CHAPTER II
BACKGROUND AND LITERATURE REVIEW

2.1 Tire and Waste Tire Problem

Typically, a tire composes of natural rubber (NR), styrene-butadiene rubber (SBR), and butadiene rubber (BR) (Williams and Besler, 1995). The rubber chains are cross-linked by sulfur after vulcanization. Sulfur may be present in the vulcanization network in a number of ways such as monosulfide, disulfide, or polysulfide (Blow and Hepburn, 1982). It may also be present as dependent sulfides, or cyclic sulfides. The content (wt%) of sulfur in the tire depends on the manufacture, but generally in the range of 1-2% (Blow and Hepburn, 1982). Table 2.1 summarizes the typical composition of a tire (Qu *et al.*, 2006).

Table 2.1 A typical composition of a passenger tire (Qu *et al.*, 2006)

	Natural Rubber	Syrene-Butadiene Rubber	Butadiene Rubber
wt%	58	27	15

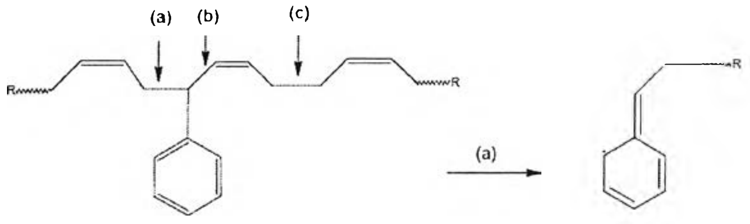
Due to the growing population, the world demand of tire keeps increasing. Consequently, over $6x10^6$ tons of waste tire are globally produced annually (Galvagno *et al.*, 2002). This, together with the fact that tires are designed to be resistant to chemical, biological and physical degradation, has been causing serious environmental problems. Owing to the low bulk density of this waste, it occupies large volumes and, if buried, disrupts the integrity of landfill sites. Moreover, fires at tire deposits are very difficult to control and generate high levels of pollution to the soil, atmosphere and water (San Miguel *et al.*, 2006). For those reasons, the environmental regulations concerning the waste tire become more and more stringent. This waste hierarchy favors the valorization and recycling alternatives. At the same time, the gradually depletion of petroleum reserves has created interest in finding alternative source of energy. Thus, over recent years, tire pyrolysis, a recycling process, has attracted renewed significant attention.

2.2 Pyrolysis of Waste Tire

Pyrolysis of waste tire essentially involves the degradation of the tire components by exposure to high temperatures in the absence of oxygen. The result is a carbonized char, condensable oil and a gas fraction. The yields and nature of these products depend on many factors *e.g.* temperature, the size of tire particle, the type of reactors, pressure..., etc. The oil and gas can be used as fuels or chemical feedstock, whereas the solid residue can be recycled in worthwhile applications such as smokeless fuel, carbon black or low-grade activated carbon.

2.2.1 Mechanistic Study

Chen and Qian (2000) investigated the decomposition of polybutadiene under different temperatures. At lower temperatures, the rubber is decomposed mainly by scission, followed by unzipping to yield monomers, whereas at higher temperatures, the hydrogen transfer reaction takes place, and chain scission mainly occurrs at the β-positions accompanied by cyclization and aromatization.



Scheme 2.1 SBR decomposition (Choi, 2000)

In the pyrolysis of natural rubber (NR), the β-scission is also much more preferable because of the low bond dissociation energy, leaving the allylic radicals (Chen and Qian, 2002). For SBR, the thermal degradation is favored at the position (a) than (c) in **Scheme 2.1** as suggested by Choi (Choi, 2000), and no product resulted from the dissociation at the position (b) was observed.

The complex structure of tire makes it difficult to understand clearly the multi-reactions occurring during tire pyrolysis. However, Jitkarnka *et al.* (2007) proposed that the breakdown of a tire molecule was initialized by breaking S-S bonds, and then spread out along the chains.

2.2.2 Pyrolytic Oil

Among the pyrolysis products, the tire-derived oil has attracted much more attentions due to its high heating value [21], its storage advantage, and its property, which was reported to be similar, to a certain extent, to that of commercial naphtha (Benellal *et al.*, 1995). Pyrolytic oil is a complex mixture of hydrocarbons (HCs) with high concentration of aromatics, particularly single-ring aromatic HCs (Cunliffe and Williams, 1998). However, this concentration is not high enough to obtain an economically separation process. And, the aromatic property of the tire-derived oil (Benallal *et al.*, 1995), especially its remarkable content of polycyclic HCs, has limited its application as a direct-usable fuel. This is due to the fact that these compounds together with the sulfur-containing compounds found in the oil (Pakdel *et al.*, 2001) cause a lot of smoke, HC and CO emissions, and also oil sticking on the nozzle stem and sac of diesel engine (Murugan *et al.*, 2009).

The formation of polycyclic aromatics during the pyrolysis of waste tire was investigated by Williams and Taylor (1993). They suggested that the pyrolysis of tire led to the production of ethylene, butadiene..., which could react to form cyclic olefins, followed by dehydrogenation to produce aromatic compounds and. As a result of subsequent associative reaction, the formation of polycyclic aromatics might occur. And a poly-aromatic compound, such as phenathrene, was formed after the formation of naphthalene, a di-aromatic compound. Moreover, no evidence proving the direct formation of aromatics from cyclization of alkanes was observed.

Pyrolytic oil also has a considerable amount of sulfur-containing compounds, such as benzothiophene, thiophene and their derivatives (Williams and Bottrill, 1995; Pakdel *et al.*, 2001). However, the formation of these compounds during pyrolysis is still remained unelucidated.

2.2.3 Effects of Pyrolysis Conditions

Table 2.2 summarizes the yields of gas and oil generated by waste tire pyrolysis using different reaction systems. Accordingly, the yields are strongly dependent on the type of reactor as well as pyrolysis conditions.

Table 2.2 Yield of pyrolysis products for different systems

Authors	Gas (%wt)	Oil (%wt)	Temperature (°C)	Reactor
Williams *et al.*, 1990	2.4-14.8	3.6-58.8	300-720	Static batch
Laresgoiti *et al.*, 2000	4.8-38.5	7.6-19.3	300-700	Autoclave
Cunliffe and Williams, 1998	4.5-8.9	53.1-58.1	450-600	Static batch
Berrueco *et al.*, 2005	2.4-4.4	30-42.8	400-700	Static batch

Temperature is one of the most important factor controlling the yield and nature of the products evolved in pyrolysis. Therefore, its influences on the degradation of waste tire have been investigated extensively. Generally, it was found that the tire can be completely decomposed at 500°C (Roy *et al.*, 1999; Rodriguez *et al.*, 2001). Pyrolysis at temperatures higher 500°C did not change the yield of the carbonaceous char, except the yield and nature of other products (Laresgoiti *et al.*, 2004). Cunliffe and Williams (1998) observed a decrease in the yield of oil in accordance with an increase in gas yield as the pyrolysis temperature was risen over 600°C. And the concentration of aromatic compounds in oil also increased at the expense of aliphatic hydrocarbons with increasing pyrolysis temperatures. Similar observation was reported by Laresgoiti *et al.* (2004), on which the temperatures were varied in the range of 300°C – 700°C. Pyrolysis temperature also affects the calorific value of the derived oil (Diez *et al.*, 2004). Namely, the oil had high calorific value, and the value increased along with pyrolysis temperature.

Another operating factor that normally found to affect the yield and nature of the obtained products is the residence time, which is typical controlled by the flowrate of the carrier gas. Mastral *et al.* (2000) observed a slight increment in the yield of oil as the velocity of the carrier gas increased. Also, the variation of the flowrate of the carrier gas changed of the oil compositions. However, using different carrier gas insignificantly influenced the yield and compositions of the derived oil. Similarly, the decrease in the yield of oil as the residence time increased was reported by Leung *et al.* (2002) and Barbooti *et al.* (2004), which was attributed to the existence of greater and deeper cracking reactions.

2.2.4 Catalytic Pyrolysis of Waste Tire

Due to the high content of aromatics in the tire-derived oil, catalysts have sometimes been introduced to the pyrolysis, aiming at enhancing the yield of valuable aromatic compounds. Generally, the use of acid zeolite catalyst in the pyrolysis of waste tire increases the yield of gaseous product at the expense of oil yield due to its cracking activity. And, the effect is more pronounced with increasing the amount of acid zeolite catalyst used, *i.e.* increasing the catalyst-to-tire ratio (Boxiong *et al.*, 2007; Williams and Brindle, 2002). And the catalyst-to-tire ratio also affects the compositions of oil and gas products. Boxiong *et al.* (2007) found that benzene and toluene concentrations peaked at the catalyst-to-tire ratio of 0.5, whereas that of xylenes increased with increasing the value of this ratio.

Williams and Brindle (2002) studied the catalytic pyrolysis of waste tire using two types of zeolites, Y and ZSM-5, and reported an increase in the concentration of single-ring aromatic hydrocarbons, *i.e.* benzene, toluene and xylene. Y zeolite produced the higher amount of these aromatics with respect to ZSM-5 due to its lower Si:Al ratio and larger pore size. Later, with the aim to obtain much higher concentration of certain single-ring aromatic, Boxiong *et al.* (2007) used USY and ZSM-5 as catalysts in the pyrolysis of waste tire. The experimental results indicated the high concentrations of benzene, toluene, and xylenes, which could be achieved with USY zeolite.

The high concentration of aromatics, particularly poly- and polar-aromatic hydrocarbons (PPAHs), as mentioned earlier, has limited the use of tire-derived oil as fuel. However, this limitation is still remained unsolved. Actually, no study has been found so far aiming at the reduction of PPAHs in this oil.

2.3. Noble Metal-Supported Catalysts

2.3.1 Monometallic Catalysts

Bifunctional catalysts have been extensively studied for the reduction of aromatics in fuel (Lugstein *et al.*, 1999). Metals can catalyze the hydrogenation of the feedstock, making it more reactive for cracking and heteroatoms (sulfur, oxygen) removal (Ali *et al.*, 2002). And a high level of aromatic hydrogenation at moderate hydrogen pressures can be achieved with noble metals catalysts (Eliche-Quesada *et al.*, 2006). This intrinsically-high hydrogenation activity can also help reducing steric effects that impede the direct elimination of the sulfur heteroatom (Pecoraro and Chianelli, 1981) in the hydrodesulfurization (HDS).

Albertazzi *et al.* (2003) studied the hydrogenation of naphthalene with noble metals supported on MCM-41 aluminosilicate catalysts. They found that Rh showed high activity although it favored partial hydrogenation to tetraline than complete hydrogenation to decaline. And, this Rh-supported catalyst can also catalyze ring-opening and cracking reactions, especially at high temperatures. Similarly, Jacquin *et al.* (2003) observed the high activity of Rh-based catalysts for upgrading diesel. Further, in their work it was reported that decreasing H_2 pressure caused a sudden drop in the yield of high molecular weight products, whereas that of lighter products increased. Besides, Rh-supported catalyst was shown to be a good candidate for the hydrogenolysis cleavage and skeletal rearrangement of C-C bonds (Teschner *et al.*, 2002). The single splitting of C-C bonds was catalyzed at high hydrogen coverage. Decreasing partial pressure of H_2 caused “deepening” of hydrogenolysis, and the hindrance in the re-hydrogenation of the surface intermediates were proposed to explain the successive breakdown of the molecules. It is also worthy mentioned that for very low metal loadings, the carbon-supported rhodium exhibited activities higher than the ruthenium one (Harris and Chianelli, 1984).

Rhenium sulfide was reported to be highly active for the hydrodesulfurization (HDS) reactions, in some cases even higher than the classic Mo and W sulfide, either in the unsupported state (Pecoraro and Chianelli, 1981; Lacroix *et al.*, 1988) or supported on carbon (Ojeda *et al.*, 2005). Nacheff *et al.* (1987) studied the characterization of Re/Al_2O_3 and $Pt-Re/Al_2O_3$ and their activity in several reactions. Re^0 sites were found to be very active for olefin hydrogenation; however, after presulfiding, this hydrogenation activity (of Re/Al_2O_3) was drastically lowered. Besides, Re-supported γ-alumina was an active catalyst promoter for the conversion of hydrocarbon (Okal and Kubicka, 1998).

In 2005, Eliche-Quesada *et al.* studied the hydrogenation and hydrogenolysis/hydrocracking of tetralin in the presence of sulfur, and reported the excellent activity of ruthenium supported on zirconium doped MCM-41. One year later, the same authors found that Ru-supported mesoporous phosphate heterostructures also exhibited high performance for the hydrotreating of aromatics (Eliche-Quesada *et al.*, 2006). Additionally, the catalysts also showed a very good balance between the yields of hydrogenation and hydrogenolysis/hydrocracking products. In the work of Akhmedov *el al.* (2000), Ru catalyst was the most active one for the hydroconversion of hydrocarbon over for a considerable amount of metals-supported catalysts. A high C-C splitting of the tested HCs was also observed for Ru catalyst due to the presence of highly dispersed ruthenium particles on the zeolite support. Gao and Schimidt (1989) showed that the rate of ethane hydrogenolysis could be changed significantly for ruthenium by oxidation and reduction treatments during catalyst preparation. Highly-active sites were formed by oxidation and low temperature reduction. It was believed that the oxidation step may lead to highly dispersed Ru-containing intermediates, which the reduction under reaction conditions may provide very small metal particles.

It is well-accepted that the amount of metal loaded strongly affects the catalytic activity of a metal-supported catalyst. To a certain extent, the catalytic activity generally increases with increasing metal loading. For the HDS of dibenzothiophene, the experimental results of Eliche-Quesada *et al.* (2007) showed an increase in activity when the ruthenium loading was increased up to 7 wt%, whereas the further addition of ruthenium produced a slight decrease. These phenomena were attributed to the fact that high dispersion of ruthenium was obtained and maintained up to 7 wt%, whereas bigger ruthenium crystal was formed with the loading amount higher than 7 wt%. Besides, it was also reported that the excellent hydrogenation of tetraline could be achieved over a catalyst with a high ruthenium content (Eliche-Quesada *et al.*, 2005).

The activity of a noble metal-containing catalyst can also be improved by selecting a proper support. A series of zeolite-catalysts were investigated to determine the support effect for the C-C bond splitting activity of Ru-containg catalysts (Sajkowski *et al.*, 1990; Wu *et al.*, 1990). It was found that these zeolites allowed one to prepare highly dispersed catalysts where most of Ru particles were apparently located on the internal surface of the zeolite crystallites. The increase in activity for these catalysts was mainly due to the presence of highly dispersed Ru particle made possible by the zeolite support. The use of HMOR as a support for Ni and Pt catalysts was reported to exhibit higher activity toward cracking reactions than HBETA zeolite due to its small and one dimensional structure (Escobar *et al.,* 2008). Also, the crystal size of mordenite is usually larger than that of BETA zeolite, and in the case of cracking it would be more favored over mordenite. A part from zeolite structure, the acid property of the support also plays important role in catalytic activity. Kinger and Vinek (2001) studied the hydroconversion of n-nonane over Ni and Pt containing HMFI, HMOR, and HBETA zeolites, and reported the linear relation between the reaction rate and the number of acid sites. In the same year, noble metal supported on HFAU was proved to be more active than on alumina for toluene hydrogenation, mainly due to the higher acidity of the former support (Chupin *et al.*, 2001). Zheng *et al.* (2008) showed that the activity of Pd-supported on USY for naphthalene hydrogenation in the presence of benzothiophene decreased with increasing SiO_2/Al_2O_3 ratio in the tested range (12 to 80). The beneficial effect of acid sites of the support in the hydrogenation of aromatics with noble metal-supported catalyst is attributed to the hydrogenation of molecules adsorbed on acidic sites by hydrogen spilled-over from the metal sites. It is noted that there generally exists an optimized acid density of the support. In the work of Yasuda *et al.* (1999), the hydrogenation activity of Pd-Pt supported on USY increased with increasing SiO_2/Al_2O_3 ratio, peaked when the ratio was in the 150 - 40 ranges, and then decreased as the ratio increased further. The authors believed that the decrease in both activity and sulfur tolerance, when the SiO_2/Al_2O_3 increased from 40 to 680, may be primarily due to the decrease in the amount of electron-deficient Pd-Pt, resulting from the decrease in Lewis acidity.

Summarily, noble metal supported catalysts can effectively catalyze the hydrogenation of aromatic hydrocarbons. However, one major limit of noble metal is its low resistance to sulfur poisoning. Interestingly, the sulfur tolerance can be enhanced by modifying the physicochemical characteristics of the metal atoms by

(i) using acidic carriers (Barbier *et al.*, 1990), (ii) changing the metal particle size, or (iii) alloying with other metals (Lee and Rhee, 1998).

2.3.2 Bimetallic Catalysts

Bimetallic catalysts have been received a great deal of attention because they might exhibit superior activity, selectivity, and deactivation resistance than their corresponding monometallic samples (Sinfelt, 1983; Ponec and Bond, 1995). The variations of catalyst performance are often explained on the basis of electronic and/or geometric effects. The ligand effect speculates the change in adsorption bond strength between chemisorbed adsorbates and surface-active metal atoms. The ensemble theory considers the addition of an inactive metal, resulting in a dilution of the surface-active metal atoms, and then, in a decrease of the active ensemble size. However, the geometric and electronic factors often cannot be easily separated as independent parameters. For instance, the electron bandwidth of the metal, as well as the nature of the exposed planes and the topology of the surface sites, can change with the size of the metallic particle.

In 2002, Crisafulli *et al.* reported that the bimetallic Ni-Ru supported on SiO_2 showed much higher activity and stability than its corresponding mono metallic samples. The different behavior was related to the formation of Ni-Ru cluster on silica and an obvious surface enrichment in nickel, leading to an increase in the metallic dispersion of nickel. Ishihara *et al.* (2005) studied the HDS of sulfur-containing poly-aromatic compounds in light gas oil using noble metal catalysts. They found that, in the case of straight run-light gas oil (SR-LGO), the dibenzothiophen (DBT) HDS activity was remarkably enhanced with using Ru-Rh bimetallic system, revealing a synergistic effect between Rh and Ru. Recently, in the work done by Navarro *et al.* (2009), it was documented 0.5%RuNiMo catalyst was less prone to deactivation than the NiMo reference sample for the HDS of dibenzothiophene. Especially, in the hydrotreatment of a SR-GO, the sulfided 0.5%Ru/NiMo/Al_2O_3 catalyst was proven to be more active in the HDS and HDA reactions than a commercial NiMO/Al_2O_3 catalyst. This high activity was explained by the formation of small particles inducing some preferential exposed planes, favoring hydrogenation properties with the introduction of ruthenium.