



CHAPTER II

LITERATURE REVIEW

Used tire is a waste material, which is hard to degrade in environment; therefore, it causes various problems to the environment. Then, there have been some studies about the recovery of waste tire. Since tire is mainly composed of basic rubbers such as polyisoprene, polybutadiene and co-polymer styrene butadiene (SBR), it can be recycled as a fuel. Singh *et al.*, (2009) reported on the usage of waste tire to produce energy in a power plant, which also can reduce NO emission. Although waste tire is a good raw material for oil or gas, it has a complex structure; then, it is hard to be processed easily. Three thermal conversion techniques for recycling tires are incineration, gasification, and pyrolysis.

Incineration is a thermal treatment, which is usually operated at high temperatures for combusting organic materials in an oxygen-rich atmosphere. The products from incineration are flue gases, particulates, and incinerator bottom ash. The flue gases are not usually friendly for the environment. Moreover, incineration releases heat from combustion which can in turn be used to generate electric power (<http://en.wikipedia.org/wiki/Incineration>).

Gasification is a process to produce syngas that can be used as a fuel and an intermediate for producing other chemicals. This process operates at high temperature with using oxygen and/or steam to convert carbonaceous materials (coal, petroleum, biofuel, and biomass) to carbon monoxide and hydrogen (<http://en.wikipedia.org/wiki/Gasification>).

Pyrolysis is a thermal decomposition process in an oxygen-free atmosphere. Without oxygen, this process produces low emission to the environment. The primary products are gas, tars (oil), and char. The gas and liquid products can be used as fuels and petrochemical feedstocks, because their carbon number range is in the neighborhood of fuels and petrochemical feedstocks. The solid contains carbon black, which is a main component that can be used for the production of activated carbon and low grade carbon black. Many techniques similar to pyrolysis are the production of hydrolysis depolymerization and depolymerization with microwave.

There are many parameters that affect to the yields and quality of products such as feed stock, operating condition, the size of reactor, the design of reactor, and residence time etc.

There is a research showing the usage of pyrolysis products such as Roy *et al.*, (1999). They mentioned that the solid pyrolysis products in the form of carbon can be used as a commercial carbon black filler. The light fraction in the liquid product mainly consisted of limonene, which can be blended with gasoline. The rest was gas product, which can be used as a fuel for this process or energy for other applications.

2.1 Pyrolysis without a Catalyst

Since pyrolysis is interesting, then there have been many researchers who studied the conditions that gave a high amount of products from the pyrolysis of waste tire. Cunliffe and Williams (1998) used a static bed reactor purged with nitrogen at the temperature range of 450°C to 600°C. The results showed the gas yield of about 4.5-9 %wt, the oil yield in the range of 53-58 %wt, and the solid yield of 37-38 %wt. And, they found that when temperature increased, the oil yield decreased, but the gas yield increased. Leung *et al.*, (2002) operated tire pyrolysis at a high heating rate of 1200°C /min in a special reactor. The temperature was also varied between 500°C to 1000°C. The results showed the gas yield between 5-23 %wt, the liquid yield in the range of 43-58 %wt, and the solid yield of 34-37 %wt. Barbooti *et al.*, (2004) used a fixed-bed reactor purged with nitrogen gas for pyrolysis experiment. They investigated for the optimum condition, which gave a high amount of oil and gas. The variables that they studied were pyrolysis temperature, nitrogen flow rate, and particle size. They found that the optimum condition was 430°C of pyrolysis temperature, the nitrogen flow of 0.35 m³/hr, and the particle size of 10 mm. At the optimum condition, the yields of carbon black, oil, and gas were 32.5 %, 51.0 %, and 16.6 % by weight, respectively.

Next, many articles focused on the composition in the products of high values obtained from pyrolysis. For example, the gas product can be used as a petrochemicals feedstocks and fuels. In addition, researchers concerned the product

yield, calorific value, the amount of propylene and butylenes, the amount of methane and hydrogen as green energy with high heating values, and the yield of ethylene and propylene as chemical feedstocks. Leung *et al.*, (2002) showed that the gas composition in the gas products from pyrolysis in a fast heating condition consisted of H₂, CO, CO₂ and light hydrocarbons such as CH₄, C₂H₄, C₂H₆ etc. And, the gas product had the heating value in the range 20 - 37 MJ/m³. Diez *et al.*, (2004) used a horizontal reactor for studying the effect of final pyrolysis temperatures at 350°C, 450°C, and 550°C. The results showed that the higher amount of hydrogen and methane was obtained at a higher temperature. The calorific value at the highest temperature was about 39.6 Mj/m³. Recently, Kaminsky *et al.*, (2009) have studied the pyrolysis of synthetic rubber (tire) and natural rubbers (polyisoprene) at 600 – 700°C. And, the results showed that the pyrolysis of tire at the higher temperature gave the greater amount of ethylene and propylene in gas.

Moreover, the oil products mainly focused for daily uses are gasoline and diesel. A sufficient concentration of aromatic and isomerized hydrocarbons, which enhance the octane number of gasoline, is needed, and the amount of polycyclic aromatic hydrocarbons (PAH) needs to be limited because their hazards to health. Williams *et al.*, (1993) studied the pyrolysis of polystyrene plastic in a static bed reactor at a temperature of 500°C, 600°C and 700°C. In this research, they focused on polycyclic aromatic hydrocarbon (PAH) in liquid products, and found that the PAH content increased when pyrolysis temperature increased. Cunliffe and Williams (1998) found that the components with a high concentration in the liquid product were limonene and aromatic compounds. The oil product also had a similar heating value with light fuel oil. The amount of limonene and aromatic compounds in the liquid products increased with pyrolysis temperature. Polycyclic aromatic hydrocarbons (PAH) which cause emission were also increased with temperature. Laresgoiti *et al.*, (2004) used an autoclave reactor with varied temperature between 300°C to 700°C. The report showed that aromatic compounds mostly consisted in the liquid products from tire pyrolysis. The concentration of aromatic compounds was increased when the temperatures were in the range of 300 - 500°C, and then decreased. Kaminsky *et al.*, (2009) have found that liquid product had high amount

of the aromatic compounds. Moreover, when natural rubber (polyisoprene) was pyrolyzed, it gave a higher amount of toluene or xylene than benzene.

Solid product from the pyrolysis of waste tire was mainly carbon which can be used as carbon black filler or activated carbon. There were some researches having tried to compare the quality of pyrolytic carbon black with commercial carbon black. Huang *et al.*, (2005) studied the effect of temperature (500°C and 700°C) on the solid products (carbon black). The results showed that carbon black from pyrolysis at a low temperature had lower quality than that of commercial carbon black due to a higher amount of inorganics in the pyrolytic carbon black. Murillo *et al.*, (2006) studied the solid products, and found that they have low surface area, but can be used as adsorbents after activation processes. Another application was that they can be used for energy production because of their high heating value. Kaminsky *et al.*, (2009) also have studied about the properties of solid product from pyrolysis with varied pyrolysis temperatures. The results showed that, at 600°C, the carbon black can be used as a filler. But the pore of carbon black was blocked at higher than 600°C, resulting to low quality.

2.2 Catalytic Pyrolysis using Zeolite Catalysts

Then, from the above it has been shown that there were many interests on the pyrolysis of waste tire. Many researchers have found that studied the products were not good enough to be used as fuels or chemical feedstocks, then they attempted to improve their selectivity, quality, and quantity of products by using special catalysts in pyrolysis. In this work, Y-zeolite is focused due to its potential to enhance the quantity of desired products (oil and gas) and reduce the quantity of some components such as aromatic compounds. Since Y-zeolite is an acid catalyst, it can enhance aromatization by H-transfer ability. William and Brindle (2002) used a fixed-bed reactor in order to study the influence of the temperatures in the catalytic pyrolysis using catalysts with two different pore sizes and surface activity; that is Y-zeolite (CBV-400) and ZSM-5 which have the pore size of 7.8 Å and 5.6 Å, respectively. The temperatures of this experiment were between 430°C and 600°C. They reported that Y-zeolite gave higher aromatic yield and lower liquid yields than

those of ZSM-5 catalyst because Y-zeolite has larger pore size and higher surface acidity. They explained that a smaller pore size of catalyst limited the hydrocarbon reactants to enter to the pore structure, and then the liquid yield was lower. Moreover, alkyl substituted aromatic compounds were also decreased with increasing temperature. After that in 2003, they studied the surface acidity and pore size effects of catalysts on the yield of single ring aromatics. The scrap tires pyrolysis was performed with three catalysts (ZSM-5, Y-zeolites (CBV-780 and CBV-400)). They reported that CBV-400 was the best catalyst in giving the highest yield of BTX (benzene, toluene, m/p/o-xylene) due to the highest pore size and surface acidity. In addition, for the influence of zeolite catalysts, the liquid products decreased, possibly because the catalysts provided other pathways. And, in the same year year, Williams *et al.*, used USY, ZSM-5 and Y-zeolites in studying the effects of pore size and surface acidity since the Y and USY zeolites had same pore size. They found that at a high catalyst/tire ratio the light naphtha fraction (<160°C) in liquid products was increased. The results indicated that the amount of oil produced by using USY zeolite was less than that of ZSM-5 and Y-zeolite catalysts; however USY zeolite gave higher total concentration of BTX. Heating rate also affected to aromatics, olefins, and coke formation. Hall *et al.*, (2009), had studied the effect of Y-zeolite catalysts on the yield of aromatic compounds such as toluene and xylenes obtained from the pyrolysis of waste rubber gloves. They found that, in the presence of Y-zeolite, the yields of toluene, xylene, methyl benzenes, ethyl benzenes, and naphthalene increased dramatically because Y-zeolite also catalyzed the limonene decomposition. In the report of Boxiong *et al.*, (2006), the scrap tires were pyrolysed in a fixed-bed reactor using USY zeolite as a catalyst. They studied the effect of USY zeolite on pyrolysis products and the composition of oil products. The studied parameters were pyrolysis temperature, catalytic temperature, catalyst/tire ratio, and heating rate. The results showed that all parameters had an influence on the yield of products. When catalytic temperature and catalyst/tire ratio were increased, the liquid yield decreased. Also, the total concentration of BTX was increased with increasing catalyst/tire ratio. USY gave the higher total concentration of BTX than ZSM-5. Olazar *et al.*, (2008) studied the effect of acid catalysts under fast heating conditions on the yield of pyrolysis products. The three zeolite catalysts used were HZSM-5,

HY, and HBeta. The results showed that adding HY zeolite, which favored hydrogen transfer capacity for the reaction, led to the formation of solid and aromatic C_{10-} . The HZSM-5 catalyst cracked non-aromatic C_{10-} , and enhanced dealkylation. Then, the amounts of solid and light aromatic C_{10-} were increased via olefin condensation and hydrogen transfer from suitable catalysts which had micropore and acidity. Moreover, the yield of gas was also increased. HBeta zeolite had an intermediate behavior. Marcilla *et al.*, (2009) have studied the products from the catalytic pyrolysis of polyethylene. HUSY zeolite was used in their experiment, and the results showed that the major pyrolysis products were 2-cis-butene, propane, isoprene, and isobutane. The catalytic pyrolysis of LDPE with HUSY gave a high aromatic compounds (the carbon distribution in range $C_1 - C_{29}$), but when HUSY was used for the pyrolysis of HDPE, most isoparaffins and olefins with carbon number distribution in the range of $C_1 - C_{19}$ were obtained

Acid catalysts such as ZSM-5 and MCM-41, which had different pore sizes and surface acidity were compared with Y zeolite. Adam *et al.*, (2005) studied the pyrolysis of biomass by using Al-MCM-41 catalysts. The report showed that using Al-MCM-41 in biomass pyrolysis gave the large structures of products (especially phenolic compounds) due to the large pore size and the low acidity of Al-MCM-41. Later, Antonakou *et al.*, (2006) also studied the biomass pyrolysis using MCM-41 with varied Si/Al ratio of Al-MCM-41. They found that lower Si/Al ratio (higher surface acidity) and large pore size resulted in the increased yield of aromatic compounds such as naphthalene. Miguel *et al.*, (2006) studied the conversion of tire rubber to hydrocarbon products using various acid catalysts. They used five catalysts in the experiments, which were three types of zeolites (standard ZSM-5, monocrystalline n-ZSM-5, and beta zeolite) and two types of mesostructured materials (Al-MCM-41 and Al-SBA-15). The results showed that three zeolite catalysts had good selectivity to aromatic compounds, especially toluene, m/p-xylene, and benzene. The mesostructured catalysts showed the similar results of those obtained by Adam *et al.*, (2005) and Antonakou *et al.*, (2006). Al-MCM-41 and Al-SBA-15 were good catalysts for aromatization and benzene alkylation due to their had weaker Lewis acidity and larger pore sizes, which allowed larger molecules of products to enter.

2.3 Catalytic Pyrolysis using Bifunctional Catalysts

Pyrolysis with using a special catalyst helps improving the quality and quantity of products, but it is sometimes not sufficient. Then one way to improve the catalyst performance is to load metals to obtain bifunctional catalysts. A large amount of information about bifunctional catalysts has been documented, especially Pt and Pd used for improving the activity on hydrogenation, hydrocracking, isomerization, the ring opening of aromatic compounds and for reducing sulfur tolerance. The hydrogenation and ring opening reaction of PAH have been performed to enhance the quality of diesel oil from pyrolytic oil products. For example, Smermiotis and Ruckenstein (1994) studied the effect of Pt/USY and Pt/L composite in reforming the mixture of n-hexane, methylcyclopentane, and methycyclohexane. The results showed that the composite catalysts increased the selectivity to aromatic $C_{>6}$, and decreased the selectivity to benzene. Next, Corma *et al.*, (1997) also studied the hydrogenation of aromatics in diesel fuel using Pt/MCM-41 and Pt/USY catalysts. They found that, during the hydrogenation, high sulfur tolerance was obtained with using USY and Al-MCM-41. Then, Pt was loaded on Al-MCM-41 surface, resulting to the higher hydrogenation activity of naphthalene than other conventional Pt-containing supports because of the higher sulfur tolerance. In 2000, Park and Ihm studied Pt on several zeolite catalysts in order to obtain a high conversion of n-hexadecane hydroisomerization. Using the Pt/HY catalyst, which had moderate acid strength, a good selectivity to isomerization was obtained. Moreover, the nature of catalyst also affected to catalysis reaction. For examples, Pt/H-beta and Pt/ZSM-5 with strong acid sites were good for cracking. In 2002, Arribas and Martinez used Pt/USY (1 %wt Pt) catalyst for the coupling hydrogenation and ring opening (ROP) of 1-methylnaphthalene. The major products of hydrogenation and ROP of 1-methylnaphthalene were C_{11} alkylbenzene, C_{11} cyclohexane, and C_{11} cyclopentane, which possibly improved the quality of diesel. Moreover, when the Bronsted acidity of catalyst increased, the selectivity of ROP was decreased at over 375°C because the catalyst quickly cracked components to lower molecular weight. They mentioned that the role of Pt was to catalyze hydrogenation products from the hydrocracking of 1-methylnaphthalene followed by

to ROP. Santikunaporn *et al.*, (2004) studied the effect of HY and Pt/HY on ring opening reactions. The results showed that bifunctional catalysts reduced polycyclic aromatic in liquid products, and then it helped to reduce emission to the environment. They mentioned that Pt loaded on acid catalyst improved ring opening reactions.

After that, Arribas and Martinez (2004) focused on the hydrogenation and ring opening (ROP) of tetralin by using Pt/USY. The results showed that when Pt loading on Y-zeolite increased, the rate of isomerization and ROP were increased. Pathway reactions were started from the hydrogenation of tetralin followed by the isomerization of naphthalenic ring of decalins to produce high cetane products.

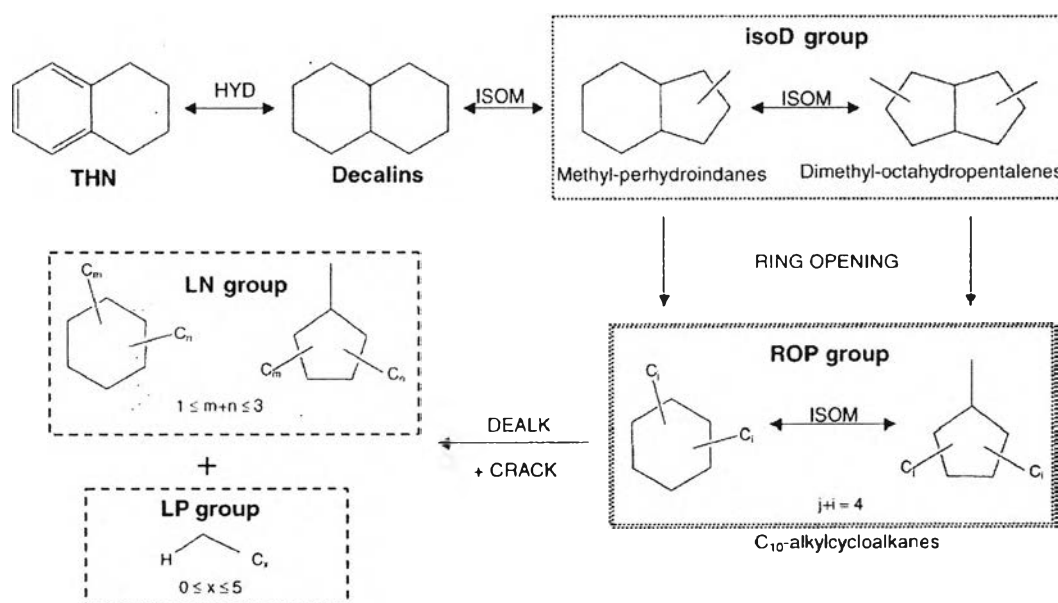


Figure 2.1 Proposed reaction scheme for the hydroconversion of tetralin on bifunctional catalysts (Arribas and Martinez 2004).

Chusuton (2007) studied the influence of bifunctional catalysts on the quality and quantity of pyrolysis products. He reported that Pt/USY improved the quality of liquid product by reducing asphaltene fraction. For the gas products, when the bifunctional catalysts (Pt/USY or Pd/USY) were used, the gas yield increased because the bifunctional catalysts enhanced cracking reaction. In terms of aromatic

compounds, using Pd on various zeolites increased the total concentration of aromatic compounds.

2.4 Catalytic Pyrolysis using Bimetallic Catalysts

Bimetallic catalysts are of researchers' interest due to the distinguished ability of each metal. For example, Lee *et al.*, (1998) studied the sulfur tolerance of Pt-Pd/Beta zeolite for isomerization of n-hexane. They reported that the amounts of sulfur and coke depositing on the bimetallic catalyst were lower than the monometallic one due to the interaction of Pd and Pt, which reduced sulfur adsorption, and then, reducing coke formation. Lee *et al.*, (1998) studied the monometallic and bimetallic catalyst on H β . In their experiment, the monometallic (Pt/H β) for n-hexane isomerization can be deactivated by coking and sulfur depositing. When they used the bimetallic catalysts (Pt-Pd/H β), sulfur tolerance was enhanced due to the interaction between the two metals. Other bimetallic catalysts (Cu-Pt/H β , Ga-Pt/H β and Ni-Pt/H β) did not improve sulfur tolerance. Funez *et al.* (2008) studied hydroisomerization in the liquid phase of C7-C8 by using bimetallic catalysts (Pt/Ni on Beta zeolite). Loaded Pt catalyst was good for linear hydrocarbons conversion. The results showed that using 0.25Pt0.75 NiBeta increased the yield of naphenic compounds (methylcyclohexane and dimethylcyclopentane), and increased the RON value. Kaneda *et al.*, (2009) tried to improve the thermal stability of Pt/Al₂O₃ by adding Pd for NO oxidation. The results showed that Pt/Al₂O₃ was highly active after adding Pd because the sintering of Pt was prevented, and the size of metal cluster was decreased.

Catalyst preparation methods had been also focused as they have some effects which are related to the activity of catalysts. Massa *et al.*, (2006) studied the effects of different preparation methods: impregnation, co-impregnation, and co-precipitation with a surfactant on phenol conversion. The catalyst used was 1%Ru/5%CeO₂-Al₂O₃, and the results showed the impregnated catalysts were active for oxidation phenol. They also mentioned that catalysts prepared by co-precipitation were not good due to the low dispersion of metal. Several catalyst preparations played an important role to metal dispersion on the support, affecting to pyrolysis

products yield. Roldan *et al.*, (2008) studied the effects of different preparation methods (co-impregnation and successive impregnation) of Pd-Pt/ β catalyst on the hydroisomerization of alkanes. From their experiments, successive impregnation method in which Pd was loaded firstly showed the best catalytic activity was compared to other methods, and caused the greater activity of the Pd-Pt/ β due to more homogeneous from more distribution of Pt-Pd bonds.

The sulfur resistance of bimetallic catalysts was the important property for condition which has infected sulfur. Many researchers studied the enhancement of sulfur tolerance. Yasuda *et al.*, 1999 reported that it was well known that acidic H^+ on a zeolite reduced the e^- density of supported metal, thereby weakening the bonding energy between an e^- deficient metal and an e^- acceptor sulfur. The electronic influence of the two metals may make the Pd atoms less sulfur sensitive and thus more catalytically active (Niquille-Röthlisberger and Prins 2006). Medrano *et al.*, 2009 reported their work that the adsorption of H_2S and S over such Pd^+ did not occur due to their high e^- deficiency, which significantly reduced metal affinity with the e^- acceptor S atom. Roldan *et al.*, 2008 also studied the sulfur tolerance of Pd-Pt/ $H\beta$. They found that Pd presence in the on the sulfur tolerance may be attributed to the increase in the amount of e^- deficient metal sites which in turn reduced the electrophilic S adsorption and S-induce coke.

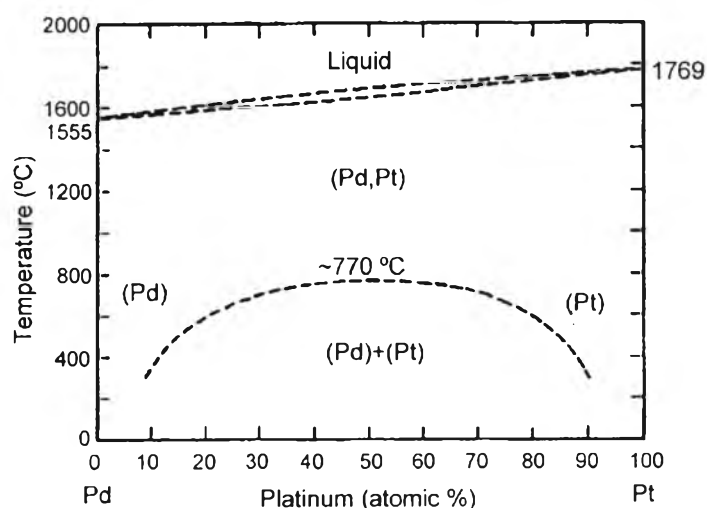


Figure 2.2 Phase diagram for Pd-Pt alloy (Massalski, 1992)

In the region below 770 °C, the phase compositions vary with temperature and Pt/Pd atomic ratio. This region contains three phases: single-phase Pd, segregated Pd-Pt, and single-phase Pt. The solid solutions are divided into two separate phases consisting of Pd and Pt, which is a Pd-rich solid solution with a maximum 15 % of Pt at 500 °C, and a Pt-rich solid solution with a maximum 15 % of Pd at 500 °C, respectively. At points under the miscibility gap, the homogeneous solid solutions for bimetallic Pd–Pt systems might be expected in Pd or Pt under conventional reducing temperatures (Yoshimura *et al.*, 2007).

From the above literature review, using a bimetallic catalyst is a good way to improve the quality and quantity of a desired product. In this work, bimetallic catalysts were used for studying on tire pyrolysis.

Y zeolite has a 3-dimensional pore structure. It has 12 memberring with 7.4Å pore diameter. Figure 2 showed ten sodalite cages connected on their hexagonal faces forming some cavities or supercages. Typically, the void volume fraction, Si/Al ratio, and thermal decomposition Y zeolite are 0.48, 2.34, and 793°C, respectively (<http://www.personal.utulsa.edu/~geoffrey-price/zeolite/fau.htm>).

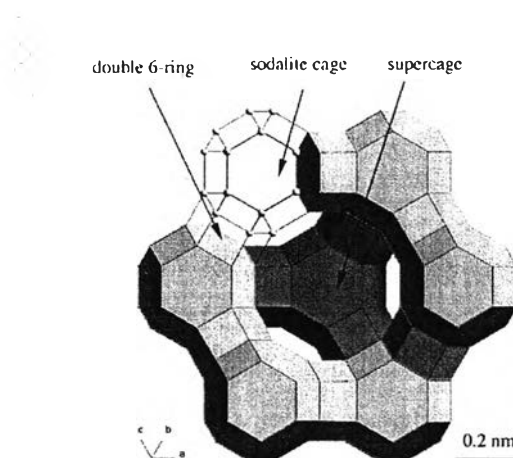


Figure 2.3 Schematic diagram of the zeolite-Y.

(<http://www.rsc.org/ej/JM/2000/b002473m/b002473m-f1.gif>)

Pt was used for catalytic reforming (isomerization, hydrogenolysis, and hydrocracking) to enhance quality of oil, but it easily deactivates by coking and sulfur poisoning. Moreover, Pd loading can enhance the sulfur tolerance due to

interaction between Pt and Pd. For this work, it was hypothesized that using bimetallic Pt and Pd catalyst can enhance the quality and quantity products. Moreover, the preparation method and metal ratio can also affect to the activity of catalysts. Then, the catalysts were also prepared by different preparation methods with various metal ratios.