# CHAPTER II
# THEORETICAL BACKGROUND AND LITERATURE REVIEW

## 2.1 Pyrolysis of Waste Tire

Waste tire pyrolysis is the process that transforms the large molecules of tire into lower molecular-weight compounds under a high temperature and the absence of oxygen. The products after pyrolysis of waste tire consist of gas, oily liquid and char. Among these three products, the liquid or tire-derived oil is the most attractive because it contains of olefins, paraffins, and aromatics. Some aromatics in tire-derived oil are valuable mono-aromatics such as benzene, toluene and xylenes, which are raw materials for petrochemical production.

### 2.1.1 Mono-aromatics as Upstream Petrochemicals

The global demand for valuable aromatics (benzene, toluene, and xylenes) continuously increases because these aromatics are used to produce intermediate and downstream petrochemicals. For example, benzene is used as a raw material in the production of ethylbenzene, cumene, cyclohexane, nitrobenzene, alky benzene, and chlorobenzene, and then these intermediate chemicals are used as raw materials in manufacturing of polymers, detergents, synthetic fibers and dyes. Toluene can be used not only as a solvent in paints and lacquers, but also as a raw material in the production of intermediate chemicals (benzene, benzoic acid, toluene di-isocyanate etc.). These chemicals, which are produced from toluene, are used in the production of pharmaceuticals, dyes, and cosmetic nail products. Generally, xylenes have three different isomers, which are meta-xylene, ortho-xylene, para-xylene. Meta-xylene is used as a raw material in the production of isophthalic acid, 2,4- and 2,6-xylidine, and then these chemicals are used in the manufacture of polyamide resins and unsaturated polyesters. Ortho-xylene is also used as an upstream chemical for the production of phthalic anhydride and polyethylene naphthalate. Para-xylene is used as a raw material in the production of terephthalic acid and dimethyl terephthalate, which are used in the production of polyethylene terephthalate (PET) plastic bottles and polyester clothing. As a result, products,

which are produced from valuable mono-aromatics, are essential for living. Therefore, seeking for a new technology or alternative resources for the valuable mono-aromatic production is a key factor in order to meet the demand of daily use products.

### 2.1.2 Catalytic Pyrolysis Using Zeolites as a Catalyst

Because of the high demand of valuable mono-aromatics, several groups of researchers attempted to improve the production of valuable products from waste tire pyrolysis. Zeolites play an important role in increasing the valuable mono-aromatics production. The typical zeolites, which have been used in the catalytic pyrolysis of waste, are HMOR, HBETA, Y, HZSM-5, and KL. The properties of zeolite are shown in Table 2.1.

**Table 2.1** Properties of zeolites (Tosoh Corporation, Singapore, 2014)
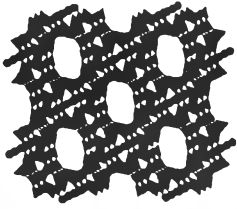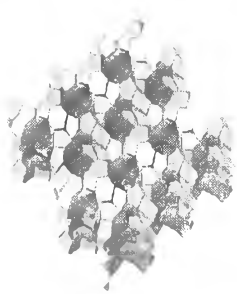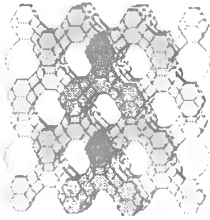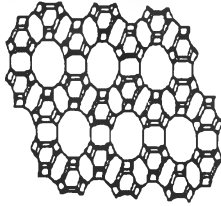
| Zeolite | Channel Structure | Membered Ring | Pore Size ($\text{Å}$) | Pore Structure |
|---------|-------------------|---------------|------------------------|----------------|
| HMOR | 1D | 12 | 6.5x7.0 |  |
| HBETA | 3D | 12 | 6.4x7.6 |  |
| HZSM-5 | 3D | 10 | 5.5x5.1 |  |

**Table 2.1** Properties of zeolites (Tosoh Corporation, Singapore, 2014) (con't.)

| Zeolite | Channel Structure | Membered Ring | Pore Size (Å) | Pore Structure |
|---------|-------------------|---------------|---------------|----------------|
| HY | 3D | 12 | 7.4 |  |
| KL | 1D | 12 | 7.1x7.1 |  |

Several researchers used HBETA zeolite as a catalyst in waste tire pyrolysis. In 2011, Wehatoranawee reported that HBETA provided the highest yield of cooking gas among HMOR, Y, and KL zeolites. In addition, HBETA zeolite also produced the highest amount of saturated hydrocarbons and the lowest yields of total aromatics among the other zeolites. The author explained that the highest Si/Al ratio of HBETA promoted the high cracking activity. On the other hand, HBETA zeolite gave high amount of polar-aromatics as compared to the other zeolites due to the high acid strength of HBETA zeolites. Manchantrarat (2011) indicated that HBETA produced saturated hydrocarbons in the kerosene and gas oil ranges, and also reduced the total-aromatics in the both kerosene and gas oil fractions.

HMOR zeolite was studied by several researches. In 2007, Choosuton found that the HMOR zeolites produce high amount of saturated hydrocarbons. In addition, HMOR catalyst increased the total aromatic contents in tire-derived oil, especially the polar-aromatics yield because of the high acid strength and the cracking ability of the zeolites. Wehatoranawee (2011) indicated that HMOR zeolite produced higher cooking gas yield than that obtained from the KL zeolite. In addition, the yield of polar-aromatic that obtained from using HMOR as a catalyst was relatively high as compared to Y zeolite. The author explained that the formation of aromatics increased with the increase of acid strength.

KL zeolite also provided aromatics contents in oil, particularly polar-aromatic yields (Wehatornawee, 2011). The polar-aromatic possibly produced by aromatization via basic pathway. Moreover, Muenpol (2014) indicated that KL gave the high mono-aromatic production, but the mono-aromatic contents in oil were not valuable. On the other hand, KL catalyst reduced the sulfur contents in tire- derived oil.

HZSM-5 zeolite was widely used in the pyrolysis of waste tire. Olazar *et al.* (2008) reported that HZSM-5 catalyst increased gas yield because the high acidity converted the liquid fraction to gas products. Similarly, HZSM-5 zeolites enhanced the light olefin production and promoted cracking of tar to gases and aromatics (Aguado *et al.*, 2014). In addition, Muenpol (2014) revealed that HZSM-5 selectively produced cyclohexane, and reduced the sulfur contents in tire-derived oil.

HY and USY zeolites were commonly used in the catalytic pyrolysis of waste tire. The ultrastable Y-zeolite provided higher the mono-aromatic production than the Y and ZSM-5 zeolites (Shen *et al.*, 2006). The concentrations of benzene, toluene and stylene in tire derived- oil were governed by the catalyst to tire ratio (Boxiong *et al.*, 2007b), pore size and silica to alumina ratio (Boxiong *et al.*, 2007a). Olazar *et al.* (2008) reported that HY produced higher aromatic yields than HZSM-5 and HBETA since the larger pore size of HY generated more aromatics via Die-Alder condensation. Additionally, Y-zeolite enhanced the saturated hydrocarbon yields (Saparakpunya, 2011) and reduced the di- and polar-aromatic contents in tire-derived oil (Wehatornawee, 2011). Recently, Aguado *et al.* (2014) stated that HY zeolites enhanced the production of aromatics and tar due to the shape selectivity of zeolite. In addition, the author explained that HY zeolite promoted the production of aromatics by increasing the condensation and alkylation of limonene and gasoline.

Different zeolites provide different product distribution because each zeolite has unique properties. As a result, several researchers attempted to understand the effect of zeolite properties (acidity, pore size, and pore structure) on the waste tire pyrolysis products in order to improve or upgrade the production of desirable products. In 2003, William and Brindle studied the effects of pore size and Si/Al ratio of zeolites on the waste tire pyrolysis. The author indicated that Y zeolite with the Si/Al ratio of 5.4 produced a higher amount of single ring-aromatics than the Y-

zeolite with the Si/Al ratio of 40. In addition, they found that the larger pore size of Y-zeolite produced more single-ring aromatics than the smaller one of ZSM-5 catalyst. The authors explained that the large hydrocarbon molecules entered the larger pore more easily than the smaller one.

Recently, Muenpol and Jitkarnka (2015) also studied the effect of zeolites on waste tire pyrolysis products. The author found that the 3D pore channel structure of HBETA gave higher full-range naphtha yields and lower heavy compounds in oil than HMOR with 1D pore channel due to the long residence time in pore. In addition, HBETA produced higher aromatic yields, and lower paraffin and olefin yields than HMOR. HBETA catalyst produced higher benzene, ethylbenzene, toluene and cyclohexane yields than HMOR. Moreover, he concluded that HBETA selectively produced benzene and ethylbenzene, and HMOR catalyst significantly enhanced the styrene production. In addition, the effect of different pore sizes of zeolites was studied by using HZSM-5 and HBETA zeolites. The full-range naphtha production produced from HBETA zeolite was higher than that from HZSM-5 zeolite. Since HZSM-5 had a smaller pore size than HBETA, it therefore gave the lower amount of benzene, toluene, and ethylbenzene. The small pore size of a zeolite provided a lower amount of valuable mono-aromatics. Moreover, the KL, which is a basic zeolite, produced a lower amount of styrene, ethylbenzene, toluene, m-xylene, cumene, and full range naphtha than the HMOR catalyst due to the low cracking ability of KL. Yuwapornpanit (2014) also studied the effect of acidity of HY and HBETA zeolites. The results showed that HY produced a higher amount of mono-aromatics and a lower amount of di-and polar-aromatics than HBETA due to the higher cracking ability of HY. Moreover, the author concluded that the HBETA catalyst selectively produced benzene and ethylbenzene, and HY catalyst selectively produced benzene and toluene.

According to above research works, the products from catalytic pyrolysis of waste tire are governed by the zeolite properties such as acidity, pore size and pore structure. The high acidity of zeolites highly converts the liquid products into gas products. In addition, high acidity can promote the aromatic yields by Die-Alder condensation of olefins. The complexity of pore structure provides lighter products because reactants spend a long time staying in the pore. Moreover, a

small pore size of zeolite reduces large compound formation in the pore; then, the production of light hydrocarbons increases. However, a small pore size of zeolites limits large molecules to diffuse into the pore. Therefore, the balance of acidity, pore size and pore structure is necessary in order to increase of valuable mono-aromatics production in tire-derived oil.

### 2.1.3 Catalytic Pyrolysis of Waste Tire Using Supported Nickel Catalysts

Because of the low price and excellent catalytic performance of nickel catalyst, several researchers introduced nickel metal on zeolites. In 2011, Pinket studied the effect of Ni loading amount over KL zeolite. The results showed that the amount of mono-aromatics in tire-derived oil increased when the amount of nickel loading increased. Although the concentration of mono-aromatics increased with increase of nickel loading, the concentration of light mono-aromatics (C6-C8) obtained from 20 % Ni/KL was only 0.04 wt %, which was the lowest yield among those obtained from 1 % Rh/KL and 5 % Co/KL. The increase of nickel loading slightly decreased saturated hydrocarbons because they might be cracked to light hydrocarbons. The yields of di- and poly- aromatics also decreased with the increase of nickel loading due to the hydrogenation and ring-opening activity on nickel sites. In addition, the author also reported that nickel over KL zeolite reduced sulfur contents in tire-derived oil by approximately 47-71 %.

Since nickel can promote hydrogenation/dehydrogenation and ring-opening reaction, like noble metals, Saeaeh (2012) studied the possibility of using Ni over HMOR and HBETA zeolites for replacing a noble metal. The author found that when the percentage of nickel loading increased, the yield of saturated hydrocarbons slightly decreased. Furthermore, 5 % Ni/HBETA and 10 % Ni/HBETA gave a higher yield of saturated hydrocarbons than 1 % Pd/HBETA. 5 % Ni/HBETA can produce a high amount of naphtha and saturated hydrocarbons as similarly as 1 % Pd/HBETA. In addition, nickel over HBETA zeolite reduced the sulfur contents in tire derived-oil since nickel metal sites broke the C-S bonds due to desulfurization activity of nickel. Moreover, 5 % Ni/HMOR gave 7 times higher yield of BTXs than 1 % Pd/HMOR. The yield of olefins, cooking gas and mixed C4 decreased with the increase of percentage of nickel loading because nickel metal enhanced the activity of

dehydrogenation and aromatization via Diels-Alders condensation of olefins. Nickel supported on HMOR zeolite also reduced sulfur contents in oil. The author concluded that 5 % Ni/HMOR could be used to substitute 1 % Pd/HMOR in order to produce mono-aromatic and valuable gases. From the previous studies, it is reasonable to conclude that nickel-promoted catalysts can improve the production of valuable products and reduction the sulfur contents in pyrolytic oil.

### 2.1.4 Limitations of Tire-derived Oil for Commercial Applications

Tire-derived oil mostly contained aromatics. Aromatic species in tire-derived oils, which can contain sulfur or nitrogen atoms, are carcinogenic substances. Pyrolytic oil is not directly used as fuels or chemical feedstock because the toxic substances in tire-derived oil have harmful effect on human health. The reduction of these aromatic species, which are called polar-aromatics, is a challenging problem for catalyst developers.

Previous research articles on the catalytic pyrolysis of waste tire reported that sulfur and nitrogen compounds still remained in tire-derived oils. One possible reason is that the diffusion of large molecules is limited by a small pore of zeolites. The diffusion of heavy molecules is not possible during reaction time; then, the molecules could not be converted to valuable products. Therefore, some groups of researchers attempted to use mesoporous molecular sieves that have a larger pore size than zeolites. Dũng *et al.* (2009) reported that the catalytic pyrolysis of waste tire using MCM-41 as a catalyst produced high naphtha and kerosene yields and a low concentration of poly- and polar-aromatic in tire-derived oil. On the other hand, using MCM-41 as a catalyst significantly increased mono- and di- aromatics. Therefore, it is reasonable to conclude that MCM-41, which has a low acidity, can promote cracking reaction. In addition, Ru supported on MCM-41 produced 4 times higher light olefin yield than the non-catalyst case. In addition, the pyrolysis of waste tire using Ru/MCM-41 increased the concentration of mono-aromatics, and decreased the polycyclic aromatic species in tire-derived oil. The introduction of ruthenium on MCM-41 provided high aromatic hydrogenation activity. Therefore, the partial hydrogenated polycyclic aromatics were cracked, or their rings were opened on the acid sites of support. Moreover, Dũng (2010) synthesized mesoporous

SBA-1, and studied the catalytic performance in the pyrolysis of waste tire. They found that SBA-1 did not play any role in the reaction since the yields of saturated hydrocarbon, mono-, di-, poly- and polar- aromatics unchanged in comparison with the non-catalytic pyrolysis of waste tire.

In summary, the increase in the pore size of catalysts is not sufficient for use in pyrolysis application. Consequently, the balance of pore size and acidity of the catalyst is a grand challenge in the development of catalyst.

## 2.2 Composite of Microporous and Mesoporous Materials

Composite materials have been used in catalytic applications because they combined both advantages of microporous zeolites, and mesoporous molecular sieves. The advantages of these materials are large pore size, and high surface acidity distribution. Therefore, the composite materials are expected to give higher conversion and better selectivity in cracking heavy molecules than conventional zeolites or mesoporous molecular sieves. However, the properties of composite materials depend on how they are synthesized.

### 2.2.1 Synthesis of Composites of Mesoporous and Microporous Materials

From the past until now, there have been several ways to synthesize biporous composite materials. The first method to synthesize a composite of mesoporous and microporous materials was proposed by Zhu *et al.* (2001). They prepared bifunctional porous material from nanocrystal zeolites by using highly-ordered MPS (Sulfate modified monodisperse polystyrene) latex arrays as templates. Firstly, the authors deposited sulfate-modified monodisperse polystyrene beads on a filter surface, followed by adding the mixture of nanocrystal zeolites and deionized water on the filter surface. The TEM image of bifunctional porous material shown in Figure 2.1 illustrates that the macrophase is tightly connected with the microphase.
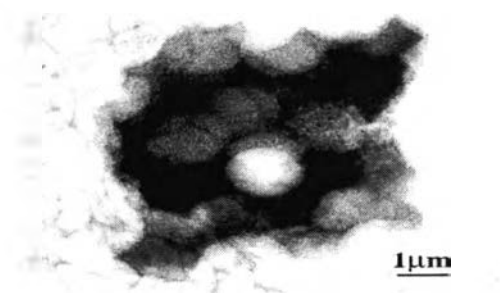
**Figure 2.1** TEM image of bifunctional porous material (Zhu *et al.*, 2001).

The second method to synthesize a composite material was proposed by *Wang et al.* (2004). They synthesized a composite material by using Modernite zeolite as a silica-alumina source and CTAB as a template. Firstly, MOR zeolite was dissolved in alkaline solution, followed by adding hexadecyl trimethyl ammonium bromide (CTAB) surfactant. The mesophase was formed by recrystallization of MOR gel around the CTAB micelle. However, the main drawback in these two methods is that materials are not hydrothermally stable.

The third method to create a composite material was proposed by Groen *et al.* (2008). The biporous material was synthesized from silicon extraction of BETA zeolite framework via alkaline treatment. Firstly, they synthesized BETA zeolite by using tetraethylammonium ions as a template. The second step was alkaline treatment of BETA zeolite. However, the mesophase and microphase were unclearly observed on the TEM image using this method (see in Figure 2.2).
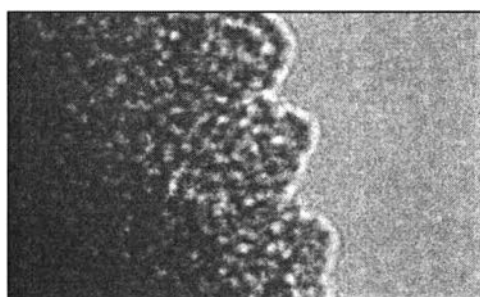


**Figure 2.2** TEM image of alkaline-treated zeolite (Groen *et al.*, 2008).

The next method to synthesize a composite material was proposed by Li *et al.* (2013). The hierarchical meso/microporous material was prepared by using hexadecyl trimethyl ammonium bromide (CTAB) and tetrabutylammonuim hydroxide (TBAOH) as meso- and microporous templates, respectively. Firstly, they synthesized the ZSM-5 zeolite seeds by using tetrabutylammonuim hydroxide as a template, followed by the addition of CTAB, ethanol, and water. Finally, the mixture was crystalized by using steam-assisted crystallization. The structure of mesoporous zeolite is displayed in Figure 2.3(a). Figure 2.3(b) indicates the structure mesophase of mesoporous zeolite that looks like a sponge, which is called wormhole-like mesoporous structure.
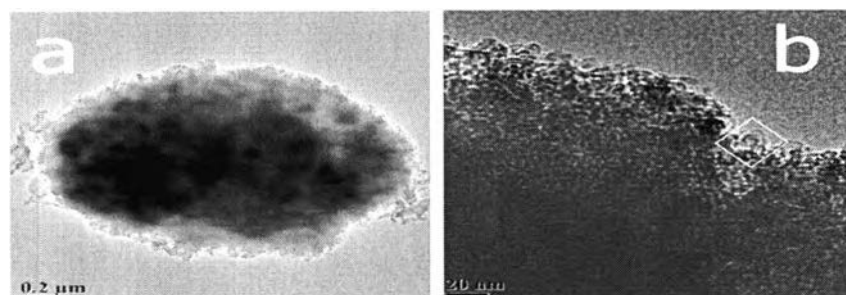


**Figure 2.3** TEM images of hierarchical meso/microporous material: (a) mesoporous zeolite structure, and (b) a wormhole-like mesoporous structure (Li *et al.*, 2013).

However, there are two main difficulties of the above methods. The first difficulty is the way to connect the mesopores and micropores in a single dimension, which is not a mixture or random connection. Composite materials having a random connection of mesopores and micropores contain two orientations of mesoporous and microporous layers; that are, the orientation of mesoporous layer over the microporous layer, and the orientation of microporous layer over the mesoporous layer. Therefore, using composite materials with a random connection of micropores and mesopores as a catalyst difficultly forecasts the desirable products because the molecular sizes of desirable products mainly depend on the orientation. For example, if reactants firstly react in micopores and then react further in mesopores, the obtained products might have a larger molecular size than those obtain from a material having a connection of mesopores to micropore. The reason

for this case is that the large pore size of mesophase governs the large molecular size of products. The second difficulty is that the way to adjust the proportion of mesophase and microphase in order to properly use in different catalytic applications. For example, composite materials are used for cracking reaction, should have a high proportion of microphase to mesophase because microphase contains a high acidity, which can boost up cracking activity.

### 2.2.2  Core-shell Structure Composite Materials

Several researchers attempted to find other ways to overcome these two above difficulties, and proposed a new composite material, which is called "core-shell" composite material. There are several methods to synthesize them; however, there are three main methods, which are most commonly used.

*(b)  Growth of Mesoporous Shell on the Surface of a Zeolite*

This method is the most convenient way to synthesize core-shell structure composite materials in comparison with the other two methods. In 1996, Kloetstra *et al.* created a thin layer of mesoporous MCM-41 on the surface of a faujasite zeolite. Firstly, they prepared the MCM-41 gel by mixing sodium silicate, Cab-osil M5, and water. Second, the mixture was added to the mixture of cetytrimethylammonium choride and water. Third, they prepared the faujasite zeolite gel by adding NaY into the mixture of cetytrimethylammonium choride (CTACl) and water. Finally, the MCM-41 gel was mixed with the faujasite zeolite gel, and then the mixture was transferred to crystallize in a Teflon-lined stainless steel autoclave. The authors verified the core-shell structure by using transmission electron microscopy, and proposed that MCM-41, which was prepared by CTACl surfactant, possibly coated on the surface of zeolite as displayed in Figure 2.4.
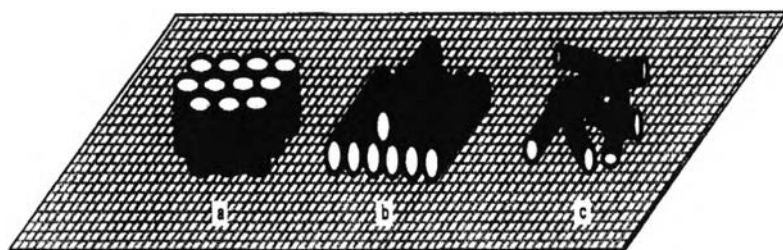


**Figure 2.4**  Drawing of possible orientations of MCM-41 on the zeolite surface (Kloetstra *et al.,* 1996).

In addition, Zhang *et al.* (2008) synthesized the core-shell composite of MCM-41 and Y zeolite under an alkaline condition. Firstly, NaY was added to the MCM-41 gel, previously prepared by mixing the ☐etraethyl-lorthosilicate (TEOS), CTAB, sodium hydroxide (NaOH), and water. Finally, the mixture was crystallized by hydrothermal crystallization. They verified the core-shell structure by TEM. The TEM image clearly illustrates that the Y-zeolite surface is covered by a MCM-48 layer with 50-100 nm thickness (See in Figure 2.5).
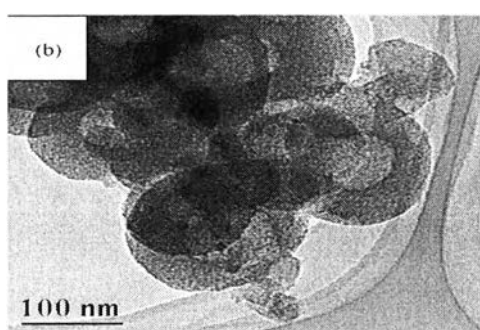


**Figure 2.5** TEM image of composite of MCM-48 and Y zeolite (Zhang *et al.*, 2008).

Moreover, some researchers studied the synthesis of core-shell composite materials under an acidic condition. Jia *et al.* (2013) synthesized core-shell composites of USY and SBA-15 by separating assembly before crystallization in different acidic conditions. Firstly, they added TEOS in dilute hydrochloric acid (HCl) solution. Secondly, they added the USY zeolite in the mixture of HCl and P123 surfactant. Finally, the mixture of TEOS and HCl was added to the mixture of P123 surfactant, HCl, and USY zeolite, followed by crystallization. Wang *et al.* (2011) also prepared a composite of MCM-41 and Y-zeolite by overgrowing MCM-41 on the surface of Y-zeolite under an acidic system. Firstly, they dissolved the CTAB in the HCl solution, followed by adding the mixture of USY zeolite, $Na_2SiO_3$, and water. Finally, the mixture was crystallized in an autoclave.

These two research groups stated that the synthesis of composite materials via an acid condition has more benefits than via a basic synthetic condition; for example, it requires shorter synthetic time and lower

surfactant concentration, and produce controllable structure. Moreover, there is a drawback of synthesis under a basic condition; that is, it is not favorable to link micropores and mesopores in single dimension since both zeolite and Si precursor have a negative charge that makes the repulsive force between them.

*(b) Mesoporous Core and Wormhole Structure of Aluminosilicate*
   *Shell*

In 2005, Zhai *et al.* prepared a mesoporous composite, which contained mesoporous MSU-S core and aluminosilicate shell. Firstly, they added the MSU-S in the mixture of CTAB, $NaAlO_2$ and water. Finally, the mixture was crystallized in a Teflon-lined stainless steel autoclave. They verified the core-shell structure using TEM. The authors explained that the shell had a wormhole pore structure as displayed in Figure 2.6.
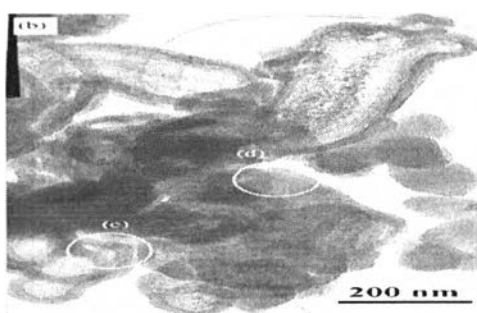


**Figure 2.6** TEM image of core-shell structure of MSU-S and aluminosilicate (Zhai *et al.,* 2005).

*(c) Yolk Shell or Egg Shell Composite Materials*

Peng *et al.* (2013) prepared a yolk shell composite material, which consisted of the titanosilicate TS-1 as a core and the mesoporous carbon as a shell. Firstly, the authors prepared the core-shell structure composite of TS-1 and mesoporous carbon, followed by treating with tetrapropylammonium hydroxide (TPAOH). The yolk-shell structure of composite material was confirmed using transmission electron microscopy (TEM). The TEM image in Figure 2.7 clearly displays that the composite material has a void between core and shell. Therefore, they concluded that the synthetic material was a yolk shell composite material.
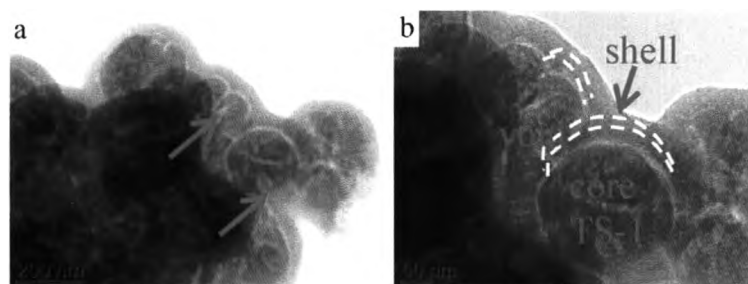
**Figure 2.7** TEM images of the yolk-shell or egg-shell composite material: (a) a void between mesoporous carbon shell and TS-1core, and (b) a high magnification image of t yolk-shell materials (*Peng* et al., 2013).

Parameters in synthesis that have the effect on mesophase formation, acidity and mesoporous shell thickness of the composite materials are the ratio of $SiO_2$ to zeolite, pH, aging time, calcination temperature, and templates. For instance, the thickness of mesoporous shell was controlled by adjustment of the mass ratios of TEOS to zeolite (Lv *et al.*, 2013). Jia *et al.* (2013) also found that the adjustment of TEOS/USY ratio from 1.26 to 2.52 can control the mesoporous SBA-15 shell thickness in the range of 20-60 nm. Therefore, it can be concluded that the thickness of mesoporous shell can be controlled by the ratio of silica source to zeolite. The acidity of a core-shell structure of composite material can be adjusted by the $SiO_2$/zeolite ratio. Alsobaai *et al.* (2007) synthesized composite materials by coating MCM-48 layer on a USY zeolite. They revealed that the adjustment of ratio of $SiO_2$/USY did not clearly change the amount of strong acid sites, but the total and weak acid sites significantly in creased when $SiO_2$/USY ratio decreased due to the increase of USY zeolite. In addition, different Si/Al ratio of micro-phase can be adjusted by changing the crystallization time and temperature (Wang *et al.*, 2011). Moreover, pH, aging time, calcination temperature, and template type can affect mesophase formation of core-shell structure of composite materials. Wang *et al.* (2011) reported that the pore size, order, and wall thickness of meso-phase can be adjusted by adding 1,3,5-TMB and pH adjustment. Ooi *et al.* (2004) synthesized a composite material of MCM-41/BETA by using seeding method and two-step

crystallization. They found that a long aging time was unable to promote the meso-phase formation because the synthesis gel converted to beta zeolite. Jiang *et al.* (2012) synthesized core-shell composite materials of MCM-41 and Y-zeolite. They found that the mesoporous order of composite molecular sieve decreased when the calcination temperature increased. Moreover, the specific area and pore volume significantly decreased with the increase of calcination temperature. In addition, Li *et al.* (2009) performed the overgrowth of MCM-41 over HY zeolite by using different templates. They found that, using CTABr as a template, the thin layer (less than 20 nm) of MCM-41 covered the HY zeolite. On the other hand, the HY zeolite was buried independently in the meso-phase with using CTACl as a template.

### 2.2.3 Utilization of Composite Materials as a Catalyst in Cracking Reaction

Composite materials are widely used in the catalytic cracking. For example, the composite zeolites of MOR and FAU were studied in isopropylbenzene cracking by the Zheng *et al.* (2013). The results showed that the proportion of FAU and MOR in the composite zeolites can be adjusted by varying crystallization time. The acidity of composite zeolites depended on the ratio of FAU to MOR zeolite, and the medium-strong acid sites increased with the increasing amount of MOR zeolite. In addition, the pore size of meso-phase increased with the increasing hydrothermal treatment time. Using MFZ composite zeolites in isopropylbezene cracking improved isopropylbenzene conversion, and reduced the coke formation. Alsobaai *et al.* (2007) also studied the hydrocracking of petroleum gas oil over NiW/MCM-48-USY composite catalysts. The hydrocracking cracking activity and amounts of gasoline, kerosene, and diesel increased with increasing the $SiO_2$/USY ratio. On the other hand, the coke formation reduced with the increase of $SiO_2$/USY ratio. Moreover, the catalytic activity increased when NiW metal was introduced to the composite material. The metallic W prevented the coke formation by saturating of the olefins and aromatics in the feed, whereas the roles of Ni promoter were on the enhancement of hydrodesulfurization activity and the balance of surface acidity.

In addition, the MCM-41/BETA composite material was studied in the waste palm oil cracking by Ooi *et al.* (2004). The results showed that the conversion and the selectivity of gasoline in liquid product decreased with the

increase of aluminum content in meso-phase because the disorder of meso-phase occurred with higher loading of aluminum. Moreover, hydrocracking of heavy oil using a core-shell composite of USY and SBA-15 as a catalyst was investigated by Jia *et al.* (2013). The authors discovered that the selectivity of liquid yield (C5-C15) from n-hexadecane cracking was improved with the introduction of Al in the core-shell composite catalyst. The NiW supported on USY/SBA-15 gave high activity, selectivity, and cetane number of middle distillate oil obtained from hydrocracking of heavy oil. Liu *et al.* (2013) reported that composite Y/MCM-41 treated with $Na_2SiO_3$ solution gave a higher conversion of vacuum gas oil than the one treated with NaOH due to its higher mesophase, pore volume, and surface acidity. Therefore, the treatment of $Na_2SiO_3$ promoted the cracking of heavy gas oil molecules because it gave a suitable pore size, which increased the diffusion efficiency of bulky molecules.

### 2.2.4 Utilization of Composite Material as a Catalyst in Desulfurization of Fuel

Ren *et al.* (2008) investigated the hydrodesulfurization of dibenzothiophene catalyzed by Ni-Mo sulfides supported on core-shell composites of MCM-41 and HY-zeolite. The composite catalysts were prepared by overgrowing MCM-41 over HY zeolite, and physical mixing of MCM-41 and HY zeolite. TEM images indicated that HY zeolite was covered by a thin MCM-41 layer in composite catalysts. Both composites of HY zeolite and MCM-41 gave higher hydrodesulfurization activity than HY zeolite and mesoporous MCM-41 due to the increase of surface acidity by the introduction of HY zeolite. Similarly, Li *et al.* (2009) studied hydrodesulfurization performance of Ni-Mo supported on the core-shell composite of HY and MCM-41. They found that the hydrodesulfurization via hydrogenation (HYD) pathway was significantly increased by the introduction of HY zeolite in the composite catalyst. However, the hydrocracking activities of Ni-Mo supported on the composites of HY and MCM-41 were low because the hydrodesulfurization of dibenzothiophene possibly occurred in the mesopore. Zhou *et al.* (2010) studied hydrodesulfurization of dibenzothiophene catalyzed by Pd supported on core-shell composite of MCM-41 and HY. Pd metals supported on the

composite materials exhibited the high activity and stability of hydrodesulfurization (HDS) of dibenzothiophene since the acidic support promoted HDS activities and HYD selectivity. In addition, the core-shell structure of composite materials increased the HDS performance, especially sulfur resistance.

## 2.3 Nickel-promoted Catalysts

Since sulfur contents in tire-derived oil are high, the pyrolytic oil is not suitable for direct use in combustion process. Desulfurization of pyrolytic oil, which is derived from waste tires, is a significant process of oil production before it can be utilized in the transportation application. Catalysts with high desulfurization activity are attractive for improvement of sulfur removal efficiency, and one of those catalysts is nickel. Nickel-promoted catalysts have been widely used for several industrial applications, especially desulfurization, because nickel is inexpensive, and has excellent catalytic activities such as desulfurization, hydrogenation/ dehydrogenation, and ring opening activities.

### 2.3.1  Desulfurization Activity of Nickel-promoted Catalysts

Nickel-based catalysts were reported to have a high desulfurization activity. Nickel supported on mesoporous materials provided the better desulfurization activity than conventional supports since the mesoporous materials had high surface area and large pore size. Nickel supported on the mesoporous SBA-15 were used in adsorptive desulfurization of diesel by Ko *et al.* (2007). The results showed that the sulfur removal efficiency increased with the increase of nickel loading, and then decreased because high nickel loading caused the agglomeration of nickel particles, and reduced the active sulfur adsorption sites. Sentorun-Shalaby *et al.* (2011) studied the adsorptive desulfurization of commercial ultra-low-sulfur diesel fuel using nickel supported on mesoporous molecular sieve. The effects of ultrasonic aid in incipient wetness impregnation were studied, and it was found that they significantly enhanced adsorptive desulfurization (ADS) performance due to the increase in the dispersion of nickel on the surface. The ADS breakthrough capacity increased with the increase of the total number of exposed Ni atoms. Using 20 wt%

nickel loading on the MCM-48 gave sulfur removal activity higher than the same loading on the SBA-15 because of the high dispersion of nickel on MCM-48 surface. Moreover, the authors suggested that the desulfurization reactivity of alkyl dibenzothiophene on the nickel supported mesoporous molecular sieve depended on the number and the size of the alkyl substituents at the 4- and 6-positions of the dibenzothiophene.

The effect of acidity on desulfurization activities of nickel supported on the mesoporous MCM-41 and AlMCM-41 was investigated by Subhan and Liu (2011). They found that 15 wt% nickel loading on MCM-41 and AlMCM-41 gave the highest breakthrough volumes (8.6 and 30 mL/g). It can be concluded that the higher acidity significantly enhanced the sulfur removal efficiency. In addition, the effect of pore size on the adsorptive desulfurization was studied by Sarda *et al.* (2012). As a result, the sulfur removal efficiency of activated alumina was higher than that of ZSM-5 because large sulfur molecules in diesel fuel diffused more freely in the large pores of activated alumina. As the Ni loading increased, the percentage of sulfur removal increased until the maximum was reached, and then decreased later. A high nickel loading caused the agglomeration of nickel, which reduced the active site of nickel metal. 8-10 wt% Ni/Alumina was more effective for removal of sulfur compounds from commercial diesel than $Cu/Al_2O_3$ adsorbent.

In summary, the amount of nickel loading is an important factor for improvement of sulfur removal efficiency. However, the excess nickel loading decreases the sulfur removal efficiency due to the reducing of active site of nickel metal. Moreover, catalyst supports with suitable surface area are preferable because the metal catalyst can be highly dispersed on the surface of supports. Therefore, selecting the suitable catalyst supports and seeking for the optimal nickel loading are the keys to get the maximum sulfur removal efficiency.

### 2.3.2 Cracking and Isomerization Activities of Nickel-promoted Catalysts

Nickel-based catalysts have been widely used for not only desulfurization of fuel but also chemical reactions. Nickel-based catalysts were reported to have a high cracking and isomerization activities. Nickel-supported HZSM-5, HBETA, and HMOR catalysts were used in cracking of n-octane and C8

isomers by Lugstein *et al.* (1999). The results showed that Ni/HZSM-5 provided higher conversions of n-octane, 2,5-dimethylhexane (2,5DMH), and 2,2,4-trimethylpentane (2,2,4TMP) than Ni/HMOR and Ni/HBETA because the pore size of HZSM-5 was suitable for the sizes of n-octane, 2,5DMH, and 2,2,4TMP. On the other hand, the authors concluded that Ni/HBETA and Ni/HMOR significantly promoted isomerization reaction. Maia *et al.* (2011) investigated the effect of Ni/ZSM-5 on light olefin production from isobutene and n-butane cracking. They found that the addition of nickel significantly increased the ethylene and iso-C4 formations. Therefore, Ni on ZSM-5 promoted the hydrogenation reaction. Botas *et al.* (2014) studied the catalytic conversion of rapeseed oil to raw chemicals and fuels over Ni-Mo modified nanocrystalline ZSM-5 zeolite. The results showed that the fresh ZSM-5 zeolite provide high yields of light olefins (C2-C4) and gasoline fraction (C5-C10). With the pore size and high acidity of ZSM-5, the obtained products were mainly light olefins and aromatics (Benzene, toluene and xylenes) Moreover, the introduction of nickel in HZSM-5 significantly enhanced cracking activity, which promoted the formation of light olefins. With the high acidity of Ni/HZSM-5, the coke formation on Ni/HZSM-5 was higher than on Mo/HZSM-5. On the other hand, Mo/HZSM-5 selectively produced liquid hydrocarbons, especially aromatics.

Nickel supported on ZSM-5 zeolites were used in cracking of n-hexane by Maia *et al.* (2010). The authors discovered that the introduction of nickel on the ZSM-5 increased the ethylene yield. The ratio of ethylene to butane with using nickel loading on ZSM-5 by impregnation method as a catalyst was higher than that of the one prepared by ion-exchange method. Escola *et al.* (2011) studied the catalytic hydroreforming of the polyethylene thermal cracking oil over Ni supported hierarchical zeolites and mesostructured aluminosillicates. Ni over hierarchical ZSM-5 and Beta zeolites promoted the hydrocracking reaction, which led to more gas and gasoline production. In addition, mono-aromatic yields obtained from using all catalysts significantly increased. Nevertheless, nickel supported on the hierarchical Beta zeolite produced higher di-aromatic yields than the one on the hierarchical ZSM-5 zeolite due to the larger microporous size. Nickel-supported mesoporous molecular sieves provided broad hydrocarbon distribution due to their

large pore size and mild acid strength. However, their hydrocracking activity was reduced, which led to more light diesel yield. Based on the above research works, the introduction of nickel on ZSM-5 zeolites promoted the cracking ability of catalysts, and the selectivity of products mainly depends on the pore size of and acidity of catalyst supports. In addition, the role of metal promoters on the supports mainly depends on the interaction between metal and support.

### 2.3.3 Aromatization Activity of Nickel-promoted Catalysts

Nickel-based catalysts promote not only cracking and isomerization reactions but also aromatization reaction. For example, Yin et al. (2005) investigated the transformation of olefin over Ni/HZSM-5 catalyst. The results showed that using the catalyst transformed olefins into aromatics and iso-paraffins. Moreover, using the catalyst at a low temperature promoted cracking and double-bond isomerization while the skeletal isomerization and aromatization activity increased at a high temperature. In addition, the sulfided Ni/HZSM-5 displayed higher aromatization activity than the metallic Ni-supported catalyst.

## 2.4 Research Motivation

Based on the literature review, nickel was used as a promoter in waste tire pyrolysis. Nickel exhibited the good performance in desulfurization of tire-derived oil and enhanced the mono-aromatics production. However, the species of products from waste tire pyrolysis using Ni catalysts have not been identified in the previous work.

Di-, poly and polar-aromatics still remained in tire-derived oil with using a zeolite as a support. Therefore, there are two possible reasons that can explain. The first possible reason is that the high acidity of zeolite promotes the aromatics productions. The second reason is that the small pore size limits the diffusion of heavy molecules of aromatics species. Therefore, heavy molecules cannot be cracked to the small valuable products. Using core-shell structure composite materials might be able to reduce heavy aromatics such as di-, poly- and polar aromatics, and increase the production of valuable mono-aromatics because of the balance of acidity

and combination of the micropore and mesopore. The possible structure of core-shell composite materials of a zeolite and MCM-41 is displayed in Figure 2.8. The MCM-41 shell might be able to crack bulky compounds such as di-, poly- and polar-aromatics in tire-derived oil. Smaller molecules of hydrocarbons, which are previously cracked by MCM-41 shell, can easily diffuse to the zeolite core, and might be further cracked into valuable mono-aromatics. The types of mono-aromatic products are governed by the zeolite type. From the previous studies, HY and HBETA zeolites had the high potential to produce the valuable mono-aromatics. Therefore, using MCM-41 as a shell and HY as a core are expected to improve the production of valuable mono-aromatics, especially benzene and ethylbenzene, and reduce bulky polycyclic hydrocarbons in pyrolytic oil. Likewise, using MCM-41 as a shell and HBETA as a core might be able to enhance the production of value mono-aromatics, especially benzene and toluene, and also decrease heavy polycyclic hydrocarbons in the tire-derived oil. Moreover, the thickness of the MCM-41 shell might affect the cracking ability of catalysts and product selectivity.
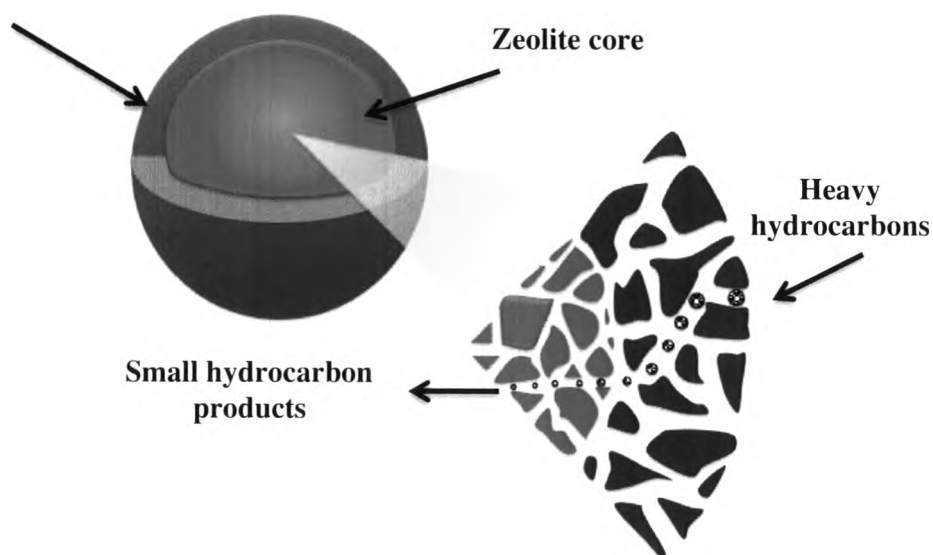


**Figure 2.8** Schematic of core-shell composite materials.

In this work, the effects of nickel-promoted catalysts and different zeolite cores of core-shell structure composite materials on the species of waste tire pyrolysis were therefore investigated. In the first part, the amount of nickel loading on the different zeolites (HMOR, HBETA, KL, HZSM-5 and HY), and mesoporous material (MCM-41) were fixed at 5 wt% for investigating the effect of presence of nickel. In the second part, the MCM-41 shell and HY and HBETA zeolites cores of the composite materials were studied for the effect of zeolite cores, and the MCM-41 shell thickness was controlled by adjustment of the mass ratio $SiO_2$ to zeolite. The species of pyrolysis products from using the zeolites and mesoporous MCM-41 were compared.

## 2.5 Objectives

a. To investigate the effect of nickel supported on different zeolites (HMOR, HBETA, KL, HY, and HZSM-5) on the species of waste tire pyrolysis products, and

b. To investigate the different zeolite (HY, HBETA) core of the core-shell composite materials on the species of waste tire pyrolysis products.

## 2.6 Scope of Research

The scope of this research covered as follows:

a. Pyrolysis of waste tire (Bridgestone TURANZA GR-80) was operated in a bench-scaled autoclave reactor.

b. Particle size of catalyst, particle size of shredded tire, $N_2$ flow rate, heating rate, the amount of shredded tire and the amount of catalysts were fixed at 40-60 mesh, 20-40 mesh, 30 ml/min, 10 °C min, 30 g and 7.5 g, respectively.

c. For the first part, nickel was loaded on the different supports:
   o Nickel was loaded using the incipient wetness impregnation method.
   o The amount of Ni was fixed at 5 %wt.
   c The zeolites that were used in this section are HMOR, HBETA, HY, KL, and HZSM-5.

Experiments are designed as shown in the Table below:

**Table 2.2** Experimental design of nickel-loaded catalysts

| Supports | Non-metal Loading | Nickel Loading (wt%) |
|----------|-------------------|----------------------|
| HMOR | - | 5 |
| HBETA | - | 5 |
| HY | - | 5 |
| KL | - | 5 |
| HZSM-5 | - | 5 |

    d.    For the second part, the core-shell structure composite materials were synthesized using different zeolite cores with fixed thickness of shell.

    o    The shell of all core-shell composite materials was synthesized by growing MCM-41 shell on a zeolite core.

    o    The shell of all core-shell composite materials was MCM-41, and zeolite cores of core-shell composite material are HY and HBETA.

Experiments are designed as shown in the table below:

**Table 2.3** Experimental design of core-shell composite catalysts

| Shell | Core |
|-------|------|
| MCM-41 | HY |
| MCM-41 | HBETA |