θ) range using a scan speed of 2° (2θ)/min. The surface area and pore volume of catalysts were measured using N_2 adsorption-desorption isotherms with Quantachrome AS1-MP instrument. Transmission electron microscopy (TEM) was performed on JEOL JEM-2010 and JEOL JEM-2100 instruments with an acceleration voltage of 200 KV. 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 (20 ml/min) on a Perkin Elmer/Pyris Diamond (Thermogravimetric/Differential Thermal Analysis, TG/DTA). The sample were heated up from room temperature to 900°C with the ramping rate of $10^\circ\text{C}/\text{min}$. CHNS analyzer was used to determine the sulfur and nitrogen content on spent catalyst using LECO®Elemental Analyzer.

7.3.3 Waste Tire Pyrolysis

The schematic pyrolysis system is displayed in Figure 7.1. 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 ones, the temperature of two zones was kept at desired temperature for 2 h. The resulting products were separated into gas and liquid fractions by an ice-salt condensing system. Gas product was collected in Tedlar PVF bag.

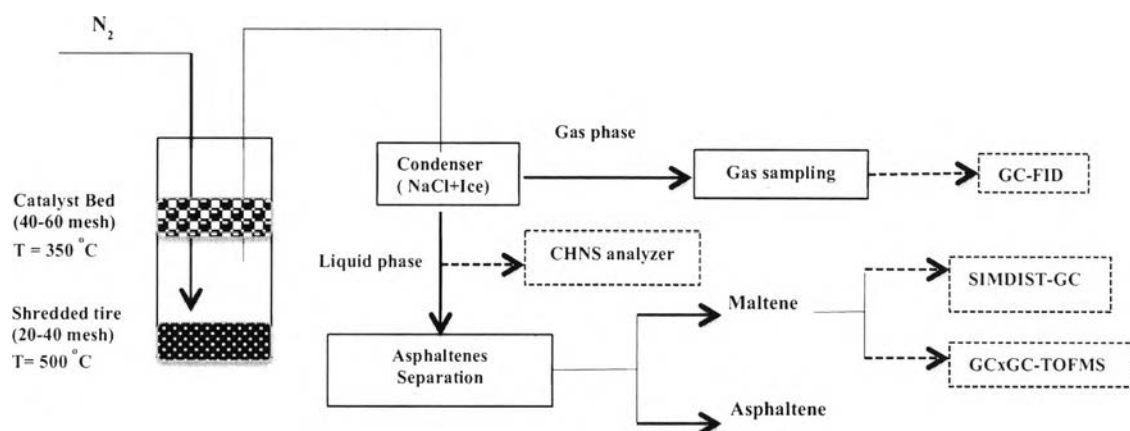


Figure 7.1 Schematic of waste tire pyrolysis system for collection and analysis of products.

7.3.4 Product Analysis

Liquid and solid products were weighed to determine the product yield. The gas yield was determined by mass balance. The gaseous product was 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 product was 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 solution was 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 x 0.25 μm) and the 2nd GC column was an Rxi®-17MS(1.790m x 0.1mmID x 0.1 μm). 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 final temperature was reached, it was held at 310 °C until the analysis was finished. For the secondary column, the column temperature 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 $^{\circ}\text{C}$), kerosene (149-232 $^{\circ}\text{C}$), gas oil (232-343 $^{\circ}\text{C}$), light vacuum gas oil (343-371 $^{\circ}\text{C}$) and heavy vacuum gas oil (>371 $^{\circ}\text{C}$). Moreover, sulfur and nitrogen content in tire-derived oil and char were determined by LECO®Elemental Analyzer (TruSpec®CHNS). Furthermore, sulfur content in gas product was determined by mass balance.

7.4 Results and Discussion

7.4.1 Characterization of Core-shell Composite of HBETA and MCM-41

The XRD patterns of core-shell composite catalysts, HY zeolite and MCM-41 are shown in the Figure 7.2. (100) The scattering peaks are clearly reflected at $2\theta = 2.1^{\circ}$ in the XRD patterns of both MCM-41 and HBETA/MCM-41 catalysts, indicating that the mesostructures are well present in the both catalysts. Furthermore, the diffraction peaks at high diffraction angles in the XRD pattern of HBETA/MCM-41 are similar to those in the XRD pattern of HY zeolite, indicating that HY zeolite is also present in the composite catalyst.

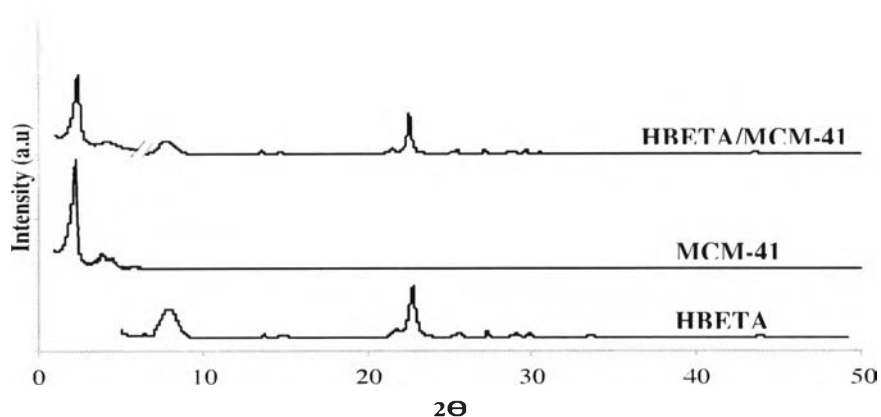


Figure 7.2 XRD patterns of HBETA, MCM-41 and composite of HBETA and MCM-41.

The N_2 adsorption-desorption isotherms of MCM-41, HBETA, and HBETA/MCM-41 catalyst are shown in Figure 7.3. HBETA zeolite exhibits the type I adsorption isotherm, which presents the characteristic of micropore. On the other hand, MCM-41 and HBETA/MCM-41 display the IV adsorption isotherms. These isotherms exhibit three steps of N_2 adsorption. The slightly rising step at $P/P_0 < 0.25$ indicates the presence of micropore in both composite and MCM-41 catalysts. The steep rising step with the relative pressure P/P_0 range of 0.25-0.4 results from the capillary condensation with mesopore, indicating that the framework-confined mesopores are present in the catalysts (Bordoloi et al., 2006). Moreover, the slope of this step indicates the uniformity of pore size distribution. Therefore, it is reasonable to conclude that the MCM-41 catalyst has a more uniformity of pore size distribution than the composite catalyst, which well agrees with the pore size distribution in Figure 7.4. The third step with relative pressure P/P_0 range of 0.9-1.0 indicates that the existence of macropore in the both composite and MCM-41 catalysts. All results indicate that the composite material contains micropores, mesopores, and some macropores.

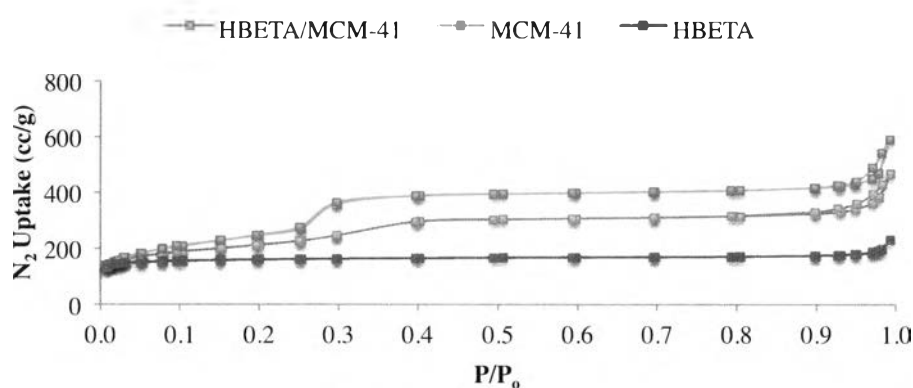


Figure 7.3 N_2 adsorption-desorption isotherms of HBETA, MCM-41 and HBETA/MCM-41.

The BJH pore size distribution of MCM-41, HBETA, and the composite of HBETA and MCM-41 in the range of 0-10 Å, indicating the existence of micropore in all three catalysts. The mesopore size distribution of MCM-41 is narrower than that of the HBETA/MCM-41 catalyst. The textural properties, such as BET surface area,

pore volume and average pore size are summarized in Table 7.1. The BET surface area of HBETA/MCM-41 composite is higher than the HBETA zeolite but lower than MCM-41, indicating that the higher surface area of composite material results from the mesopore of MCM-41.

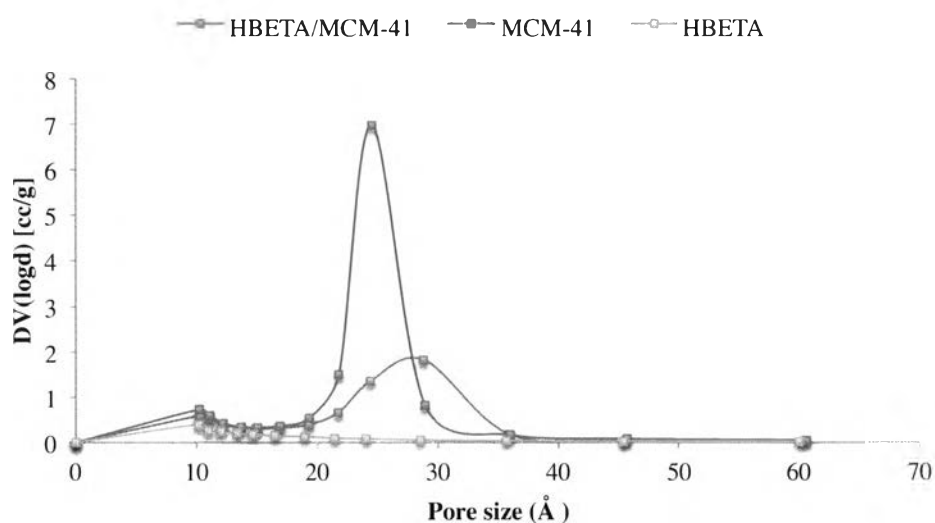


Figure 7.4 Pore size distribution of HBETA, MCM-41 and HBETA/MCM-41.

Table 7.1 Textural properties of HBETA, MCM-41 and HBETA/MCM-41 composite

Catalyst	BET Surface Area (m ² /g)	Pore Volume (cm ³ /g)	BJH Average Pore Size (nm)
HBETA	490	0.19	10.1
MCM-41	1064	1.00	24.6
HBETA/MCM-41	754	0.69	28.8

Figure 7.5 displays the TEM image of composite of HBETA/MCM-41. It found that the HBETA zeolite particles are wrapped by the thin layer of MCM-41 (50-100 nm). The layer of MCM-41 has a less density than the zeolite particles. Moreover, the energy dispersive X-ray spectroscopy (EDS) is used to determine the chemical composition of the microporous phase and mesoporous phase.

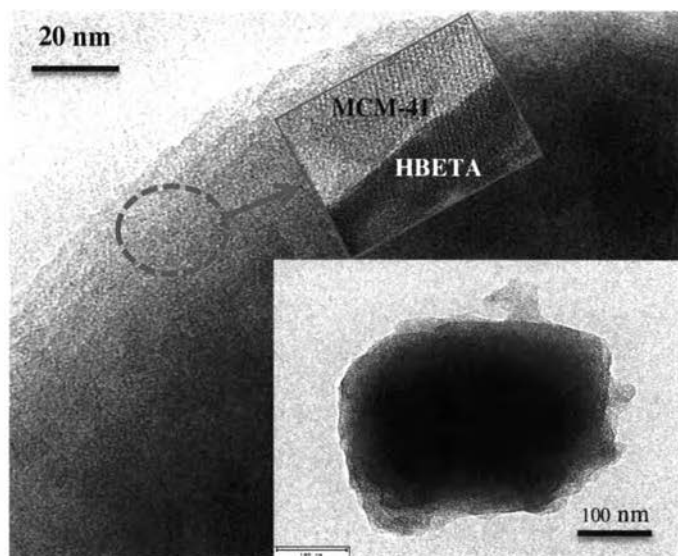


Figure 7.5 TEM image of composite of HBETA and MCM-41.

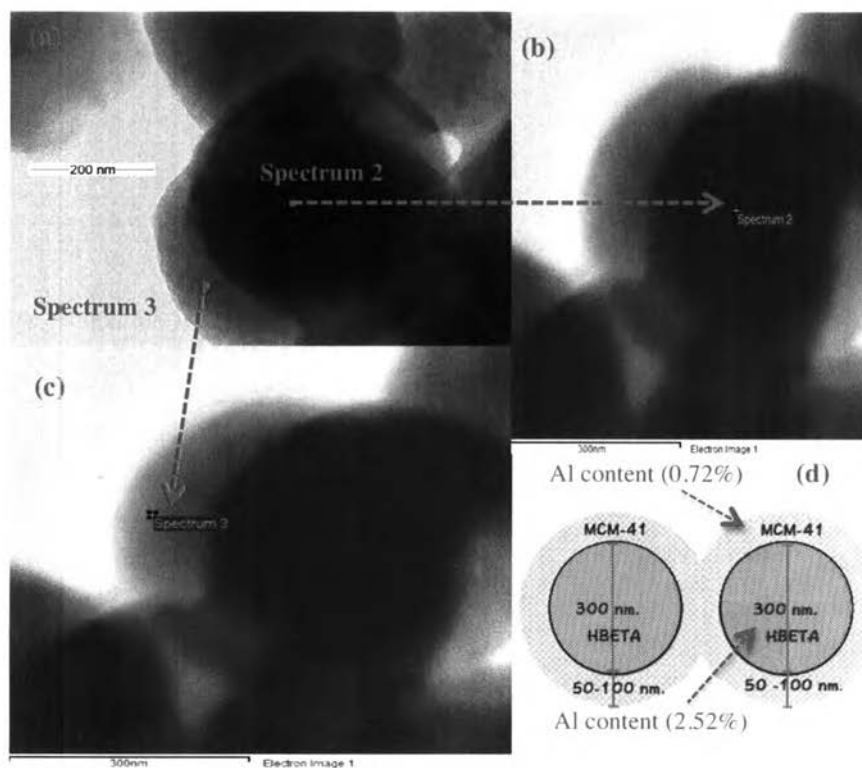


Figure 7.6 EDS positions (a-c) taken on TEM and STEM images of HBETA/MCM-41 core-shell composite, and (d) drawing of HBETA/MCM-41 core shell composite.

Figure 7.6 displays the EDS spectra from the STEM image. After EDS was taken at the position that was believed as HBETA core (see Figure 7.6(b)), the result shows that O, Na, Al, Si, Cr, C and Cu elements are detected, which are the elements in the Cu grid used in the experiment. Moreover, the mass ratio of Si/Al is about 17.51 (see Figure 7.7(a)), which is close to Si/Al ratio of parent HBETA. Thus, the core of composite is proven to be the HBETA zeolite. Furthermore, the Al content at the position that is believed as a MCM-41 shell (see Figure 7.6(c)) is lower than the first position, which is proven to be a HBETA core and the mass ratio of Si/Al ratio of this position is about 53.2 (see Figure 7.7(b)). The high ratio of Si/Al indicate that MCM-41 is likely to be in the shell. However, some Al content in MCM-41 shell is contaminated from either precursor or zeolite during synthesis. Therefore, it is reasonable to conclude that the composite catalyst, containing of MCM-41 in the shell and HBETA in the core, has been successfully synthesized.

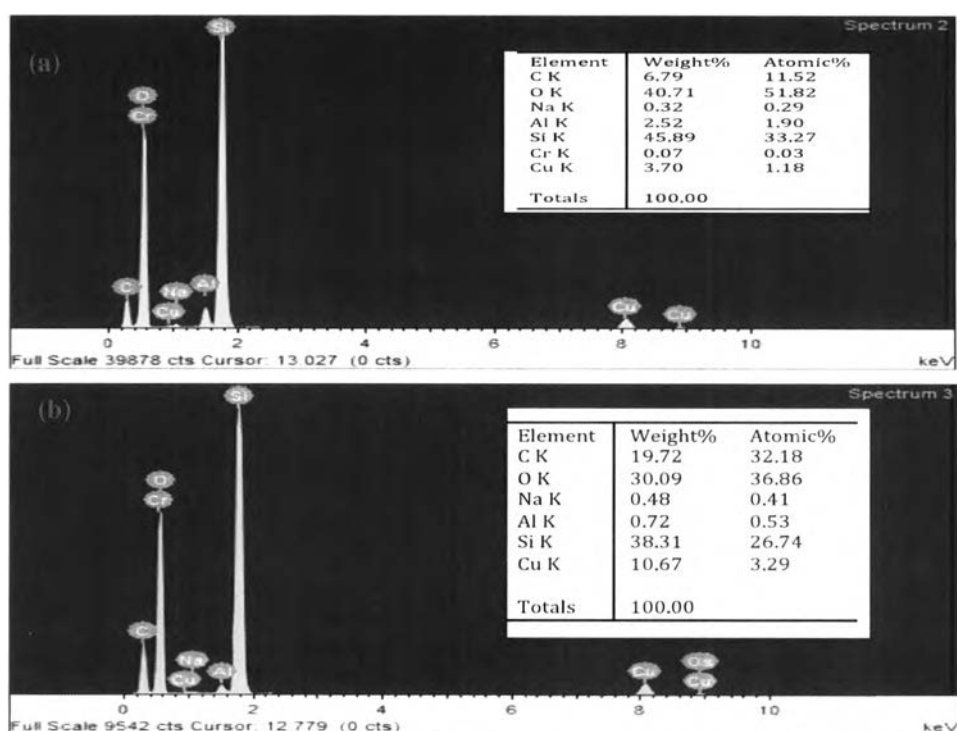


Figure 7.7 EDS spectra of (a) HBETA core and (b) MCM-41 shell.

7.4.2 Pyrolysis Yields

The pyrolysis product distributions from using parent HBETA zeolite, MCM-41, and HBETA/MCM-41 catalyst displayed in Figure 7.8 are not significantly different, indicating the composite in the core-shell formation does not significantly alter the product distribution. HBETA catalyst provides a slight higher yield of gas than that obtained from MCM-41 catalyst since the HBETA zeolite with strong acid sites that provide a higher cracking activity than MCM-41 with weak acid sites. On the other hand, the presence of core-shell composite of HBETA and MCM-41 slightly increases liquid yield, whereas the yields of solid and coke decrease as compared to parent MCM-41 and HBETA zeolite. These results indicate that the growth of MCM-41 shell over HBETA core provides a higher cracking activity than the parent MCM-41 catalysts and enhance the resistance of coke formation. It can be explained that the mesoporous MCM-41 shell might provide free channel for cracking products diffusing from the HBETA core, resulting in reduction of excessive cracking, and then leading to a lower coke formation on the catalyst and a higher yield of liquid.

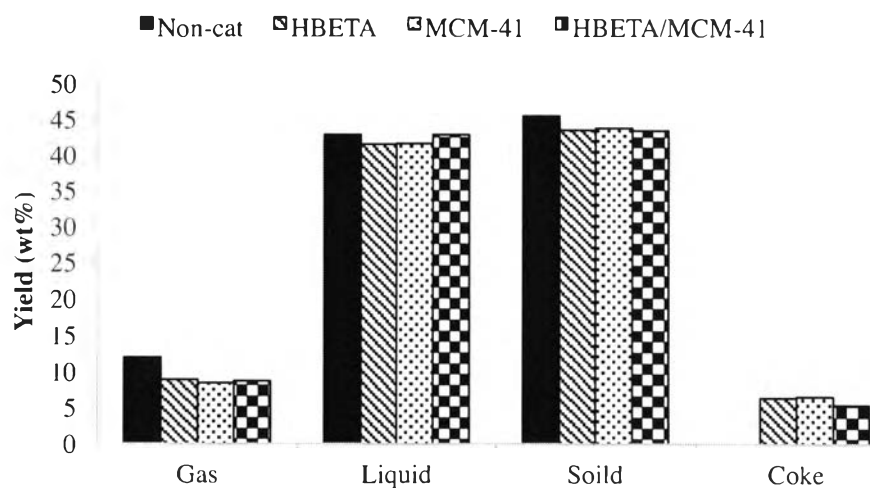


Figure 7.8. Pyrolysis yields from using HBETA, MCM-41 and their core-shell composite.

7.4.3 Waste Tire-derived Gas

Figure 7.9 provides the information about the species of gaseous products. The amount of mixed-C4 and mixed-C5 gases is one of indicators that can indicate the cracking ability of catalysts since the mixed-C4 and mixed C5, which are monomers of tire molecules, can be directly formed by breaking of carbon bond of styrene-butadiene and isoprene rubbers. It can be observed that the presence of core-shell composite of HBETA zeolite and MCM-41 provides a higher formation of mixed-C4 and mixed-C5 gases than those produced by the parent MCM-41 catalyst since the hydrocarbon molecules might be cracked by MCM-41 shell, and then further cracked by HBETA zeolite core, leading to the higher formation of lighter hydrocarbon products. Using the parent MCM-41, propane, ethane, propylene and mixed-C5 increases, whereas the other gaseous products decrease as compared to the non-catalytic case. On the other, the presence of HBETA catalyst significantly enhances the formation of mixed-C4 and mixed-C5 gases, which are higher than those obtained from MCM-41 catalyst. Therefore, it is reasonable to conclude that HBETA zeolite provides a higher cracking activity than MCM-41 catalyst. Therefore, the combination of HBETA and MCM-41 can provide a higher cracking activity of catalysts than MCM-41 catalyst.

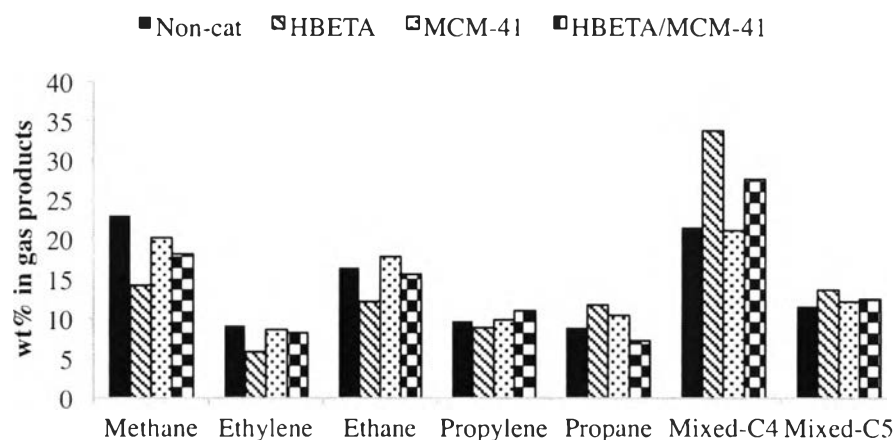


Figure 7.9. Compositions of gaseous products from using HBETA, MCM-41 and their core-shell composite.

7.4.4 Waste Tire-derived Oil

Figure 7.10 provides the information about composition in maltene. MCM-41 with mesopore and weak acid sites provide higher amounts of mono-aromatics, olefins and paraffins, whereas the amounts of di- and poly-aromatics, and naphthenes decrease as compared to the non-catalytic case. These results indicate that the low acidity of MCM-41 catalyst can promote the aromatization of naphthenes, leading to the formation of mono-aromatics. It can be explained that the cracking ability of MCM-41 associates with silanol group, which also generate carbenium ions when interacting with hydrocarbon molecules. Moreover, the mesopore of MCM-41 clearly promotes the transformation of heavy aromatics such as di- and poly-aromatics to lighter aromatic, olefins and paraffins.

In the case of the core-shell composite, the products obtained from the MCM-41 shell subsequently diffuse into the HBETA core, and undergo further reaction. The presence of core-shell composite of HBETA and MCM-41 provides a higher amount of mono-aromatics than the pure HBETA and MCM-41 catalysts since the mono-aromatics can be formed via transformation of di-, poly and polar-aromatics and aromatization of olefins and paraffins, diffusing from the MCM-41 shell. Furthermore, the two pore sizes of composite catalysts can further decrease the formation of di- and poly-aromatics in maltene as compared to HBETA zeolite, which only possesses a micropore. It can be seen in Figure 7.10 that parent HBETA zeolite itself can enhance the amounts of mono-, di-, and poly-aromatics, but provides lower amounts of naphthenes and olefins than the non-catalytic case. These results indicate that HBETA with micropore pore and strong acid sites favors the formation of aromatics via two pathways; cracking of polar-aromatics and aromatization of naphthenes and olefins. However, the reduction of poly- and di-aromatics by the core-shell composite is quite similar to that obtained from MCM-41 since the some cracking products, that escape from HBETA surface, might have undergone some reactions, forming poly-aromatics as well. On the other hand, the weak acid sites of MCM-41 shell might be not sufficient to convert all of polycyclic aromatics to intermediate cracking products, which can diffuse to micropore of HBETA core, resulting in the slight reduction of polycyclic-aromatics. However, it

has been found that the concentration of 1,5-diphenyl-3-(3-cyclopentylpropyl) pentane and 1,1'-(1,2-Dicyclopropyl-1,2-ethanediyl) dibenzene decreases as compared to those obtained from using pure HBETA and MCM-41 as catalysts. These results also indicate that the combination of two different pore sizes and acidity can more effectively crack some poly-aromatics than the pure HBETA and MCM-41 catalysts due to the limitation of HBETA pore size and MCM-41 acidity. The higher cracking of MCM-41 shell might be associated with the incorporation of aluminium, which are generated by dealumination of HBETA zeolite during the synthesis of composite material.

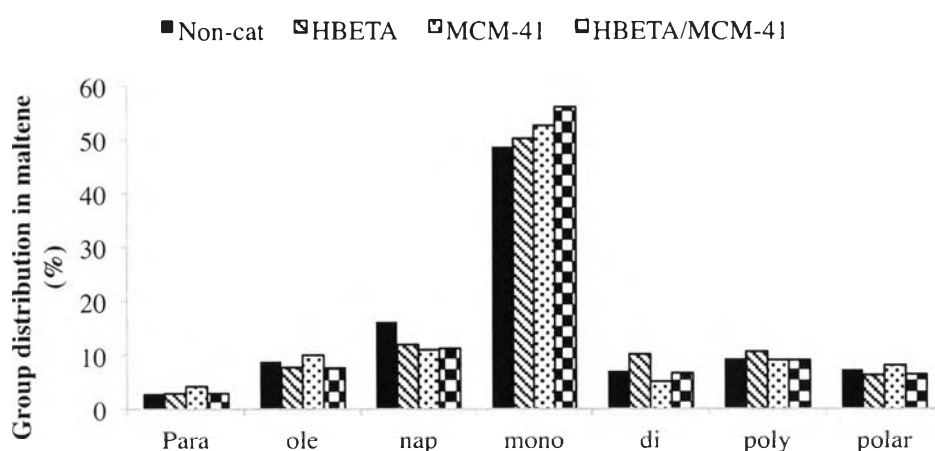


Figure 7.10 Maltene compositions (pare=paraffins, ole=olefins, nap=naphthenes, mono=mono-aromatic, di=di-aromatics, poly=poly-aromatics, and polar=polar-aromatics) from using HBETA, MCM-41 and their core-shell composite.

The quite similar results are observed in petroleum fractions. The use of the core-shell composite further reduced the gas oil and LVGO content in oil, as compared to the results from the individual component, resulting in the enhancement of gasoline fraction. It can be observed that with using pure MCM-41 as a catalyst, the gasoline fraction enhances, while the fractions of LVGO and HVGO are suppressed. It is evident that the presence of pure HBETA zeolite provides the lighter oil with higher proportion of gasoline and kerosene than the non-catalytic case. Therefore, it can be concluded that the larger pore size of MCM-41 allows more heavy hydrocarbons, which cannot be cracked in the micropore of zeolite, to diffuse

inside the mesopore of MCM-41 and then are cracked into more lighter hydrocarbon products, especially hydrocarbons that have boiling points in the gasoline range. The fact that the presence of core-shell composite of HBETA and MCM-41 provide higher amounts of gasoline and kerosene with the lower amounts of gas oil and LVGO than pure HBETA and MCM-41 catalysts indicate that some heavy hydrocarbons can be cracked at the weak acid sites of MCM-41 shell into smaller hydrocarbons, which can effectively diffuse to the zeolite core, and then the smaller hydrocarbons further cracked at the strong acid sites of HBETA core, resulting in lighter products than pure HBETA and MCM-41 catalyst. Moreover, the composite catalyst provides the oil with the high proportion of lighter hydrocarbons since the cracking products, that diffuse out of the HBETA surface, can then diffuse through the MCM-41 shell channel without the excessive cracking.

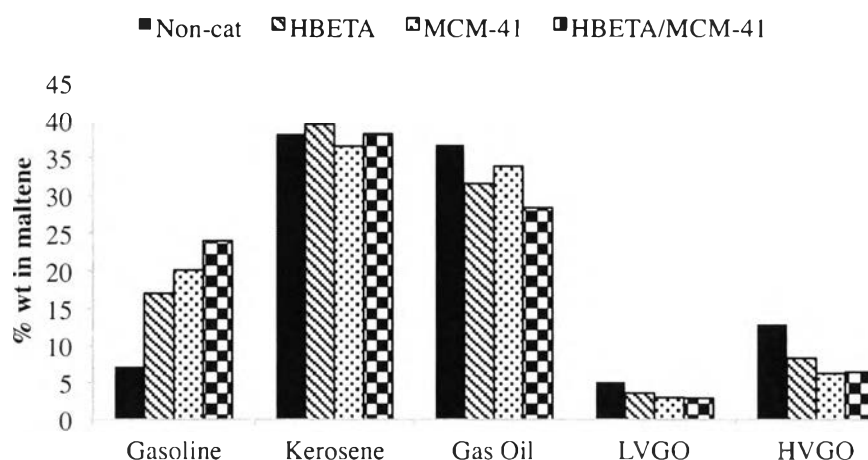


Figure 7.11 Petroleum fractions in maltenes from using HBETA, MCM-41 and their core-shell composite.

Regarding to petrochemical species in maltenes, pure MCM-41 also enhances the formation of ethylbenzene, toluene, mixed-xylenes, cumene and styrene in maltene. The pure HBETA zeolite itself has the ability to enhance the formation of ethylbenzene, toluene, mixed-xylenes and styrene in maltene. The presence of core-shell composite provides a higher petrochemicals selectivity in maltene, resulting

from a higher formation of benzene, ethylbenzene, toluene, and mixed-xylenes than those obtained from the pure HBETA and MCM-41 catalysts (See Figure 7.12 (a)).

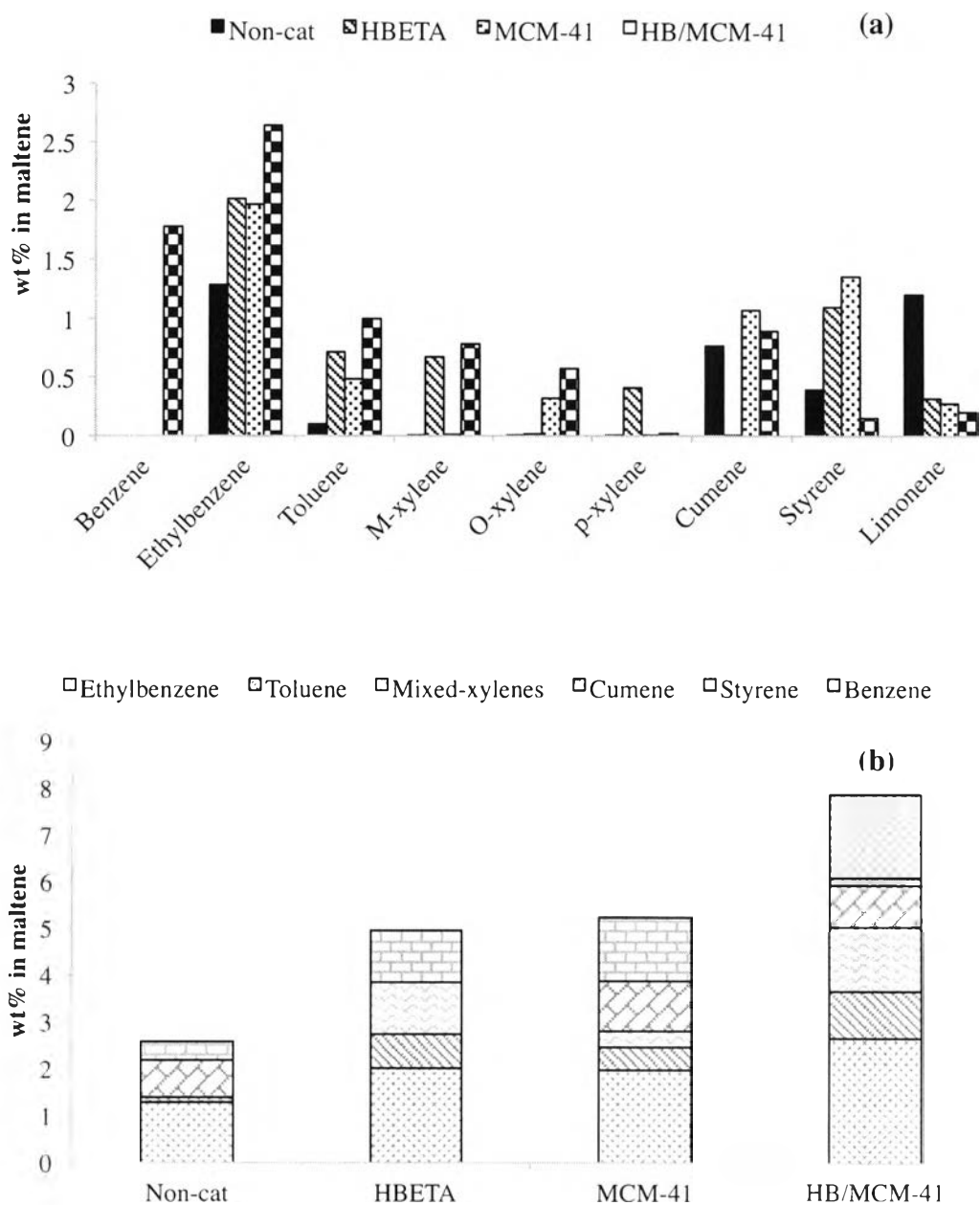


Figure 7.12 Concentration of petrochemicals in maltenes.(a-b) and concentration of biphenyl in maltene (c).

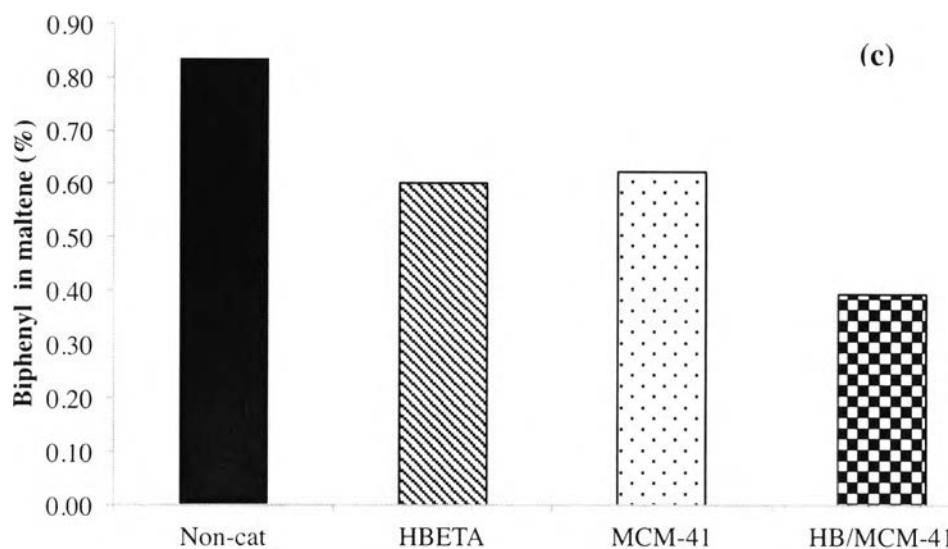


Figure 7.12 Concentration of petrochemicals in maltenes.(a-b) and concentration of biphenyl in maltene (c). (Con't.)

The presence of composite catalyst promotes the transformation of di-, poly- and polar- aromatics to valuable petrochemicals since some heavy aromatics are cracked at the weak acid sites of MCM-41, which are generated by silanol groups and aluminium oxide that come from dealumination of zeolite, forming intermediate aromatics that later can diffuse more effectively to the zeolite core and are then cracked further on strong acid sites of HBETA zeolite, resulting in the markedly enhanced formation of valuable aromatics. Moreover, the MCM-41 shell might provide some free channels, which allow some valuable aromatics that escape from HBETA zeolite, diffuse throughout MCM-41 channel without the transformation of valuable aromatics to other hydrocarbons. Furthermore, the concentration of biphenyl has been found to decrease (see Figure 7.12(c)), so biphenyl might be converted to benzene as displayed in **Scheme 1**. After the carbon-carbon scission at the position between two benzene rings, benzene and benzene radical can be directly formed. If H_2 can be produced sufficiently, a radical of benzene can react with H_2 , forming another benzene molecule. Moreover, the concentration of styrene has been found to significantly decrease, so the styrene might react with available H_2 to form ethylbenzene as displayed in **Scheme 2**. In addition, ethylbenzene can undergo

dealkylation reaction, forming benzene as displayed in **Scheme 3**. Since the concentration of benzene has not been found to increase when using non-composite catalyst and the concentration of styrene is suppressed by the presence of core-shell structure, possible reaction pathways in **Scheme 2** and **Scheme 3** might be promoted by the synergy of MCM-41 shell and HBETA core.

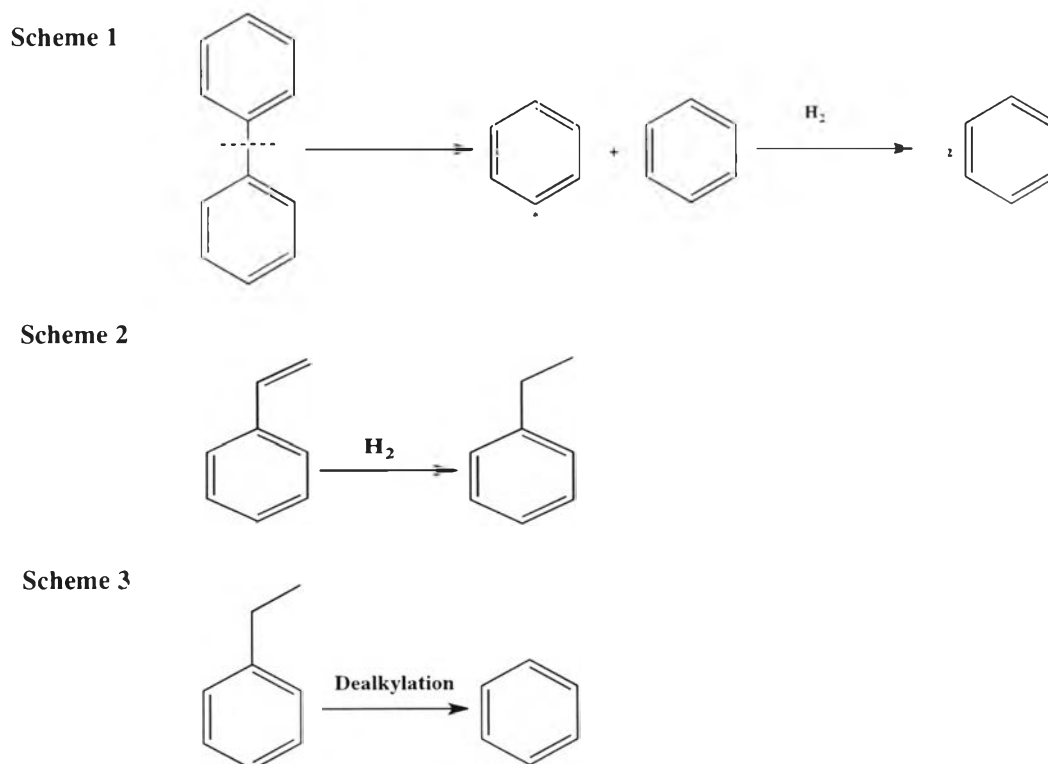


Figure 7.13 Possible reaction pathways for transformation of biphenyl and styrene to valuable aromatics using the core-shell composite of HBETA and MCM-41.

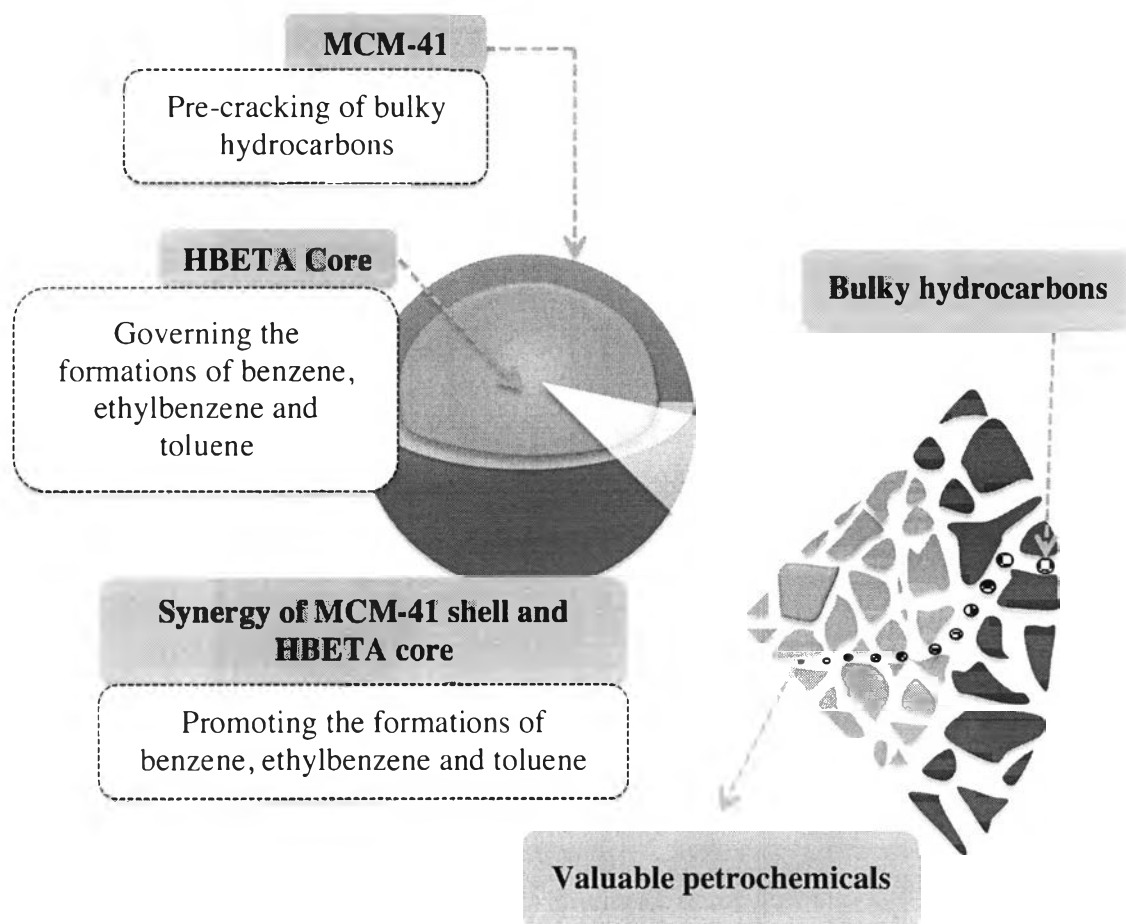


Figure 7.14 Role of core-shell composite of HBETA and MCM-41.

7.4.5 Sulfur Distribution and Sulfur Content in Oils

The sulfur content in oils significantly decreases with the presence of catalysts. HBETA zeolite has the ability to provide a lower sulfur content in oil than MCM-41 since the acidity of MCM-41 are weaker than that of HBETA zeolite, resulting in the lower desulfurization activity. Therefore, it can be suggested that the acidity is also an important factor that should be considered when the catalysts have a large enough pore size, which can allow all sulfur-containing compounds to go inside the pore. Moreover, the sulfur content in oil produced by the core-shell composite of HBETA and MCM-41 is lower than those produced by HBETA and MCM-41 catalysts due to the good balance between the acid sites and pore size of composite, resulting in high desulfurization activity. The composite catalyst favors to

break C-S and C-N bond of sulfur-containing compounds in oil, leading to high sulfur distribution in the gas products (see Figure 7.15(b)).

Table 7.2 Sulfur contents in pyrolysis oil

Catalyst	Non-catalyst	HBETA	MCM-41	HBETA/MCM-41
Sulfur content in oil (wt%)	0.96	0.83	0.88	0.79
Sulfur reduction (%)	Base	14.1	8.3	17.7

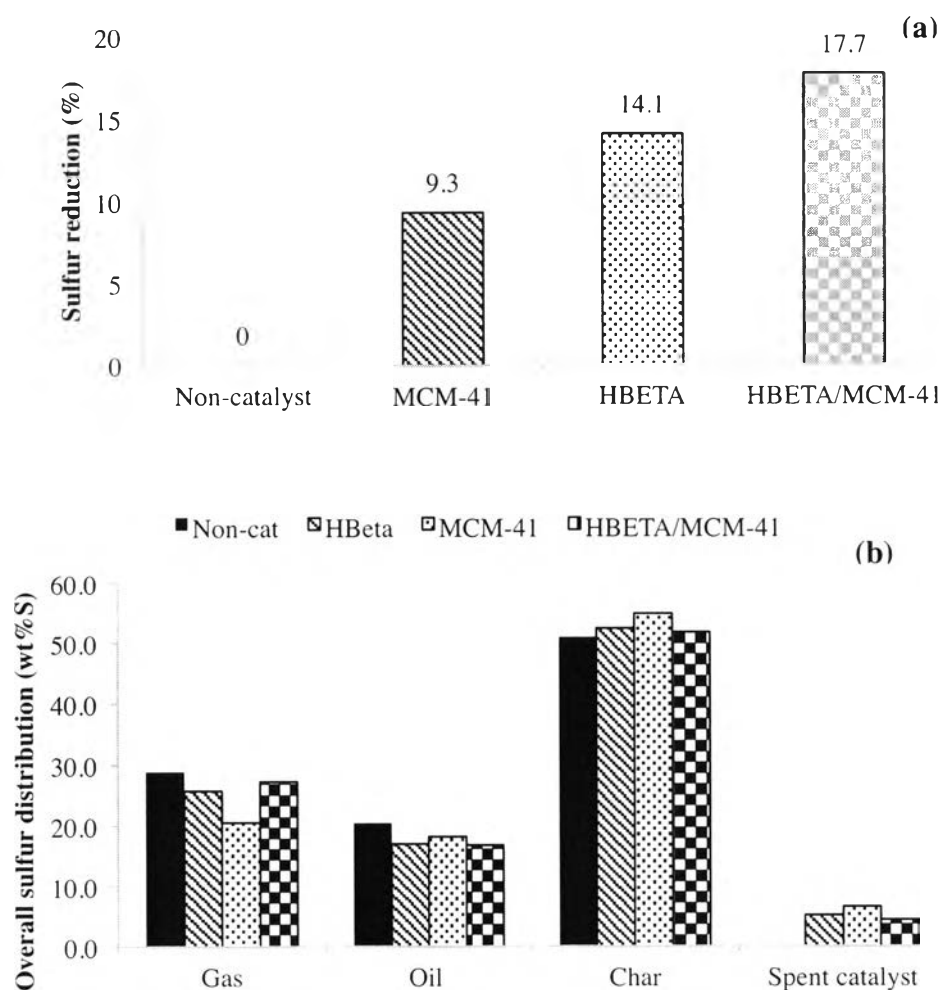


Figure 7.15 Sulfur reduction (a), overall sulfur distribution on pyrolysis products and spent catalysts (b), and Distribution of sulfur-containing compounds in maltenes from using HBETA, MCM-41 and their core-shell composite (c).

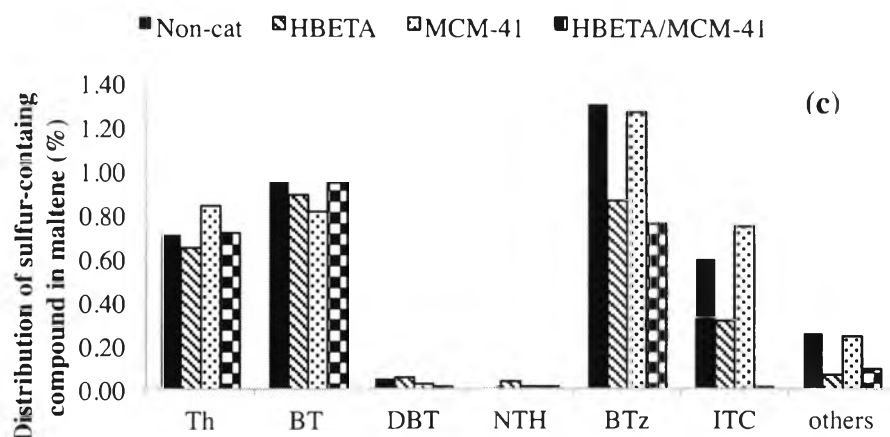


Figure 7.15 Sulfur reduction (a), overall sulfur distribution on pyrolysis products and spent catalysts (b), and Distribution of sulfur-containing compounds in maltenes from using HBETA, MCM-41 and their core-shell composite (c). (Con't.)

Regarding to the distribution of sulfur-containing compounds in maltene, sulfur-containing compounds in maltenes are classified into six groups, following Yuwapornpanit and jitkarnka (2015); that are, thiophenes (Th), benzothiophenes (BT), dibenzothiophene (DBT), naphthothiophenes (NT), benzothiazoles (BTz), isothiocyanates (ITC) as displayed in Figure 7.15(C). MCM-41, which possesses a large pore size and weak acid sites, slightly decreases the formation of benzothiophenes and benzothiazoles as compared to the thermal pyrolysis. On the other hand, the pure HBETA catalyst itself, which possesses strong acid sites and micropore, decreases the formation of thiophenes, benzothiophenes, benzothiazoles, and isothiocyanates since the pore size of HBETA allows thiophenes, benzothiophene, benzothiazoles and isothiocyanates to diffuse inside the zeolite channel, and then are desulfurized. Moreover, the formation of thiophenes and isothiocyanates significantly increases as compared to thermal pyrolysis and HBETA zeolite. These results can be explained by two reasons; (i) the large pore size of MCM-41 catalyst might promote the cracking of heavy sulfur-containing compounds, such as DBT, NTH and etc, resulting in the high formation of slightly smaller sulfur-containing compounds, such as thiophenes and isothiocyanates; and (ii) desulfurization by a zeolite or MCM-41 without a metal promoter does not only need a large pore size, but also the suitable acidity that can break the C-S bonds and C-N

bonds of sulfur-containing compounds. Significant changes are observed in the formation of sulfur-containing compounds with using core-shell composite of HBETA and MCM-41. The presence of composite catalyst provides a lower the formation of benzothiazoles and isothiocyanates than the pure HBETA and MCM-41 catalysts. These results indicate that the combination of the MCM-41 shell that possesses the weak acid sites and large pore size and the HBETA core with strong acid sites and micropore can overcome the limitation of both components on desulfurization of sulfur-containing compounds. The limitation of zeolite is that zeolites possesses a small pore size that cannot allow the some sulfur-containing compounds such as DBT, NTH, BTZ and ITC to be effectively desulfurized in its channel. On the other, the limitation is that MCM-41 possesses only weak acid sites that cannot effectively desulfurized and denitrogenized of BTz and ITC. Moreover, the formation of sulfur-containing compounds, except benzothiophene is lower than that of MCM-41 catalyst since the core-shell composite provides a higher possibility for desulfurization of sulfur-containing compounds. The bulky sulfur-containing compounds might be desulfurized at weak acid sites of MCM-41 shell, and the slightly-smaller sulfur compounds are further desulfurized at strong acid sites of HBETA core, leading to the a higher desulfurization activity than MCM-41.

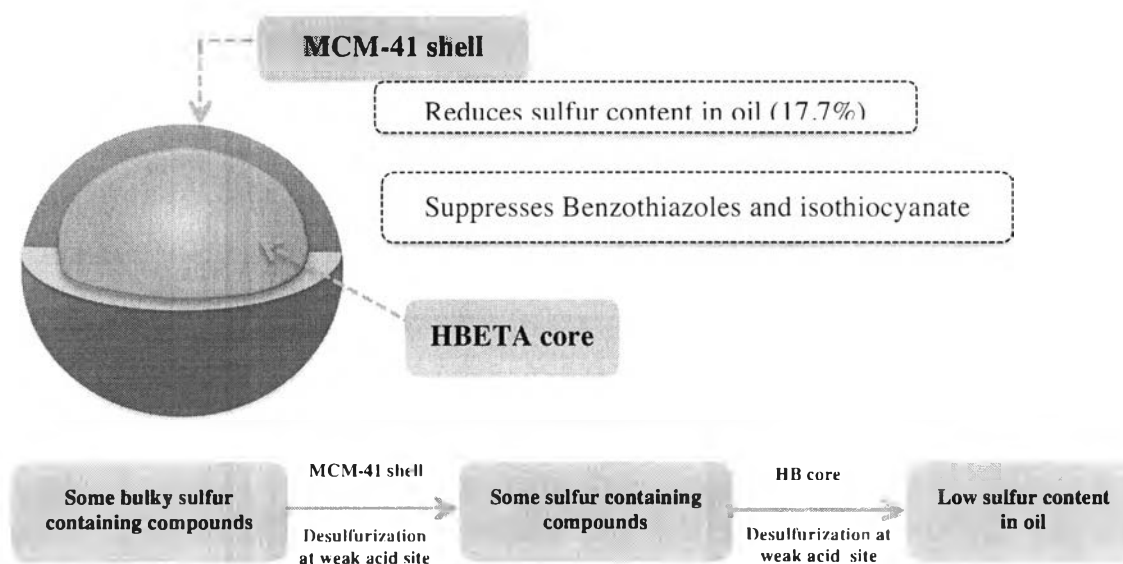


Figure 7.16 The role of core-shell composite on sulfur removal from tire-derived oil.

7.5 Conclusions

The core-shell composite comprising HBETA zeolite core and mesoporous MCM-41 shell with a thin shell thickness (50-100 nm.) can be considered an promising catalyst for enhancement of petrochemical production and reduction of poly-cyclic aromatics from waste tire-derived oil. The results show that the core-shell composite catalysts strongly promoted the production of gasoline, indicating that the cracking activity of composite catalysts was higher than the pure HBETA and MCM-41 catalysts. Moreover, the formation of di-, poly- and polar-aromatics in oil significantly increased as compared to pure HBETA zeolite since these aromatics cannot be sufficiently cracked in micropore of HBETA zeolite. Furthermore, the core-shell composite catalyst provided an excellent catalytic performance in the transformation of hydrocarbons to valuable aromatics. The core-shell composite of HBETA and MCM-41 strongly enhanced the formation of benzene, ethylbenzene, toluene and mixed-xylenes since the composite catalyst favored to produce petrochemicals via aromatization of olefins and paraffins and transformation of poly-cyclic aromatics to valuable aromatics. Furthermore, the composite catalyst also provided a lower sulfur tire-derived oil than the oil produced from pure MCM-41 and HBETA catalysts. Therefore, it is reasonable to conclude that the presence of single dimension connection of HBETA zeolite core and MCM-41 shell exhibits the great potential in enhancement of quality of waste tire-derived oil with a high proportions of gasoline and petrochemicals.

7.6 Acknowledgements

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7.7 References

- Bordoloi, A., Devassy, B.M., Niphadkar, P.S., Joshi, P.N., and Halligudi, S.B. (2006) Shape selective synthesis of long-chain linear alkyl benzene (LAB) with AlMCM-41/Beta zeolite composite catalyst. Journal of Molecular Catalysis A: Chemical, 253(1-2), 239-244
- Boxiong, S., Chunfei, W., Binbin, G., Rui, W., and Liangcai (2007) Pyrolysis of waste tyres with zeolite USY and ZSM-5 catalysts. Applied Catalysis B: Environmental, 73(1-2), 150-157.
- Dung, N.A., Klaewkla, R., Wongkasemjit, S., and Jitkarnka, S. (2009) Light olefins and light oil production from catalytic pyrolysis of waste tire. Journal of Analytical and Applied Pyrolysis, 86(2), 281-286.
- Dung, N.A., Tanglumlert, W., Wongkasemjit, S., and Jitkarnka, S. (2010) Roles of ruthenium on catalytic pyrolysis of waste tire and the changes of its activity upon the rate of calcination. Journal of Analytical and Applied Pyrolysis, 87(2). 256 -262.
- Huang, L., Guo, W., Deng, P., and Li, Z.X.a.Q. (2000) Investigation of synthesizing MCM-41/ZSM-5 composites. Journal of Physical Chemistry B, 104, 2817-2823.
- Jia, L., Sun, X., Ye, X., Zou, C., Gu, H., Huang, Y., Niu, G., and Zhao, D. (2013) Core shell composites of USY@Mesosilica: Synthesis and application in cracking heavy molecules with high liquid yield. Microporous and Mesoporous Materials, 176, 16-24.
- Kloetstra, K.R., b, H.W. Z., Jansen, J.C., and Bekkum, H.v. (1996) Overgrowth of mesoporous MCM-41 on faujasite. Microporous Materials, 6, 287-293.
- Li, X., Zhou, F., Wang, A., Wang, L., and Hu, Y. (2009) Influence of Templates on the Overgrowth of MCM-41 over HY and the Hydrodesulfurization Performances of the Supported Ni-Mo Catalysts. Industrial & Engineering Chemistry Research, 48, 2970-2877.

- Muenpol, S., Yuwapornpanit, R., and Jitkarnka, S. (2015) Valuable petrochemicals, petroleum fractions, and sulfur compounds in oils derived from waste tyre pyrolysis using five commercial zeolites as catalysts: Impact of zeolite properties. Cleaner Technology and Environmental Policy, DOI 10.1007/s10098-015-0935-8
- Na, J., Liu, G., Zhou, T., Ding, G., Hu, S., and Wang, L. (2013) Synthesis and Catalytic Performance of ZSM-5/MCM-41 Zeolites With Varying Mesopore Size by Surfactant-Directed Recrystallization. Catalysis Letters, 143(3), 267-275.
- Ooi, Y.-S., Zakaria, R., Mohamed, A.R., and Bhatia, S. (2004) Synthesis of composite material MCM-41/Beta and its catalytic performance in waste used palm oil cracking. Applied Catalysis A: General, 274(1-2), 15-23.
- Yuwapornpanit, R. and Jitkarnka, S. (2015) Cu-doped catalysts and their impacts on tire-derived oil and sulfur removal. Journal of Analytical and Applied Pyrolysis, 111, 200-208.