



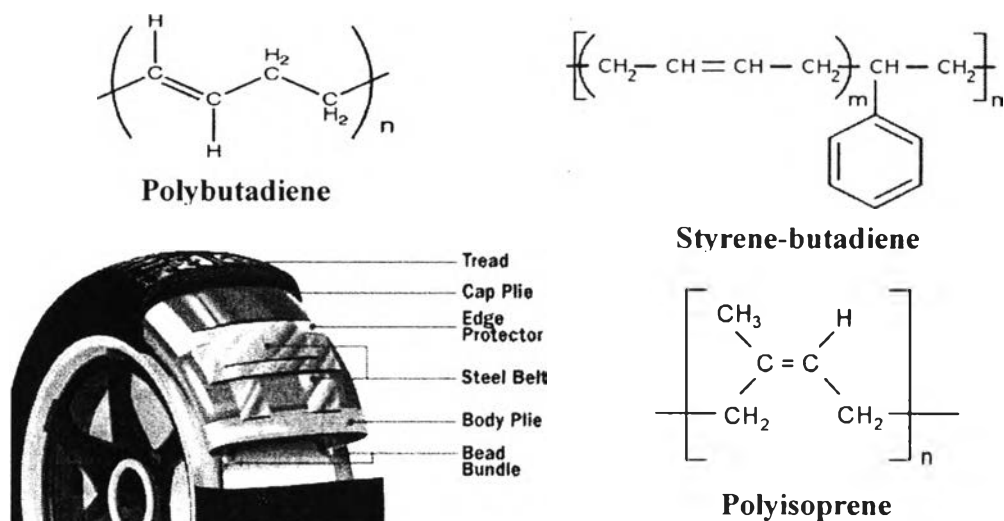
## CHAPTER II

### THEORETICAL BACKGROUND AND LITERATURE REVIEW

#### 2.1 Tire

Tire is used as moving and controlling parts for many vehicles. The pressurized air inside the tire acts as a cushion to absorb shocks. Types of tire depend on the applications and the structures of tire. The components of tire are shown in Figure 1.

One of tire materials is rubber, which consists of natural rubber (isoprene rubber), and synthesis rubber (styrene butadiene rubber, butadiene rubber, isobutene isoprene rubber etc.). The chemicals which are added into tire are vulcanizing agent, reinforcing agent, antioxidant, accelerator, and so on. Other tire materials are carbon black, nylon, polyester and steel wire. Rubbers and all chemical are blended through the vulcanization process by using sulfur as a vulcanizing agent. The chains of polymer are cross-linked together to produce a macromolecule. Moreover, carbon black is added as a reinforcing agent for tire. As a result, the overall properties of rubber become dramatically enhanced; for example, it has a higher tensile strength and durability.



**Figure 2.1** Components and main rubber compositions in tire (<http://express.howstuffworks.com/gif/tires-cutaway.jpg>).

Nowadays, according to the rapidly growth of the automotive sector, the waste tire disposal capacity is massively increased. Waste tire disposal may cause various kinds of environmental problems. For example, waste tire may hold water inside for long times, which becomes a breeding ground for mosquitoes. Moreover, burning tire produces air pollutions including the toxic gases which cause health hazards such as CO, SO<sub>2</sub>, NO<sub>2</sub>, and HCl.

## 2.2 KL Zeolite

KL zeolite is a non-acidic synthetic zeolite, and its composition is K<sub>9</sub>Al<sub>9</sub>Si<sub>27</sub>O<sub>72</sub> (Sato *et al.*, 1999). The structure consists of one-dimensional pore structure, which is connected by the channels of 12 membered rings, leading to the cavities of about 0.48 nm × 1.24 nm × 1.07 nm with 0.71 apertures (Satterfield, 1991). KL zeolite acts like an electron donor, and increases the electron density on the metal cluster (Stakheev and Shpivo, 1995). The structure of KL zeolite is shown in Figure 2. The most uses of KL zeolite are the catalyst and catalyst support for aromatization (Norberg *et al.*, 2000). Choosuton (2007) studied KL zeolite as a catalyst in the pyrolysis of tire for improving the pyrolysis products. Asphaltene in oil production drastically reduced with using KL zeolite because the complex molecules of asphaltene were cracked on the active site of catalyst. Moreover, KL zeolite was a good catalyst for gasoline production, but not for kerosene as a result of high aromatic contents distributed in the gasoline range. Therefore, the octane number should be highly improved using KL zeolite.

In 2003, Jongpatiwat *et al.* investigated the aromatization of n-octane on a Pt/KL catalyst. The results showed that ethylbenzene and ortho-xylene were produced inside the channels of the zeolite and then hydrogenolyzed to benzene and toluene as the dominant aromatic compounds. Trakarnroek *et al.* (2006) studied n-octane aromatization over Pt supported by varying the morphology and channel length of KL zeolite. They investigated four different KL zeolite morphologies: hockey puck (HOP), cylinder (CYL), long cylinder (LCYL), clam-like shape (CLAM), and nanocrystal (NCL). NCL was the small crystal size and short length, which was inappropriate for the secondary cracking reaction. Therefore, NCL showed

the highest selectivity of C8-aromatic products. HOP was a very flat cylindrical, while CYL and LCYL had a longer channel length. Therefore, CYL and LCYL had the long residence time of C8-aromatic products inside the zeolite, and produced the higher benzene and smaller molecules than HOP. Even though, the dispersion of Pt was high on CLAM and HOP shapes, but the 1%Pt/HOP exhibited the higher selectivity to C8-aromatics than 1%/CLAM.



**Figure 2.2** Structure of KL ([www.chemistry.nus.edu.sg](http://www.chemistry.nus.edu.sg)).

### 2.3 Pyrolysis

The definition of pyrolysis is the thermal degradation in the absence of oxygen. In pyrolysis, the macromolecules of a material are broken down by heat at a high temperature. Pyrolysis products contain gas fraction, liquid fraction, and solid residue. As an example, gaseous products are methane, ethane, propane, propene, butane and other light hydrocarbons. Oil products from pyrolysis are important for chemical feed stock as well as an octane booster of gasoline (Banallal *et al.*, 1995). Examples of oil products are light aromatic, poly-aromatic, polar-aromatic compounds, and especially benzene, toluene and xylenes.

Char or carbon black from pyrolysis has very low quality, which is improved to higher grade such as carbon black or activated carbon. Pyrolysis is developed and improved in the recycling technology for the degradation of a waste plastic into commercial fuels. Main types of pyrolysis process are shown in the following part.

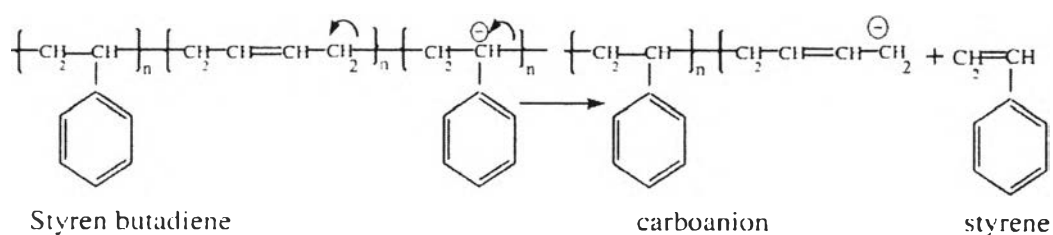
### 2.3.1 Thermal Cracking

Thermal cracking is used in many industries to crack the raw material into the desired products. This type of process is a heat sensitive operation, which means the compositions of the products are significantly affected by the pyrolysis temperatures (Scheirs and Kaminsky, 2006). The pyrolysis at low temperature promotes the oil fractions, whereas the gas fractions are increased with increasing temperatures. However, not only temperatures but also other parameters such as residence time and feed type are the significant factors, which determine the products. The products from this process are widely distributed, and have low costs.

### 2.3.2 Catalytic Cracking

Cracking with using a catalyst has been used for a long time. Catalyst can improve the operation conditions, which lead to decrease the energy consumptions; for example, it reduces residence time, and reduces the reaction temperature (Scheirs and Kaminsky, 2006). In addition, the catalytic process can increase the desired products and product quality, when it is compared with thermal cracking.

The catalytic pyrolysis using a base catalyst can break up large hydrocarbon molecules into smaller ones via anionic intermediates called carboanions (carbanions) (Jan *et al.*, 2010) as shown in Figure 2.3.



**Figure 2.3** Catalytic pyrolysis of styrene butadiene rubber via carboanions (Jan *et al.*, 2010).

This reaction starts with the abstraction of  $\text{H}^+$  from the reactant on a solid base to form carboanions. Electrons or electron pairs of anionic species can donate sites on the surface, and the reaction proceeds by a self-propagating chain

mechanism. Finally, the reaction is terminated by the combination of free radicals. Jan and co-workers studied the thermal pyrolysis and the catalytic pyrolysis of a used isobutyl isoprene rubber. The studied base catalyst in this experiment was zinc oxide. The results showed that the catalytic pyrolysis of the used isobutyl isoprene rubber gave the maximum conversion into useful products, whereas thermal pyrolysis showed the less conversion and the temperature needed was higher. The pyrolysis product consisted of the complex mixture of alkanes, alkenes, carbonyl group, and aromatic products such as benzene, toluene, xylene etc.

## 2.4 Pyrolysis of Waste Tire

The pyrolysis of waste tires has undergone many kinds of research, which is aimed to produce new energy sources. The pyrolysis conditions of waste tire have been studied for a long time for the optimum conditions and optimum products in each interested condition. The influence of operating temperature was investigated by Shen *et al.* (2006). They studied the pyrolysis of scrap tire in a fixed bed reactor with the continuous purge of nitrogen. They found that the yields of gas, oil and char were slightly different while the pyrolysis temperature was changed from 450 °C to 600 °C. The results revealed that the oil yield still showed the maximum percent weight value whereas the amount of char and gaseous product showed the low values, respectively.

Galvagno *et al.* (2002) studied the influence of the reaction temperatures between 550 °C to 680 °C. They found that the increasing temperatures promoted the gas productions such as CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and C<sub>2</sub>H<sub>4</sub>. Similarly, Berrueco *et al.* (2005) studied the pyrolysis of scrap tires at temperatures from 400 °C to 700 °C. The results showed that the sample conversion increased with increasing process temperatures. The temperatures from 400 °C to 500 °C promoted the liquid productions, whilst the gas productions were promoted with the increasing temperatures. The secondary cracking reaction was promoted with temperature higher than 500 °C. Moreover, high temperature promoted the light gas products such as CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>3</sub>H<sub>6</sub>.

In 2009, Dũng *et al.* studied the effect of pyrolysis temperature polar-aromatic content in the oil product. They found that the increasing pyrolysis temperature led to the higher amount of polar-aromatic and heavier polar-aromatic compounds, while the gas yields were decreased. Similarly, Cunliffe *et al.* (1998) reported the aromatic contents of oils were increased with the temperature increase whereas the aliphatic hydrocarbon decreased. Barbooti *et al.* (2004) studied the pyrolysis of scrap tires under nitrogen atmosphere in a fixed-bed batch reactor. They studied the effects of pyrolysis temperatures (400 °C to 460 °C) and the particle sizes of scrap tires (2 mm to 20 mm). The result showed that the thermal degradation was incomplete in the large particle sizes (16 mm to 20 mm) compared with the small particle sizes (2 mm to 10 mm). Moreover, the oil yields were decreased with the increase temperatures.

The effects of catalysts in the pyrolysis of waste tire were studied for decades. Arabiourrutia *et al.* (2008) investigated the effects of HZSM-5 and HY zeolite catalysts in pyrolysis of tires with the influence of temperatures between 425 °C and 500 °C. The HZSM-5 zeolite exhibited the activity for cracking reaction and the selectivity for producing propene, propylene, butane, and butadiene productions. On the other hand, HY zeolite promoted the condensation to produce the heavier components. Williams *et al.* (2002) studied the effect of silica/alumina ratio and pore size on ZSM-5 and Y zeolites. The report showed that Y zeolite had lower silica/alumina ratio than ZSM-5 zeolite due to an increase in the surface acidity by increasing the surface concentration of alumina. Thus, the amounts of aromatic compounds (benzene, toluene, and xylene) were found in the Y zeolite case more than the ZSM-5 zeolite case. The difference of pore size of zeolite provided the product selectivity. The small pore size showed the size and shape selectivity of hydrocarbon which passed through the pore for cracking; that is, the formation of the aromatic hydrocarbon increased in HZSM-5. Similarly, Williams *et al.* (2003) showed the influence selectivity of the different silica/alumina ratio of zeolite. They reported that the Y zeolite with the low silica/alumina ratio had high surface activity. Therefore, the high aromatic hydrocarbon content in oil was produced by using Y zeolite. In 2006, Shen *et al.* studied the influence of USY zeolite on the product yield. The results showed that the presence of USY catalyst reduced the oil yield with an increase of gas yield.

Likewise, the higher catalyst/tire ratio and the catalytic temperature also enhanced the gaseous products.

Choosuton (2007) studied the effect of zeolites and bifunctional catalysts on waste tire pyrolysis. Three metals (Pt, Pd, and Ru) and four zeolites (beta, USY, HMOR, and KL) were used to improve the product quality in the pyrolysis process. All catalysts produced the higher quality of gasoline and kerosene than a zeolite alone and than non-catalytic case. Moreover, polyaromatics in the oil products were reduced by 50%wt to 70 wt%. In addition, Phopaisarn (2010) studied the influence of platinum loaded on different zeolites (KL and Y zeolites). The results showed that Pt/Y had higher hydrocracking activity and produced higher cooking gas, light olefins and naphtha production, whereas Pt/KL zeolite exhibited higher dehydrocyclization activity in producing the total aromatic hydrocarbons.

## 2.5. Metal Supported on Zeolites

### 2.5.1 Molybdenum Supported on Zeolites

The dehydro-oligomerization of methane to ethylene and aromatics over molybdenum/HZSM-5 catalysts had been studied by Chen *et al.* (1995). The results indicated that the calcined form of molybdenum at 2-3wt% over HZSM-5 exhibited the optimum activity for the dehydro-oligomerization of methane to aromatics. Moreover, they suggested that ethylene was a primary product while benzene was a final product in the reaction. Moreover, they found that pure molybdenum trioxide showed no activity for the methane conversion, while molybdenum oxide loaded on HZSM-5 significantly improved the conversion of methane. In 1997, Wang *et al.* studied the methane dehydrogenation and aromatization in the absence of oxygen over molybdenum loaded HZSM-5 catalyst. They found that the maximum of methane conversion was around 7%, whereas the selectivity to benzene was around 70% at high reaction temperatures of 700 °C – 800 °C. Molybdenum carbide ( $\text{Mo}_2\text{C}$ ) was formed as the active species over Mo/HZSM-5 which the  $\text{CH}_4$  reactant reduced the original  $\text{Mo}^{6+}$  ion in zeolite to  $\text{Mo}_2\text{C}$ . The carbide was the active species for the activation of methane and the formation of ethylene as the primary reaction intermediate to produce benzene. Similarly, Zhang *et al.* (1998) reported the influ-

ence of molybdenum on ZSM-5 zeolite for the non-oxidative conversion of methane to benzene. The results showed that molybdenum migrated into the zeolite pore during the catalyst calcination at high temperatures, and it was converted to  $\text{Mo}_2\text{C}$  under reaction condition. The presence of  $\text{Mo}_2\text{C}$  showed the conversion of  $\text{CH}_4$  to benzene, while unsupported  $\text{Mo}_2\text{C}$  gave low conversion. Only  $\text{Mo}_2\text{C}$  mixed with HZSM-5 was active for methane conversion to ethylene and benzene, while the methane conversion on unsupported  $\text{Mo}_2\text{C}$  gave low conversion of  $\text{CH}_4$ . Moreover, benzene was not found in product yields.

Anunziata *et al.* (1999) also studied the transformation of ethane into aromatic hydrocarbons with molybdenum supported on ZSM-11 zeolite. They found that the molybdenum supported ZSM-11 zeolite showed the high activity for the ethane conversion as well as the selectivity to aromatics. After molybdenum loading, the amount of Bronsted site also decreased, and new stronger Lewis-acidic sites were created in Mo/ZSM-11 that allowed the dehydrogenation of ethane to ethylene. Ethylene was an unstable primary product; thus, the aromatic products were formed as stable secondary products, especially benzene, toluene and xylenes. Xu *et al.* (1995) investigated the dehydrogenation and aromatization of methane in the different percentages of molybdenum loading over HZSM-5 zeolite (1 wt% to 10 wt%), which the calcinations and reaction temperatures were 973 K. The results showed that 2%Mo/HZSM-5 exhibited the maximum methane conversion and the highest selectivity to benzene around 90 %. The channels and the surface area of zeolite were decreased with increasing the Mo loading. The possible mechanism for aromatic products occurs via the interaction between methane and  $\text{MoO}_3$  species in the channel of HZSM-5 zeolite to form polarized methane. The polarized molecule of methane reacts with the Bronsted acid site of HZSM-5 zeolite, and provides to the formation of molybdenum carbene-like species;  $\text{CH}_2=\text{MoO}_3$ . These species is transformed via the dimerization to produce ethylene as a primary product; then, ethane aromatization is occurred on HZSM-5 zeolite to produce mono-aromatics like benzene and methyl benzene. The increment of Mo loading showed the aggregation of Mo, which might block up the channels of catalyst. As a result, the channels and the surface area of zeolite were decreased, which led to the reduction of catalyst activity.



Shu *et al.* (1997) also improved the dehydrogenation and aromatization of methane by using Ru-promoted Mo/HZSM-5 catalysts. They found that the better reaction rate of methane conversion and a better formation rate of aromatic could be promoted by the influence of 2Mo-Ru/HZSM-5 catalyst. The strong acid sites decreased with amount of Ru loading, whereas the amount of medium and weak acid site increased with the selectivity for methane aromatization.

### 2.5.2 Rhenium Supported on Zeolites

Rhenium catalyst has the high resistance to a catalyst poison such as sulfur, nitrogen, and phosphorus (Brot, 2009). Rhenium with ZSM-5 as a support has been considered for the conversion of ethane into benzene (Solmosi and Tolmacsov, 2004). The weight percentages of Re loading were 2, 5, and 10 wt%. The results showed that 2%wt of Re loading produced the high selectivity and yield of benzene, whereas the high amount of Re loading at 5-10 wt% did not result in the further improvement of the catalyst. Rhenium has a high activity of hydrogenolysis. In 1983, Burch and Mitchell studied Re supported on  $\text{Al}_2\text{O}_3$  catalysts, consisting of 0.3 wt% of Re loading, on the activity and selectivity for the reaction of cyclopentadiene at 750 K and atmosphere pressure. They found that Re showed the high activities for the hydrogenolysis and then the ring-opening of cyclopentane. The selectivity for C1-C5 paraffins was 74.9%. Similarly, Carter *et al.* (1982) studied the rhenium on alumina catalysts with 0.3 wt% of Re loading on the methylcyclopentane conversion. The results showed that 0.3 wt%  $\text{Re}/\text{Al}_2\text{O}_3$  catalyst had the high hydrogenolysis activity, and the selectivity to C1-C6 alkanes was 84 wt%. The  $\text{Re}/\text{Al}_2\text{O}_3$  catalysts did not have the hydrogenolysis activity below 425 °C (Jothimurugesat *et al.*, 1985).

Re is considered to increase the hydrogen concentration on surface, and it could remove the coke deposited on catalysts by hydrogenation (Xiao *et al.*, 1995). The bimetallic catalyst, Pt-Re/ $\text{Al}_2\text{O}_3$ -Cl, is the most used catalyst for naphtha reforming. The presence of rhenium could decrease coke deposited on the catalyst and then increase gas products (Pieck *et al.*, 1995). Moreover, the platinum-rhenium mixed metal showed the significant improvement in the lifetime and selectivity for aromatics products. It has been most used as a reforming catalyst for aromatic productions (Xiao *et al.*, 1995). Rhenium-containing catalysts are used for hydrocarbon

transition to upgrade product yields. Krogh *et al.* (2003) studied the bifunctional catalysts, 5.7 wt% Re and 2.2 wt% Zn impregnated on HZSM-5 for ethane aromatization. They found that the differences in the deactivation of both zeolites were caused by the different coke deposited on the zeolite. Re supported on HZSM-5 showed the slower deactivation of the catalyst, and the spent Re/HZSM-5 catalyst contained less coke than Zn/HZSM-5 catalyst. Re/HZSM-5 and Zn/HZSM-5 showed the same initial aromatic selectivity. After that the aromatic selectivity of Zn/HZSM-5 catalysts decreased rapidly with time, while the selectivity of ethylene also increased fast. Re/HZSM-5 exhibited the less deactivation of acid sites than Zn/HZSM-5; thus, the aromatic selectivity was higher than Zn/HZSM-5.

The influences of rhenium supported on HZSM-5 catalyst in the hydrogenation of cyclohexene (CHE) compared with other metals, platinum (Pt), palladium (Pd) or iridium (Ir), were practically studied by Aboul-Gheit *et al.* (2005). The result showed that Pt/HZSM-5 and Pd/HZSM-5 were the most active for hydrogenation and dehydrogenation. Re/HZSM-5 acted as an inactive catalyst on the hydroconversions of CHE, whereas the bimetallic combination of Pd, Ir or Re with platinum supported on HZSM-5 catalyst enhanced the hydrogenation activity and reduced the temperature of hydrogenation of cyclohexene to cyclohexane compared with only rhenium supported on HZSM-5 (Aboul-Gheit *et al.*, 2005). Moreover, PtRe/HZSM-5 produced the lowest amounts of benzene but the highest toluene and xylenes amounts, while PdPt/HZSM-5 produced the highest amount of benzene but the lowest toluene and xylene ones. The catalytic dehydrogenation of methane was improved by using HMCM-22 and HZSM-5 supported rhenium and molybdenum catalyst (Shu *et al.*, 2003). The results showed that HMCM-22 supported catalysts had more space for the carbonaceous deposition because of the large cavities, and could pass less bulky product because of more elliptic or more slit-like pore opening than HZSM-5. Thereby, HMCM-22 catalyst was supported with rhenium and molybdenum more than HZSM-5 catalyst. The dehydrogenation and aromatization of propane were studied by Gao *et al.* (2005). They studied the effects of Re/HZSM-5 and Ga/HZSM-5 on the influence of reaction temperatures from 623 K to 923 K and the additions of CO<sub>2</sub> and CH<sub>4</sub> on the catalytic activity. The report showed that the dehydrogenation and aromatization of propane in Re/HZSM-5 exhibited the higher activi-

ties than Ga/HZSM-5. Products from the conversion were methane, ethene, propene, butane, butane, and aromatics such as benzene, toluene, and xylenes. The effects of reaction temperatures showed that Re/HZSM-5 enhanced the selectivity for methane, ethene and benzene with the increasing temperature. The propane transformation and the selectivity to aromatics were inhibited with the addition of CO<sub>2</sub> in feed stream. In contrast, the addition of CH<sub>4</sub> improved the conversion of propane to the aromatic productions.

From several research works, KL zeolite showed the high activity and selectivity in producing aromatic hydrocarbon (Bécue *et al.*, 1999). Similarly, Re and Mo supported on zeolite promoted the dehydrogenation and aromatization of light molecules such as methane and ethane to the aromatic products (Gao *et al.*, 2005), while 2%Mo supported on zeolite enhanced the conversion and selectivity of light molecule to benzene, toluene, and xylenes (Anunziata *et al.*, 1999). As a result, light molecules from cracking reaction in the pyrolysis of waste tire might be converted to aromatic products such as benzene, toluene, and xylenes with the influence of Re and Mo supported on KL zeolite.

The objectives of the research work were to investigate the optimum amount of Re and MoO<sub>3</sub> supported on KL zeolite and to study the effect of supported catalysts, %Re-1%MoO<sub>3</sub>/KL, on the quality and quantity of waste tire pyrolysis products. The scope of this research was divided into two parts. First part was on the individually-loaded catalysts (Re and MoO<sub>3</sub> supported on KL zeolite) and the second part was on the co-loaded catalysts (%Re-1%MoO<sub>3</sub> supported on KL zeolite), which are shown in Table 2.1.

This research work focused on varying the low amount of Re loading at 0.25 to 1 wt% on the effect of waste tire pyrolysis. According to the above literature review, the low amounts of Re loaded on a zeolite not only showed the high hydrogenolysis activity, but also had an economic benefit due to the expensive cost of rhenium precursor. The Re loaded on KL zeolite was aimed convert the heavy molecules of tire to lighter products via hydrogenolysis. In addition, MoO<sub>3</sub> loaded on zeolite was proven to have the high activity on the dehydrogenation and aromatization of light gas to aromatics products, especially mono-aromatics. Since many research works showed that MoO<sub>3</sub>-loaded zeolites had the high activity at as low as 2wt% of

MoO<sub>3</sub> loading, in this work, MoO<sub>3</sub> loading was varied at 1 to 10 wt% with the expectation that the light gas products can be dehydrogenated and aromatized to mono-aromatics in this range of loading. Moreover, the mono-aromatic can possibly be promoted from KL zeolite, which is usually used as a catalyst support for aromatization.

In this work, the varied percentage of co-loaded catalysts (wt%Re-1%MoO<sub>3</sub>/KL) corresponded to those of individually loaded catalysts. Therefore, the co-loaded catalysts with the varied Re loading (0.25 to 1 wt%) at a fixed 1% of MoO<sub>3</sub> loading were selected for the study the quality and quantity of pyrolysis products, especially on the production of mono-aromatic hydrocarbons.

**Table 2.1** Experimental designs in this research

<b>Individually-loaded catalysts</b>		<b>Co-loaded catalysts</b>
wt% MoO <sub>3</sub> /KL	wt% Re/KL	wt% Re-1%MoO <sub>3</sub> /KL
1%MoO <sub>3</sub> /KL	0.25%Re/KL	0.25%Re-1%MoO <sub>3</sub> /KL
2%MoO <sub>3</sub> /KL	0.50%Re/KL	0.50%Re-1%MoO <sub>3</sub> /KL
3%MoO <sub>3</sub> /KL	0.75%Re/KL	0.75%Re-1%MoO <sub>3</sub> /KL
5%MoO <sub>3</sub> /KL	1%Re/KL	1%Re-1%MoO <sub>3</sub> /KL
10%MoO <sub>3</sub> /KL		