

CHAPTER II

LITERATURE REVIEW

2.1 The Process Conditions

The products of pyrolysis process depend on the conditions of process. Rodriguez *et al.*, (2001) studied on the pyrolysis of passenger car tires with different temperature conditions. They varied temperature at 300, 400, 500, 600 and 700 °C, and found 500 °C was the optimum temperature. Berrueco *et al.* (2005) investigated scrap tire pyrolysis under nitrogen atmospheric pressure in order to study the temperature influence on the yield and gas composition. They found the liquid yield increased with increasing temperature from 400 - 500 °C, but it was constant when the temperature was over 500 °C. On the other hand, the gas yield showed a slight increase with increasing temperature from 400 to 700 °C. Barbooti *et al.* (2004) studied pyrolysis scrap tire at temperature 400-460 °C, nitrogen flow rate 0.2 - 0.5 m³h⁻³, and particle size 2 - 20 mm. Their results showed the best condition for their work was at 430 °C, 0.35 m³h⁻³, and 10 mm, respectively. Leung *et al.* (2002) studied the influence of condition on the composition and gas product for the pyrolysis of tire powder. They found that products of pyrolysis had maximum heating value at temperatures between 700 and 800 °C. The gas yield increased with residence time when the temperature was higher than 700 °C. When temperature was higher than 800 °C, the gas heating value decreased. In 2006, Murillo *et al.* studied the effect of temperature in waste tire pyrolysis. They found that at above 500 °C the conversion for scrap tire pyrolysis was the highest, and oil yield was higher than 40%. Similarity, Roy *et al.* (1999) studied the vacuum pyrolysis of waste tires for oil and carbon black products. They investigated the temperature of pyrolysis between 480 and 520 °C. The temperature did not affect the yield at temperature over 500 °C. And in 2004, Laresgoti *et al.* pyrolyzed tire under nitrogen environment in a 3.5 dm³ autoclave at 300, 400, 500, 600 and 700 °C. Above 500 °C, there was no effect of temperature on the gas and oil yield.

Ucar *et al.* (2005) studied two different scrap tires, passenger car tires (PCT) and the truck tires (TT), as hydrocarbon sources for pyrolysis. They concluded that:

- There was no difference in the effect of temperature on the product distribution for PCT.
- The amount of oil product of TT pyrolysis was higher than that from PCT whereas the amount of carbon black was less than that from PCT.
- The amounts of hydrocarbon gases, H₂S and CO₂ from PCT pyrolysis were higher than that from TT pyrolysis due to the different types of additives used in tire manufacture.
- The physical properties of oil from PCT and TT were similar, but the products from PCT pyrolysis had higher aromatic content and sulphur content in oil than that of TT.
- The pyrolytic oil obtained from PCT pyrolysis contained about 50% gasoline fractions whereas 40% gasoline fractions was found on the pyrolytic oil obtained from TT pyrolysis . The pyrolytic oil from the pyrolysis of TT can be blended with gasoline or diesel fuels after the upgrading whereas the pyrolytic oil from PCT can be feedstock for the production of basic aromatics in petrochemical industry.
- The carbon black from the pyrolysis of TT was better than from PCT.

2.2 Catalytic Pyrolysis

Nowadays, catalysts have an important influence in industries. They can increase productivity and control the selectivity of considered products. Moreover, they can reduce processing time and operating temperature. And, they can be easily separated from product and regenerated. In 2006, Shen *et al.* studied the pyrolysis of scrap tires using zeolite USY. They found that zeolite USY can reduce the oil yield with increasing gas yield. Furthermore, the oil yield decreased largely when the catalytic temperature and catalyst/tires ratio increased. Finally, they compared the oil product from the non-catalytic pyrolysis of scrap tire with those obtained from ZSM-5 and Y catalysts. They found that the product from USY zeolite had higher total

concentration of mono-aromatics. Bortnovsky *et al.* (2005) studied the cracking of 2-methyl-2-butene to C₂-C₄ light olefins over zeolites. They found that 10-MRP zeolites of ZSM5 and ZSM-11 with a low concentration of strong acid site (0.04 - 0.1 mmol/g) were the most active and selective catalysts for cracking of C₅ olefins to C₂-C₄ light olefins. Furthermore, the bridging hydroxyl in a high concentration of the H-(Fe)ZSM-5 and H-(Al)ZSM-5 was not sufficient to provide high pentene conversion. And, the 1-D 10-MRP zeolites (with elliptical channels), i.e. ferrierite CoAlPO-11, and SAPO-11, catalyzed the cracking of pentene via the β-scission of pentene molecules, whereas 12-MRP zeolites, i.e. mordenite and ZSM-12 with a high concentration of acid sites, exhibited rather high activity and high selectivity to C₂ - C₄ olefins. Li *et al.* (2004) studied effective factors on catalytic pyrolysis process. They obtained the keys to get high productivity which were the properties of feedstock and the types of catalyst. They also summarized that for different cracking feedstock, the light olefin yield could be increased over the same types of catalyst.

In 2006, Marcilla *et al.* studied the influence of different acid solids in the catalytic pyrolysis of different polymers. The catalysts used in pyrolysis were HZSM-5 zeolite and mesoporous aluminosilicates—MCM-41a and MCM-41b. The MCM-41b had higher acidity. They concluded the activity of acid catalysts depended on pore size, because reactant molecules can easily access to the active site located in the interior of the pores. Furthermore, another factor was acidity. The result showed that the activity of catalyst increased as the acidity increased. In 2008, Torri *et al.* studied on the pyrolytic behavior of cellulose in the presence of MCM-41 mesoporous materials. They used MCM-41 (Si-MCM-41) and Me-MCM-41 catalysts containing different metals (Al, Mg, Ti, Sn or Zr) in the catalyst/cellulose ratio of 1:3. The pyrolytic products were (2H)-furan-3-one, 2-furaldehyde, 5-methyl-2-furaldehyde, 4-hydroxy-5,6-dihydro-pyran-2-one, levoglucosenone, 1-hydroxy-3,6-dioxabicyclo[3.2.1]octan-2-one (LAC), 1,4:3,6-dianhydro-α-D-glucose and levoglucosan. They found mesostructured solids decreased the yields of levoglucosan with respect to non-loading catalysed cellulose, and increased the production of levoglucosenone and LAC. Similarly, Adam *et al.* (2005) studied the pyrolysis of biomass in the presence of Al-MCM-41 type catalysts. They found the effect of MCM-41 catalyst on the pyrolysis products of spruce wood was related to

the size of the pores of the catalyst. Pore size enlargement and transition metal incorporation reduced the yield of acetic acid and water among pyrolysis products. In 2006, Antonakou *et al.* studied Al-MCM-41 as a catalyst in biomass pyrolysis for the production of bio-fuels and chemicals. They found that the production of liquid was decreased compared to non-catalytic runs. The production of gas was comparable or lower, and the production of coke was higher. Reddy and Song (1996) studied the influence of mesoporous zeolite (MCM-41) on polycyclic aromatic conversion. They illustrated that a major advantage of mesoporous Al-MCM-41 catalyst was capable of converting very large molecules into smaller molecules. Aguado *et al.* (2006) studied the catalytic activity of zeolite and mesostructured catalysts in the cracking of pure and waste polyolefins. They found that mesostructured catalysts, Al-MCM-41 and Al-SBA-15, showed stronger aromatization and benzene alkylation capability because of their weaker Lewis acid and larger pore size, which provide larger molecules of products. In 2008, Dũng *et al.* studied the effects of ITQ-21 and ITQ-24 as zeolite additives on the catalytic pyrolytic oil using HMOR. The results were presented that, with increasing the catalyst-to-tire ratio, the gasoline and kerosene yield increased with the reduction of the heavier fractions. The concentration of the saturated hydrocarbons in the pyrolytic oil was found to be higher. Therefore, increasing the catalyst/tire ratio decreased the yield of liquid product.

2.3 The Mesoporous Silica Materials

In 1992, the mobil scientists first synthesized the Mobil Composition of Matter series as MCM-41, and MCM-48, which were the most of popular mesoporous molecular sieves. Their surface area is more than 1,000 m²/g. Furthermore, they have the pore diameter range between 1.5 to 20 nm, which depends on the condition of synthesis and a kind of surfactant used as the pore-directing agent.

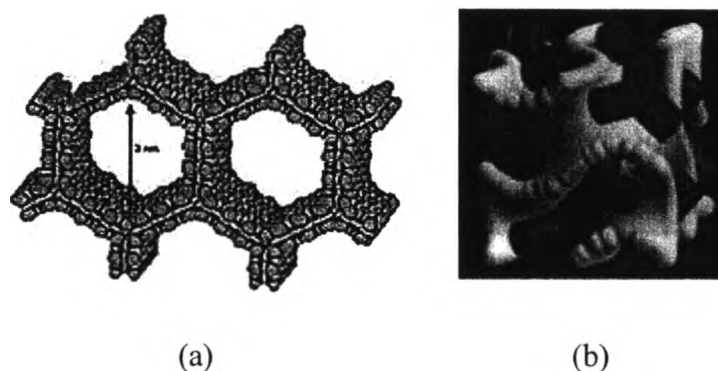


Figure 2.1 Pore structure of the Mobil composition of matter or MCM: (a) MCM-41 (1-D) and (b) MCM-48 (3-D) (http://www.chemistry.wustl.edu/research/lin_group).

The MCM-41 is a mesoporous silica material, which has one dimension hexagonal pore. The MCM-48 has three dimensional pores. They have been applied to the catalyst work as a support of heterogeneous catalysts and an adsorbent in waste water treatment. The XRD result of Jang *et al.* (2005) shows that the MCM-48 has plane 211 while the MCM-41 has plane 100 at the same 2-theta value of 2.5. It was confirmed that the MCM-41 has different structure to the MCM-48. The pore size of MCM-48 is between 1.6 nm and 3.8 nm.

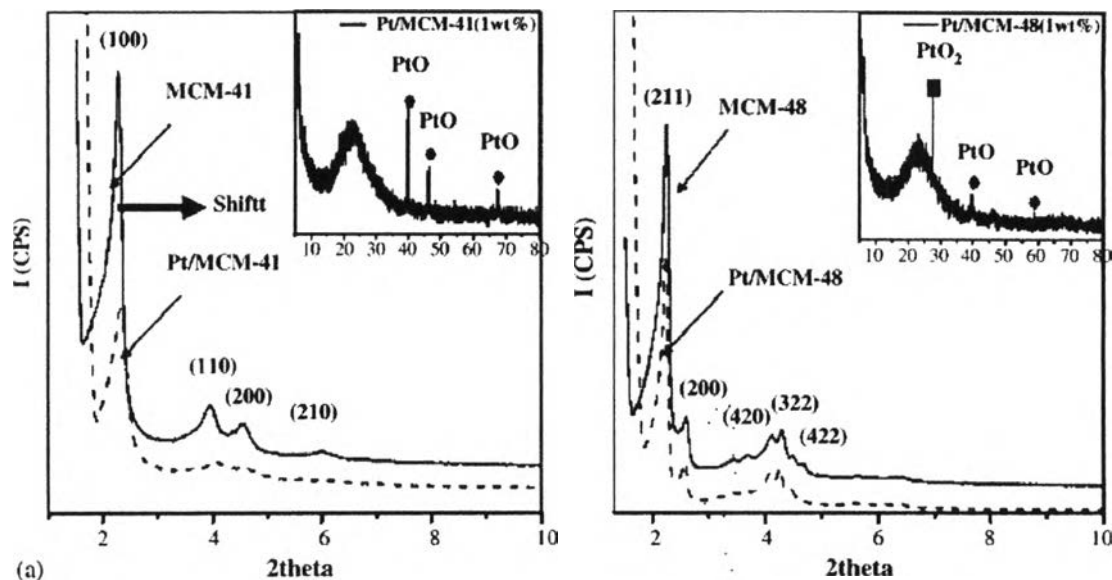


Figure 2.2 XRD results of MCM-41 and MCM-48 with and without platinum loaded (Jang *et al.*, 2005).

In 2005, Li *et al.* studied MCM-48 supported cobalt catalyst for Fischer-Tropsch synthesis. They loaded cobalt metal 5%, 10%, and, 15% on MCM-48, and found that the conversion of CO was insignificantly increased when 5% Co was used. Meanwhile, the 10% Co could reach the highest CO conversion and C5+ selectivity, but the improvement of 10% Co to 15% Co metal loaded was insignificant in CO conversion and C5+ selectivity. In addition, the MCM-41 and MCM-48 were used as supports for the selective oxidation of propane, which was studied by Peña *et al.* (2000). They found that the V-containing MCM-41 and MCM-48, which were loaded lower than 1 %wt, presented higher activity and selectivity than the SiO₂ supported catalyst. They concluded that the V-MCM catalysts had higher surface area and dispersion of vanadium than the silica-supported catalyst. Kawi and Te (1998) used MCM-48 supported chromium catalyst for trichloroethylene oxidation. Cr/MCM-48 catalysts had good catalytic activity, which was 100% conversion at 350 °C and was stable for the oxidative destruction of TCE (trichloroethylene) up to 72 hr. In addition, the Cr/MCM-48 was the catalyst which had high adsorption capacity for a destruction of TCE. Lan-Lan and Shuang (2005)

studied on phenol hydroxylation using CuO/MCM-48 as a catalyst. The CuO-containing MCM-48 had high performance for hydroxylation phenol. It exhibited higher phenol conversion than CuO and MCM-41 supported CuO. They concluded that the 3D pore structure of MCM-48 could transmit phenol better than MCM-41. In 2007, Alsobaai *et al.* used MCM-48 for coating USY in order to hydrocrack petroleum gas oil. The appropriate ratio of hydrocracking was 0.5 because it was attributed to good balance between the acidity of USY and the high pore size of MCM-48. Furthermore, the nickel and tungsten-containing composite materials of USY-MCM-48 improved higher hydrocracking activity than USY-MCM-48.

2.4 Supported Ruthenium Catalysts

In 2009, Dũng *et al.* investigated light olefin and light oil production from the catalytic pyrolysis of waste tire. They found that Ru/MCM-41 was the good catalyst for production light olefins in the gas product and high concentration mono-aromatic compounds in the oil product. Similarly, Choosuton *et al.*, (2007) studied that the effect of noble metals and supports in waste tire pyrolysis. They reported that Ru/HMOR can produce the high amount light of olefins and gas yield. And in 2008, Kongkadee *et al.* investigated the effect of Ru on HMOR and Ru on HZSM-5 on tire pyrolysis products. They presented the Ru on HMOR produced the high yield of gas product because of its high acidity for cracking. So, light olefin can be produced by Ru/HMOR.

Dũng *et al.*, (2010) studied the role of ruthenium on the catalytic pyrolysis of waste tire by using Ru supported SBA-1. They reported that ruthenium clusters increased the gas yield by approximately twice as much as compared to non-catalytic pyrolysis, and decreased poly and polar-aromatic compounds because lighter oil was produced. In addition, SBA-1 itself did not have the effect on the pyrolysis product. In 2008, Basagiannis *et al.* studied the influence of the carrier on the steam reforming of acetic acid over Ru-based catalysts. They found that Ru can help increase catalytic activity to shift toward lower temperatures process and high rates hydrogen production. In 1999, Akhmedov and Al-Khowaiter studied the hydroconversion of hydrocarbons over Ru-containing supported catalysts. The result of Ru-Re/ZSM-5

showed high selectivity in the isomerization of *n*-hexane to 2- and 3-methylpentanes, while Ni–Ru/ZSM-5 ruptured mostly the central carbon–carbon bond in the *n*-heptane molecule. The rates of hydroconversion of tested hydrocarbons for the bimetallic samples were much higher than over Ru/ZSM-5.

It can be concluded that Ru supported catalysts are good catalysts to produce light olefins (ethylene and propylene) and light products. Light olefins can be used to be used as petrochemical feedstock for producing polyethylene and polypropylene. Recently, Sritana (2010) studied the development of Ru-supported HMOR catalyst as an industrial catalyst for the production of light olefins from waste tire. It is a selective catalyst for producing light olefins because Ru/HMOR has high cracking and isomerization activities. It is composed of Ru/HMOR, clay (a matrix), and α -alumina (a binder). Furthermore, the matrix can induce heat transfer from active catalyst to prevent hot spots and over-cracking.

2.5 The Applications of Clay Minerals

Nowadays, clays have important roles in industrial catalysts because the matrix or clay can induce heat that causes hot spots. It causes over-cracking preventing undesirable products. Many pieces of research used clay minerals mixed as a catalyst matrix in catalytic pyrolysis. In 2002, Rong and Xiao studied the catalytic cracking activity of kaolin. They found that the kaolin-group minerals were: halloysite 24.3%, kaolinite 13.4%, and dickite 0%. The tested of samples property are in Table 2.

Table 2.1 The properties of the purified sample clays (Rong and Xiao, 2002)

Sample	Purified K1	Purified K2	Purified K3
Mineral composition	halloysite	kaolinite (70%), halloysite (30%)	dickite
SiO ₂ (wt.%)	46.76	46.54	46.80
Al ₂ O ₃ (wt.%)	39.12	39.54	39.67
Specific surface area (m ² g ⁻¹)	89.4	41.1	9.0
Specific surface area (calcined at 800 °C) (m ² g ⁻¹)	61.9	24.3	7.0
Retention of Specific surface area (%)	69.18	59.12	77.78
Micro-reaction activity (%)	24	13.4	0

In 1995, Xiao *et al.* investigated catalytic cracking activity and the physicochemical properties of REY zeolite mixed with kaolin clay treated by hydrothermal hot pressing (HHP) method. They found the catalytic conversion and selectivity in the cracking of pentadecane and heavy oil in a series of samples treated at different temperature (25 - 220 °C) changed significantly. In particular, the catalyst treated by HHP at 170 °C showed high catalytic activity and selectivity for gasoline, low coke formation, and high compressive strength when compared with non HHP treatment. Moreover, X-ray diffraction exhibited the stability of active REY zeolite in HHP catalysts, but above 220 °C a part of REY zeolite lost its crystalline structure.

Swarmakar *et al.* (1996) studied the catalytic activity of Ti- and Al-pillared montmorillonite and beidellite for cumene cracking and hydrocracking. The beidellite showed higher cracking than montmorillonite. The clay layers themselves also showed differences in selectivity. Beidellite had ability to crack cumene to benzene whereas montmorillonite was good cracking to α -methylstyrene (dehydrogenation). Similarly, Pan *et al.* (2010) studied that the effect of calcite and montmorillonite on oil cracking in confined pyrolysis experiments. The main observations were: (1) i-C₄/n-C₄ and i-C₅/n-C₅ in oil with montmorillonite was higher than only oil and oil with calcite, and (2) montmorillonite and calcite greatly reduced the carbon isotope fractionation during methane formation from oil cracking.

In general, a catalyst which is used for cracking is composed of 0-70% of clay, 5-99% of inorganic oxide, and 1-50% of zeolite. The zeolite is a mixture of 0-

25 wt% of Y zeolite and 75-100% of phosphorus (P_2O_5) and rare earth (Re_2O_3) (Zhicheng *et al.*, 1993). Similarly in 1980, Alafandi and Stamires have owned a patent of producing zeolitic catalysts with silica alumina matrix. Their catalysts were composed of the exchanged zeolite in the range of about 10 to 30 parts by weight, alumina 10 to 25 parts by weight, if alumina used as matrix, and silica-alumina gel 60 to 10 parts by weight, and clay 70 parts by weight. The clays were acid treated halloysite, ball clay, other kaolin and mixture thereof.

In 1971, Silverstein patented the method for inhibiting the spread of heat utilizing bentonite. They found that bentonite can inhibit heat spread for ring soldering work, orthodontic retainer soldering work and two pieces of metal welding work. So, bentonite acts as a water curtain to absorb the heat. In 1988, Gummow and Sigalas investigated that the thermal conductivity of talc as a function of pressure and temperature. The thermal conductivity for both fired and unfired talc showed a slight increase with pressure. Furthermore, the thermal conductivity of the fired was lower than the unfired.

From the several research works, the most interesting issue is the development of Ru/HMOR and Ru/MCM-48 as industrial catalysts for producing light olefins from waste tire. With the fact that the matrix can spread heat from active component, and can prevent over-cracking, the catalysts therefore consist of Ru/HMOR or Ru/MCM-48, clay, and α -alumina. In this work, the optimum composition of modified catalysts and the effect of type of matrix was investigated for the production of light olefins from waste tire pyrolysis.

The objective of this research work was to find the optimum composition of a being-developed commercial Ru/HMOR and Ru/MCM-48 catalysts. After that, the effect of types of matrix, and the composition of the catalysts on the nature product were studied with the aim for the production of light olefins.

The scope of this research covered:

- The pyrolysis of scrap tire was performed in a bench-scaled autoclave reactor.
- Holding time, N_2 flow rate, the pyrolysis temperature, the catalytic temperature, heating rate, the amount of Ru loading, the amount of sample

and catalysts were fixed to at 90 min, 30 ml/min, 500°C, 300°C , 10 °C/ min, 0.7 %wt, 30 g, and 7.5 g, respectively.

- The experiment was divided into 2 parts;

Part I: The optimum composition of catalysts was determined by varying %wt of HMOR zeolite and MCM-48 mesoporous. The binder was α -alumina, which was fixed at 10%wt. The matrix was kaolin. The ratio of active component and matrix was varied as 5:85, 10:80, 15:75, 20:70, and 100:0 (active component only).

Components	%wt				
Batch No.	1	2	3	4	5
Ru/HMOR	5	10	15	20	100
Kaolin	85	80	75	70	0
Binder (α-alumina)	10	10	10	10	0

Components	%wt				
Batch No.	6	7	8	9	10
Ru/MCM-48	5	10	15	20	100
Kaolin	85	80	75	70	0
Binder (α-alumina)	10	10	10	10	0

Part II: The ratio of active component and matrix was fixed, and the types of matrix were kaolin, bentonite, talcum, and montmorillonite.

Batch No.	%Ru/HMOR	%Kaolin	%Bentonite	%Talcum	%Montmorillonite	%Binder (α-alumina)
1	0	100	0	0	0	0
2	0	0	100	0	0	0
3	0	0	0	100	0	0
4	0	0	0	0	100	0
5	5	0	85	0	0	10
6	5	0	0	85	0	10
7	5	0	0	0	85	10