# CHAPTER II
# THEORETICAL BACKGROUND AND LITERATURE REVIEW

Nowadays, the annual world energy demand is continuously increasing, while the quantity of crude oil is decreasing in the next century, which originates the diminution of crude oil reserves. In order to deal with the increased energy demand, unconventional hydrocarbon sources such as oil shale, tar sands, heavy crude and natural gas, and alternative energy sources are adopted to compensate oil supplies and fulfill future energy needs (Roger, 1997). Pyrolysis is one of the interesting alternative ways to solve the problem, and it is widely used for worthy utilizing some valueless wastes such as plastics and tires, owing to their chemical compositions. For pyrolysis of waste tire, due to vulcanization, the sulfur contents in tire-derived oils become the most troublesome problem. Desulfurization is a potential mean to remove sulfur from the tire-derived oils, as similar as the conventional desulfurization process in petroleum refinery.

Due to considerably-decreasing conventional petroleum reserve, heavier crude needs to be worthily used; therefore, the heteroatom compounds of sulfur, oxygen, nitrogen, and aromatics become serious task for producing the high quality of liquid fuels. Besides oil qualities, the environmental regulations become more stringent, aiming to reduce sulfur emissions from combustion of oil products. Low level sulfur contents are required to meet with oil specification. For high quality transportation fuels, especially diesel, the sulfur contents are required to reduce to 15 ppm, which is the maximum of an ultra-low level (data from MSDS of ultra-low sulfur diesel).

## 2.1 Sulfur removal technologies for liquid fuels

There are many sulfur removal technologies such as extraction, oxidation, adsorption, and hydrodesulfurization, required for reducing sulfur content. These technologies have different driving forces to handle sulfur removal differently. The incorporation of non-hydrodesulfurization with hydrodesulfurization, can help reduce hydrogen consumption required for the hydrodesulfurization process (Rang *et al.*, 2006). A liquid-liquid extraction such as Merox process has been used for removing mercaptans by using a caustic solution at very mild conditions (Sullivan, 2004). Oxidative catalysts such as Mn and Co oxide/$\gamma$-Al$_2$O$_3$ catalysts can oxidize thiophenes to sulfones at 130-200 $^{\circ}$C (Sampanthar *et al.*, 2006). Adsorption mechanisms of thiophene on Cu(I)-supported HY-Al$_2$O$_3$ were reported by Tang and Shi (2011). Adsorptive desulfurization requires ambient condition; therefore, the light feed was used in their study. The best results were observed on using the HY/Al$_2$O$_3$ ratio of 3 because it balances between Brønsted site of HY and total acid site of Al$_2$O$_3$, resulting in good enough for adsorption and desorption of thiophene. 12% Cu(I) loading has more weak Lewis acid than strong Lewis acid that is related to the $\pi$-complexation reaction between Cu$^+$ and thiophene ring $\pi$-electron. Cu(I)/HY-Al$_2$O$_3$ calcined at 550 $^{\circ}$C had higher specific surface area with suitable pore structure than other temperatures. They concluded that the adsorptive desulfurization resulted from total weak Lewis acidity, and the adsorption of thiophene on Cu(I)/HY-Al$_2$O$_3$ could occur via $\pi$-complexation and sulfur-adsorbent bonds. Another verifiable result was reported by Pang *et al.* (2007). They studied the sulfur removal of atmospheric residue by taking advantages of the synergy of Brønsted and Lewis acid. Lewis acidity of Zn, V and Cu was compared, and the results showed that adsorption and conversion of thiophene molecules were benefited by a prominent increase of weak Lewis acidity due to vanadium. Therefore, they combined vanadium with rare earth-exchanged USY zeolite in order to enlarge the cracking ability of acidic protons (hydrogen transfer) on Brønsted acidity (de la Puente *et al.*, 2000). The mechanism of hydrogen transfer reactions were explained by Lappas *et al.* (2004). As mentioned above, the three technologies; extraction, oxidation and adsorption work well on mild conditions whereas hydrodesulfurization process can be operated under severe conditions.

## 2.2 Hydrodesulfurization process

Hydrodesulfurization is a conventional catalytic chemical process, which is one of the hydrotreating processes. It has been used in the petroleum industry for eliminating sulfur compounds in oil under high temperatures and pressures. This process consumes a high amount of hydrogen to attract sulfur compounds, in yielding sulfur-free hydrocarbons and hydrogen sulfide gas. Furthermore, it is well-known that high multi-ring aromatic contents bring in low cetane quality. Therefore, the process of hydrogenation (dearomatisation) is required. However, the hydrogenation of unsaturated bond makes a decrease in octane number of an oil (Takasaki *et al.*, 2010).

### 2.2.1 Structures of sulfur compounds

Other than a high level of contaminants, especially sulfur, crude oil contains heavy hydrocarbon molecules. Hereby, the methyl or alkyl groups of sulfur compounds are discussed for their steric hindrance because they obstruct sulfur atoms from contacting with the active site of catalysts.
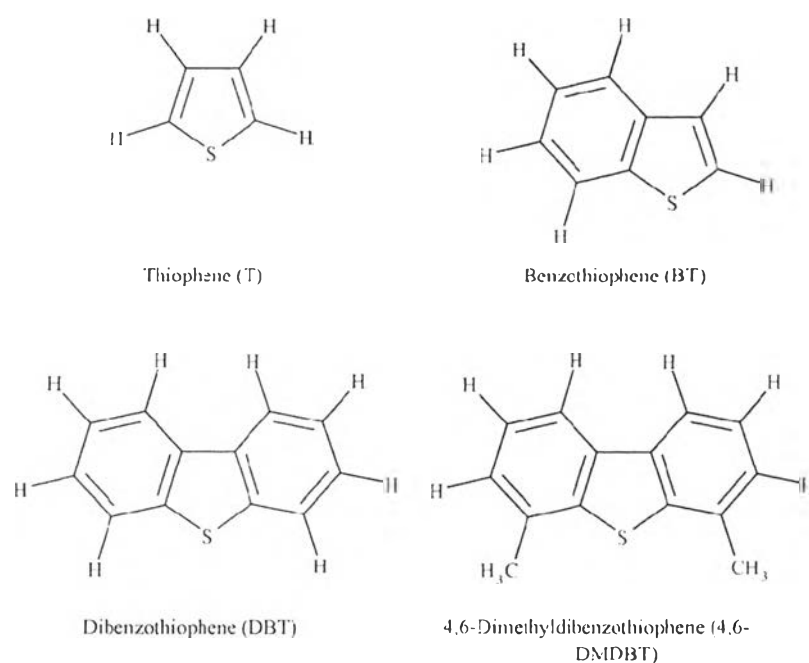


Thiophene (T)

Benzothiophene (BT)

Dibenzothiophene (DBT)

4,6-Dimethyldibenzothiophene (4,6-DMDBT)

**Figure 2.1** Thiophene and some of its derivatives (García-Cruz *et al.*, 2008).

The positions of alkyl groups of thiophenes (T), benzothiophenes (BT), dibenzothiophenes (DBT), and di-alkyl-dibenzothiophenes such as 4,6-di-methyl-dibenzothiophene (4,6-DMDBT) are shown in Figure 2.1. They can affect to desulfurization activity. The hydrodesulfurization activity of thiophenes and their derivatives is ranked in the order: T > BT > DBT > 4,6-DMDBT (García-Cruz *et al.*, 2008), relating with their boiling point (Choi *et al.*, 2004). HDS reaction scheme for 4,6-DMDBT, which is a quite large molecules, was summarized by Lecrenay *et al.* (1997). One of the reasons that large size of alkyl groups is difficult to desulfurize is that C-S bonds in the aromatic rings are rather stable than the others (Tang and Shi, 2011). Reduction of steric hindrance brings about the unsatisfaction of low sulfur specification; therefore, hydrogenating those alkyl groups can alleviate sterically-hindered sulfur compounds which drags into deep hydrodesulfurization. As mentioned above, the types of various sulfur compounds can affect the degree of sulfur removal according to Myrstad *et al.* (2000). They observed that saturated sulfur species, namely mercaptan and tetrahydrothiophene, in fluid-catalytic cracking naphtha were almost totally removed by using nickel and vanadium catalysts while thiophenes and benzothiophene were more difficult to be removed. Consequently, sulfur compounds should be promoted by chemical reactions, in particular hydrotreating and hydrocracking. Unsaturated molecules are firstly saturated; then, sulfur, oxygen, nitrogen and metal atoms are taken away from hydrogenated oil by cracking. There are two major pathways to remove sulfur, which are comprised of direct desulfurization (direct hydrogenolysis route) and hydrogenation (Pre-hydrogenation route). For the first route, sulfur atom is removed without hydrogenation. In the second route, sulfur atom is removed after at least one aromatic ring is hydrogenated (García-Cruz *et al.*, 2008). Therefore, the heavy feeds with large sterically-hindered sulfur compounds, like vulcanized rubber network, would prefer pre-hydrogenation rather than the direct desulfurization of large sulfur molecules.

## 2.2.2 Hydrodesulfurization catalysts

### *2.2.2.1 Conventional hydrodesulfurization catalysts*

It is well-known that hydrodesulfurization is the most common industrial process used for treating liquid fuels under high temperature and pressure with hydrogen feeding. The efficient catalysts for hydrodesulfurization, molybdenum or tungsten especially promoted with cobalt or nickel, have the synergistic effect between the active site of Mo or W and the Co or Ni as a promoter. Moreover, the active site should give moderate interaction with sulfur compounds in the reactant in order that sulfur-containing molecules could easily be removed on these catalysts (Chianelli *et al.,* 2002). Examples of positive effects, in case of Co promoted Mo on $Al_2O_3$, are that Co could help Mo monolayer to increase their stability, and Co-Mo-S phase formation makes Co-Mo catalysts more active than Mo catalysts alone. Villarroel *et al.* (2008) explained that hydrogen atoms generated from Co or Ni promoter under the working condition removed sulfur atoms on the Mo active site, resulting in unsaturated coordination of Mo atoms which are active phase in catalytic desulfurization. These relations make the coordinative unsaturated site facilitate the adsorption of sulfur-containing reactants and desorption of hydrogen sulfide products.

Villarroel *et al.* (2008) compared the promotion effect of the first row transition metal sulfides; Mn, Fe, Co, Ni, Cu and Zn, on Mo and W sulfides, in terms of hydrogen activation that plays important role in hydrotreating reaction under moderate to high conditions. Their hypothesis was that spillover hydrogen formed by metal sulfide promoter would help create coordinative unsaturated sites on $MoS_2$. They prepared the catalysts by promoting Mn, Fe, Co, Ni, Cu or $Zn/\gamma-Al_2O_3$ on Mo or $W/\gamma-Al_2O_3$, which were diluted with $SiO_2$, and found that the spillover factor of promoter on W was higher than that on Mo due to the lower bond energy of S-W. However, $Mo/\gamma-Al_2O_3$ was more active than that of $W/\gamma-Al_2O_3$ at 325 °C. They also found that when temperature increased, the spillover factor decreased, due to the loss of adsorption ability. Nevertheless, both Co and Ni promoters gave the maximum spillover factor when compared with the other first row transition metals, leading to the highest activity in hydrodesulfurization, which agreed with the periodic trends in the volcano curve (Chianelli *et al.,* 2002). According to the

Sabatier principle, Chianelli *et al,* (2002) concluded that moderate metal-sulfur bond strength from sulfur atom shared between Co and Mo resulted in good hydrodesulfurization activity. Rodríguez-Castellón *et al.* (2008) studied the effect of Ni and Co (5 wt% of each one) promoted on W and Mo (20 and 11 wt%) sulfide catalysts over Zr doped siliceous MCM-41. All of the catalysts showed favorite HDS activity at 3.0 MPa and 300-340 °C. The DBT conversion was ranked as follow: Ni5-Mo11 > Ni5-W20 > Co5-Mo11 > Co5-W20 in the temperature range of 320-340 °C, or can be stated that Ni-promoted catalysts had greater performance than Co-promoted catalysts at high temperatures because of high hydrogenation ability. Eventually, DBT hydrodesulfurization obtained by Ni5-W20 was more stable than by Ni5-Mo11 catalyst. This result is similar to the study of Kim *et al.* (2003). NiMo catalyst had higher activity in hydrodesulfurization of 4,6-DMDBT than CoMo catalyst because of greater hydrogenation ability. For Ni promoter, Ni-Mo and Ni-W gave similar hydrodesulfurization conversion of 93.16 and 92.48 %, respectively, for micro-sized zeolite beta (Ding *et al.,* 2009). Even though some processes require high acidity in order to achieve high activity, the higher acidity also causes a problem that was reported by Pawelec *et al.* (1997). The results from activity profiles showed that HY zeolite was faster deactivated than CoMo/Al$_2$O$_3$ along with time. The γ-Al$_2$O$_3$ support is the most widely-used for hydrotreating process because not only is it highly stable, contains both acidic and basic sites, and has high porosity and surface area, but also it causes positive interaction between itself and the promoter, especially conventional Co(Ni)Mo(W). Li-hua *et al.* (2011) evaluated the hydrodesulfurization of different loadings of Mo and Ni supported on alumina catalysts. They found that among various loadings of NiMo on Al$_2$O$_3$ catalysts, 18% of Mo and 4% of Ni showed high hydrodesulfurization activity, hydrogenation selectivity, and favored the hydrogenation of phenyl ring in the DBT molecule due to the high stacking number of MoS$_2$. Nevertheless, the main active function of pyrolysis catalysts should have high cracking ability by using acid support in order to crack the sulfur atoms, and better hydrogenation ability as well.

*2.2.2.2 Noble metal-promoted zeolite catalysts*

Modified catalysts are generally used in the hydrodsulfurization process because the high severity of process conditions not only causes the problems of high operation cost and energy expense but also the deactivation of catalysts. Transition metal sulfides, especially noble metal ones, are commonly used to enhance hydrogenation reaction that can work together with sulfur eliminating function, but they need to have sulfur tolerance to protect them from sulfur poisoning. Dũng *et al.* (2010) reported the effect of noble metal particle size on the sulfur tolerance. From TPR-$H_2$ profiles, the smallest Ru particle size resulted from using the heating rate of 5 °C/min gave the highest dispersion of the Ru metal on SBA-1 support and the strongest metal-support interaction. Those properties had a potential to improve the stability of noble metals, resulting in the lowest sulfur in oil and coke on the spent catalyst of 0.061 g/g catalyst and 1.33 wt%, respectively.

For hydrodesulfurization of thiophene at 400 °C, Rh supported on various zeolites was prepared by using $RhCl_3$ aqueous solution with impregnation method (Sugioka *et al.*, 1996a). All catalysts were calcined at 500 °C for 4 hr; then, reduced at 450 °C for 1 hr. It was proven that among Rh supported on various H-zeolites; namely USY, H-Y, M-mordenite, and H-ZSM-5, 5 wt% Rh catalysts supported on USY and H-Y were higher catalytic activity than CoMo/$Al_2O_3$. Presulfided 5 wt% Rh/USY gave the highest cracking of thiophene activity. Later, Sugioka *et al.* (1996a) therefore used USY as a support and compared the effect of Pt, Rh, Pd, Ru at 5 wt% loading. The results showed that thiophene hydrodesulfurization activities were as follows: Pt/USY > Rh/USY > Pd/USY >> Ru/ USY. In addition, Pt and Rh over USY gave the higher activity, and had a longer life than the presulfided CoMo/$Al_2O_3$ catalyst within 4 hour-running. XRD result also displayed that the dispersion of these noble metals on USY was ranked in the order: Pt/USY = Rh/USY > Pd /USY >> Ru/USY, which is in the same order as the activity. Therefore, they concluded that a high dispersion of noble metal resulted in high and stable activity for hydrodesulfurization. Finally, they combined Pt with Pd and Rh so as to improve the deactivation of catalyst, and drew a possible mechanism for proposing spillover hydrogen on these noble metals. The hydrogenation ability of noble metals was also compared in the study of Jacquin *et al.* (2003). They showed

the effect of Rh, Pt, Ir and Ru over mesopous aluminosilicates for naphthalene hydrogenation by using direct liquid crystal templating with a non-ionic surfactant in order to obtain surface acidity lower than zeolites. These catalysts gave 95-96% of naphthalene conversion at 200 °C and 6 MPa. The high-molecular weight (HMW) hydrogenolysis and/or ring-opening products (% yield) at 300 °C and 6 MPa were obtained as follows: Rh > Ru > Ir > Pt-containing-catalysts. Rh over mesopous aluminosilicates at 300 °C resulted in the highest selectivity to hydrogenolysis and/or ring-opening products. They proposed that naphthalene was hydrogenated to tetralin; then, cis- or trans-decalin before HMW hydrogenolysis and/or ring-opening compounds were formed. Hossain (2006) confirmed that Rh had the ability in hydrogen donation. He improved the performance of Co/saponite by adding Rh as a promoter, and discovered that Rh promoted Co/saponite showed apparently higher hydrodesulferization, hydrocracking, H/C ratio, saturated hydrocarbon group and gas ($C_1$-$C_5$) formation rate of vacuum gas oil than Pd and Pt promoted catalysts, or even CoMo/$Al_2O_3$ catalyst. Therefore, the introduction of Rh could reduce carbon deposition on the catalysts because of spillover hydrogen. The high performance of very low Rh loading (0.25 %) was reported by Ishihara et al. (2005). At the temperature of 390 °C, 0.25 wt% Rh/$Al_2O_3$ had higher conversion of sulfur compound groups than 16 wt% Ru/$Al_2O_3$ catalyst except for DBT group. The behavior of Rh and RhMo/γ-$Al_2O_3$ in hydrodesulfurization and hydrogenation was studied by Giraldo et al. (2008). The results showed that RhMo/γ-$Al_2O_3$ gave lower selectivity to HDS but higher HDS conversion than the monometallic ones. Furthermore, the results of 2 wt% Rh/γ-$Al_2O_3$ from using different activating agents at 673 K were presented. When using $N_2$ (without activation), Rh had moderate active for both hydrodesulfurization and hydrogenation. Using pure $H_2S$ as an active agent displayed the highest activity in HDS with 42 % HDS conversion while the greatest hydrogenation occurred at the same temperature with 17 % HYD conversion when reduced with $H_2$. These behaviors indicated that $H_2S$ had an important role to create active site for HDS activity but not for HYD one. Moreover, using an activating mixture (both 15 and 85 vol% of $H_2S/H_2$) presented low or almost no hydrogenation as well. Sidhpuria et al. (2008) studied the hydrogenation of toluene over 1 wt% Rh/HBETA, and reported that the large pore size of HBETA promoted

hydrodearomatization and Rh/HBETA had good activity for toluene hydrogenation because of hydrogen spillover on the acid site of zeolite. However, the catalyst activity in toluene hydrogenation decreased with the appearance of DBT because DBT was adsorbed and decomposed on the metal site, causing coke formation on the metal surface. It means that Rh/HBETA had the ability in desulfurization. Besides DBT and coke poisoning, they hypothesized that the active site could also be poisoned by $H_2S$ adsorption. These are similar to the deactivation observed by Sidhpuria et al. (2009). They studied thiophene reduction on nanoparticle Rh impregnated montmorillonite (Rh-MMT) in order to reach highly-dispersed Rh. During the hydrogenation of aromatic compounds, this catalyst was also poisoned by thiophene. The reaction can be achieved 100 % conversion of benzene to cyclohexane because of the high hydrogenation ability of Rh. Lee et al. (2004) reported that the DBT conversion obtained from 4 wt% sulfided $Rh/Al_2O_3$ was twice as high as the same loading percentage of sulfide $Ru/Al_2O_3$ due to the great quantity of active sites ($Rh_2S_3$ or RuS), but further increasing Rh loading did not benefit catalytic performance. They also found that low Rh loading gave higher hydrodesulfurization activity than conventional CoMo catalysts because of the easier desorption of $H_2S$.

In general, noble metals were used accompany with acidic supports, which often gave the beneficial effect for hydrodesulfurization process. On the contrary, in some case, the result from using PdMo/HY zeolite affecting the hydrodesulfurization was studied by Pawelec et al. (1997). The result showed that monometallic Pd/HY is more active in DBT conversion than bimetallic PdMo/HY. Although the catalyst consists of both noble metal and acidic support, PdMo/HY exhibited lower in HDS of DBT due to inhibitory activity effect of Mo unlike RhMo/$\gamma$-$Al_2O_3$ in the study of Giraldo et al. (2008). Hence, using Mo in form of $NiMo/Al_2O_3$ additive is a positive way to avoid inhibitory activity effect of Mo in bimetallic catalyst and increase hydrodesulfurization ability of Rh over acidic catalysts.

Even if high performance of hydrodesulfurization catalysts has been found by the cooperation of acidic support to enhance the cracking ability, the acidity of support can cause coke formation. Non-acidic zeolite is an alternative

to avoid the problem of coke formation. Fung *et al.* (2001) explained the deactivation of Pt/KL zeolite that Pt/$\gamma$-Al$_2$O$_3$ catalyst was deactivated by the major cause of acid sites and coke deposition on Pt particles during reforming process. On the other hand, using KL zeolite as a support could reduce coking of Pt metal, but Pt/KL zeolite was mainly deactivated by Pt agglomeration. Moreover, 0.6 wt% Pt/KL zeolite showed higher activity and selectivity of aromatics and methane but lower selectivity of C$_4$ and n- C$_7$ than Pt/$\gamma$-Al$_2$O$_3$ catalyst at the same loading. Treacy (1999) proposed that using short-channel KL zeolite could minimize the deactivation from Pt entombment. In aromatization, the introduction of acidity by any mean may cause a decrease in the selectivity, so non-acidic channel structure is only the active site for this reaction. Moreover, the high dispersion of Pt on short-channel KL zeolite would economize the cost of Pt by spreading Pt to the reactants. M'Kombe *et al.* (1997) compared the dispersion of Pt on KL and HY zeolites having the difference in acidity. At the calcination temperature of 350°C, the % Pt dispersions of Pt/KL and Pt/HY were 113 and 80%, respectively. It means that Pt/KL exhibited greater dispersion than Pt/HY. The hydrogenation selectivity of Ru/KL zeolite was studied by Álvarez-Rodríguez *et al.* (2005). They found that small metal particle size would interact with the wall of zeolite, and caused high product selectivity. The results from Pinket and Jitkarnka (2011) showed that KL reduced sulfur in the pyrolysis oil from 1.40 to 0.91 wt%, and further decreased extremely to 0.35 wt% with using Rh/KL. It is interesting that Rh supported on a basic catalyst has ability in desulfurization as well.

## 2.3 Catalytic pyrolysis of waste tire

The waste tires represent a source of energy and valuable hydrocarbon products because rubbers are made from constituent of petroleum hydrocarbons. The disposal of waste tires causes a major problem on environmental impacts, cost and other limits. These problems can be reduced by the production of valuable hydrocarbons from waste tires. Pyrolysis is a thermochemical process used to decompose organic materials without the cooperation of oxygen. It is an interesting solution that not only solves the problem of waste tire disposal but also treats the waste tire to valuable hydrocarbon products by decomposing the vulcanized rubber,

which has a three-dimensional network as shown in Figure 2.2. To improve tire properties, each of polyisoprene molecules was connected together with sulfidic crosslinks so as to inhibit polyisoprene chains from sliding over each other. The sulfidic bond can be monosulfidic (-S-), disulfidic (-S-S-) and polysulfidic (-S-S$_x$-S-) (Bilgili *et al.*, 2001). The effects of thermal aging on crosslink density of rubber compounds and the products from pyrolysis were studied by Jitkarnka *et al.* (2007). They concluded that the crosslink density increased within 3 weeks of aging time. The liquid product also increased with aging time because high crosslink density made it more difficult to crack. Pyrolysis oils from scrap tire have the sulfur contents of about 1.4-1.5 wt% and the gross calorific value of about 40.0 MJ/kg, which are similar to light fuel oils (Cunliffe and Williams, 1998). However, for the pyrolysis of used tire, the sulfur contents in the desired products need to be concerned.
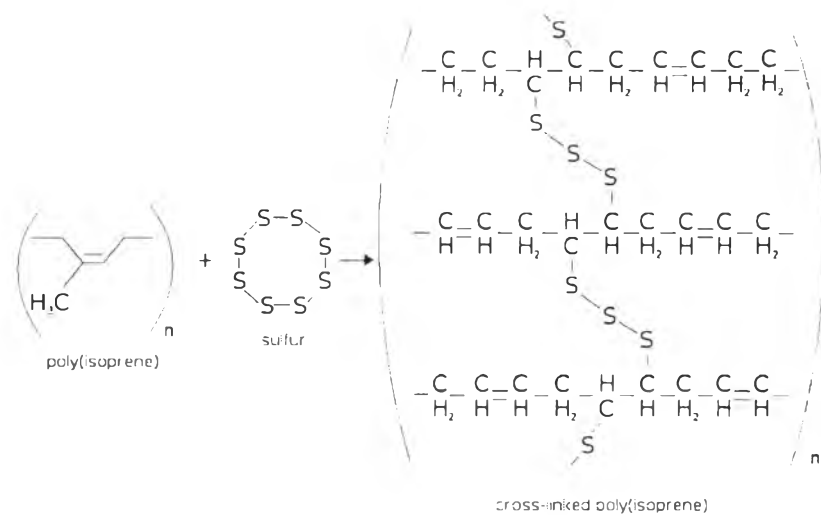
**Figure 2.2** Sulfidic bonds intercalated into tire structure (rubber) as a crosslink in vulcanization process (https://commons.wikimedia.org/wiki/File:Vulcanization.svg).

During pyrolysis, waste tire was decomposed to three products; namely solid, liquid and gaseous products with ~30 vol% $H_2$ (Aylón et al., 2007). The gaseous products had majority of methane, ethane, $C_4$-, $C_5$-hydrocarbons and the others such as ethylene, propane, propylene, $C_6$-$C_8$-hydrocarbons. The liquid products; namely saturated hydrocarbons, mono-, di-, poly-, and polar-aromatics were fractionated into gasoline, kerosene, gas oil, light vacuum gas oil and heavy vacuum gas oil by boiling point (Jitkarnka et al., 2007). Different particle sizes and pyrolysis conditions (temperature and heating rate) resulted in different yields of each composition of these three products, including the difference of sulfur contents in char and $H_2S$ in gas products (Lin et al., 1997). Unapumnuk et al. (2008) showed that the desulfurization ability obviously enhanced when temperature increased from 325 to 350°C, and remained quite constant during 400 to 1,000°C. The tendency of desulfurization ability had the same characteristic for the different heating rates (1, 5 and 10 °C/min); however, higher heating rate gave a bit greater desulfurization ability than lower ones. The effect of pyrolysis temperature was also studied by Williams and Bottrill (1995). They reported that sulfur-polycyclic aromatic hydrocarbons (PASH) in pyrolysis oils increased with the increment of pyrolysis temperature. Three years later, Cunliffe and Williams (1998) also reported the similar results. Increasing pyrolysis temperature from 450-600 °C caused polycyclic aromatic hydrocarbons (PAH) increased from 1.5 to 3.4 wt%. The highest yield of pyrolysis oil was 58.2 wt% at 475 °C, and the oil yield decreased with increasing temperature.

In order to achieve low sulfur contents of potential fuels, hydrocracking and hydrogenation become important. Dũng et al. (2009) also studied the effect of waste tire pyrolysis temperatures. They found that sulfur-containing polar-aromatics increased when the pyrolysis temperatures increased. The results show that polar-aromatics reduction activity can be ranked as follows: Pt/HBETA > Pt/HMOR > HBETA > HMOR, because higher acid strength of HBETA resulted in higher cracking ability than HMOR, and the larger pore size of HBETA would allow the bulky molecules enter inside to its pore before cracking those molecules. Large pores size of a support would help $H_2$ molecules transport between pore systems as spillover hydrogen (Song, 2002). Pt loading on different supports exhibited high

dispersion of Pt/HBETA catalyst because of the higher surface area and pore diameter of HBETA, which resulted in better hydrogenation. Finally, they concluded that the heavier polar-aromatics were prevented by hydrogenating polar-aromatic precursor to saturated compounds; then, further cracking by acid supports. Another noble metal, Ru had a potential to reduce poly- and polar-aromatic hydrocarbons by converting waste tire into light oil products and further cracking the saturated hydrocarbons in oil fraction to gaseous products (Dũng *et al.*, 2010). Shen *et al.* (2006) studied tire pyrolysis on USY zeolite. They found that this acid zeolite could increase the gas yield with the expense of oil yield. Simultaneously, coke was formed on the catalyst while the char yield kept the same during the process. The result from GC/MS chromatogram can be explained that USY zeolite gave higher amount of single-ring aromatics, like benzene, toluene and xylene than ZSM-5 catalyst due to their lower Si/Al ratio.

In order to achieve the valuable lighter product with low sulfur levels, the pyrolysis of waste tire together with the removal of sulfur in tire-derived oil are needed. According to the literature reviews, it is interesting that using Rh/KL gave a remarkable formation of mono-aromatics in waste tire pyrolysis. Pure KL could reduce sulfur in the pyrolysis oil from 1.40 to 0.91 wt%, and further decreased extremely to 0.35 wt% with using Rh/KL (Pinket and Jitkarnka, 2011), meaning that Rh/KL could potentially benefit cracking and sulfur removal simultaneously. Moreover, the acidic zeolite supports such as HY and HBETA had acid site with large pore size, necessary for cracking of bulky molecules such as a tire molecule. Since Rh/KL was found to be active for both tire pyrolysis and sulfur removal, Rh metal was also tested as a promoter on two acid zeolites: HY and HBETA. Hence, Rh/HY and Rh/HBETA was expected to promote pyrolysis process together with hydrogenation ability of Rh. The advantages of hydrogenation (cracking) and hydrodesulfurization (sulfur removal) performance of Rh noble metal on HY and HBETA (acidic zeolites) were simultaneously taken for investigation. The activities of the catalysts were also compared with those of Rh/KL (non-acidic zeolite) as the effective catalyst in waste tire pyrolysis.

Furthermore, $NiMoS/Al_2O_3$ and $CoMoS/Al_2O_3$ have been widely used as a commercial catalyst for hydrodesulfurization process of the refinery. They contained

both acid and metal sulfide functions ($Al_2O_3$ and Ni(Co)MoS, respectively) that could promote cracking and sulfur reduction simultaneously, so in this work, they were employed as the catalysts for waste tire pyrolysis. The objective of this part was to investigate the possibility of using the commercial hydrodesulfurization catalysts in waste tire pyrolysis, aiming to improve the quality and quantity of pyrolysis oil with a lower sulfur level.