CHAPTER II
BACKGROUND AND LITERATURE SURVEY

2.1 Overview of Diesel Fuel

The German engineer, Rudolph Diesel, patented the diesel engine in 1892. He initially considered powdered coal and liquid petroleum as possible fuels. Powdered coal proved difficult to inject into the engine cylinder and eventually caused an explosion that destroyed the prototype engine. As a result, Mr. Diesel turned to experiment with liquid petroleum, which later became known as "diesel fuel." Adolphus Busch built the first commercial diesel engine in the United States. Busch, a brewer in St. Louis, Missouri, had seen the diesel engine at an exposition in Munich and purchased a license from Diesel to manufacture and sell the engine in the United States and Canada.

At the end of World War I, soldiers who had operated diesel engines in submarines began to adapt them for the peacetime economy. One modification was the development of the "semi-diesel" engine used in trucks in the 1930s. These trucks were nicknamed "smokers" because of their dark, smoky emissions.

Since the advent of diesel regulations in the late 1960s, diesel engine manufacturers have substantially re-designed products to reduce emissions. Design modifications such as cooled exhaust gas re-circulation, injection-timing delay, and higher injection pressures, along with cleaner fuel, have reduced diesel engine emissions by 80 to 90% over the last 20 years. On average, today's diesel truck engines emit nearly 70 percent less nitrogen oxide and 90 percent less particulate matter than in 1987. Diesel engine manufacturers are continuing to use a combination of these and other emission control options to reduce harmful emissions.

Diesel fuel is heavier and oilier than gasoline. Because diesel fuel requires less refining, it is generally cheaper than gasoline. Diesel fuel also has a higher energy density than gasoline, which means that a gallon of diesel fuel provides more power than a gallon of gasoline. In fact, diesel engines typically offer 45 percent to 60 percent better fuel economy than gasoline engines.

In a gasoline engine a spark ignites the fuel, whereas in a diesel engine the fuel is ignited by the compression of air in the engine's cylinders. A diesel engine's ability to constantly change the mixture of air and fuel allows it to generate additional power when needed and to haul heavy loads more easily. Diesel engines are typically heavier and more expensive than gasoline engines.

Diesel exhaust contains several pollutants that, alone or in combination with other substances, can be harmful to public health. These include hydrocarbons, nitrogen oxides, fine particulate matter, carbon monoxide, and toxic air contaminants known as hazardous air pollutants (Song *et al.*, 2000).

- Nitrogen oxides (NOx) are by-products of fuel combustion and contribute to the formation of ground-level ozone or "smog." Health effects include coughing, shortness of breath, and decreased lung function.

- Fine particulate matter (PM2.5) is the term used for the mixture of solid particles and liquid droplets in the air. Because of its small size, fine particulate matter can be deposited deep in the lungs, where it can cause health problems. Nitrogen oxides and sulfur dioxides are also major sources of fine particulate matter. Recent studies have shown an association between particulate matter and premature mortality from respiratory and cardiovascular disease, and increased incidences of respiratory illness, particularly in children and the elder. For adults with heart or lung conditions, exposure to fine particulate matter can cause more illness and in some cases premature death. More than 90 percent of the particulates found in diesel exhaust are fine particles.

- Hydrocarbons (HC) are formed by incomplete fuel combustion. When combined with NOx in the presence of sunlight, HCs produce ground-level ozone or "smog," which can irritate eyes, damage lungs, and aggravate respiratory problems. Symptoms include coughing, shortness of breath, and decreased lung function. Many hydrocarbons are also considered hazardous air pollutants.

- Carbon monoxide (CO) is formed by incomplete fuel combustion. Carbon monoxide reduces the flow of oxygen in the bloodstream and is of particular concern to people with heart disease.

- Diesel exhaust contains 40 substances that the U.S. Environmental Protection Agency lists as hazardous air pollutants (HAPs) - 15 of which are considered probable or known human carcinogens. Of greatest concern are acetaldehyde; benzene, 1,3-butadiene, formaldehyde, and polycyclic aromatic hydrocarbons (PAHs).

Nitrogen oxides contribute to acid rain and to the acidification of lakes and soils. They can also affect aquatic ecosystems by providing too many nutrients to aquatic plant life, which reduces dissolved oxygen levels and can ultimately harm the ecosystem. In addition, nitrogen oxides and hydrocarbons contribute to the formation of ground-level ozone or "smog," which is highly corrosive and damages crops and forests.

Particulate matter is a major cause of poor visibility and haze in many parts of the United States. Air pollution, largely due to particulate matter, has reduced visibility in some areas from 90 miles to only 14 to 24 miles. Visibility has been affected in urban centers and in scenic rural areas as well. Fine particulate matter can remain suspended in the air for days and travel long distances.

Over the past 20 years, design modifications such as cooled exhaust gas recirculation, injection timing delay, and higher injection pressures have reduced diesel engine emissions by 80 to 90 percent. Diesel engine manufacturers will continue to use a combination of these and other emission control options to reduce harmful emissions.

Green Diesel Technology is a new engine technology that lowers emissions from diesel trucks and buses that use new low-sulfur fuels. International Truck and Engine Corporation developed the Green Diesel Technology, and in May 2000 announced plans to unveil a school bus that uses it in mid-2001.

The Green Diesel Technology optimizes combustion to lower nitrogen oxide emissions by 25 percent. It also replaces the muffler with a catalyzed particulate filter that virtually eliminates hydrocarbons and carbon monoxide, and reduces particulate matter to 50 percent below levels achieved by natural gas

engines. The Green Diesel Technology engine can be retrofitted into most trucks and buses.

There are many advantages of using the diesel engine. Firstly, they are the most economical engines to operate due to their high power density. Moreover, they are highly reliable and very durable, and there is an effective infrastructure for fuel distribution. In addition, models are available in a wide power range, and the engine can be modified to operate with alternative fuels.

Diesel oil, however, is the main source of SOx emissions due to transportation in Europe. The sulfur content in gas oil was limited to 0.2-0.3 wt% in 1992; it was to decrease to 0.05% in 1996 and could be slightly lower beyond 2000. The tendency of the cetane index is increased because of its favorable influence on emissions (mainly NOx and particulates and, to a lesser extent, CO and Volatile Organic Compounds). From a value slightly less than 50 now, its lower limit might increase to 52 or even 55 beyond 2000 (Ertl *et al.*, 1997). As there is a direct relationship between the cetane index and the aromatics content, the latter specification will also be more severe in the near future: values less than 20 vol% or even 10 vol% are being suggested for 2000 and beyond. Pour point has no influence on emissions, but it is an important specification for the good operability of diesel engines, especially in winter. Specifications concerning the pour point depend greatly on the climate and can be noticeably different from one country to another. They should not change a lot in the future.

Today, diesel oil is a blend of cuts coming from primary distillation, hydrocracking units, FCC light cycle oil, and also some products obtained by thermal treatments such as visbreaking or coking. Hydrotreated straight-run diesel oils have good cetane numbers, whereas LCOs and thermal conversion blending streams do not meet the required sulfur content and cetane indexes and even the aromatics content required.

Types of Aromatic Compounds in Petroleum Fractions

There are many types of aromatic compounds in petroleum fractions which are analyzed by several techniques such as high performance liquid chromatography (HPLC), ^{13}C nuclear magnetic resonance ($^{13}CNMR$), gas chromatography-mass

spectrometry (GC-MS), ultraviolet (UV) and infrared (IR) techniques. These techniques have shown that the aromatics found in petroleum and synthetic middle distillates mainly fall into four groups: (i) monoaromatics, (ii) diaromatics, (iii) triaromatics, and (iv) polycyclic aromatics (Stanislaus and Cooper, 1994).

Table 2.1 Aromatic compounds in Kuwait Atmospheric Gas Oil

Aromatic type	Aromatic content (wt %)
1. Monoaromatics	
C_3-C_6 alkyl benzenes	3.68
C_1-C_5 benzothiophenes	14.24
2. Bicycloaromatics	
C_0-C_4 naphthalenes	52.81
C_0-C_4 dibezothiophenes	14.38
C_0-C_4 fluorenes	4.12
C_1- benzyls+ dibenzofuran	4.07
3. Triaromatics	
C_0-C_4 phenanthrenes	6.20
C_0-C_4 pyrenes/fluoranthrenes	0.5
Total	100

The polycyclic aromatics with four or more condensed benzene rings are largely present in many high-boiling petroleum fractions (BP> 350°C), whereas the other three types are important components of middle distillates. Typical analysis data on the type of aromatic compounds present in untreated gas oil fractions of Kuwait petroleum are presented in Table 2.1. It is seen that di-aromatics (mainly alkyl naphthalene) constitute a major portion of the total content of aromatics in straight-run gas oil. However, in hydrotreated oils, monoaromatics are present in larger quantities than di- and tri-aromatics, as shown in Table 2.2.

Table 2.2 Properties of hydrotreated and unhydrotreated Gas Oils (First-stage hydrotreating)

Aromatic type	Light Gas Oil (LGO)		Light Cycle Oil (LCO)	
	unhydrotreated	hydrotreated	unhydrotreated	hydrotreated
Total aromatics	33.7	31.6	70.2	70.9
Mono-	17.7	22.4	11.2	38.5
Di-	11.5	5.7	49.5	26.9
Tri^+-	4.5	3.5	9.5	5.5
Polars	-	-	0.8	0

Condensed multi-ring aromatic compounds are hydrogenated more easily to the corresponding monoaromatics under mild hydrotreating conditions, whereas conversions of the monoaromatics remain nearly unchanged. The hydrogenation of the monoaromatics is the key step in the production of low-aromatic diesel fuel. With conventional hydrotreating catalysts this can only be achieved at high hydrogen pressures and low space velocities, generally requiring new and expensive equipment.

2.2 Hydrogenation of Aromatic Compounds

Deep hydrogenation is favored at a lower temperature. However, conventional hydrotreating catalysts are active only at relatively high temperatures (>300°C). It is therefore natural to consider deep hydrogenation at low temperatures (<300°C). The potential candidate catalysts for low-temperature hydrotreating include noble metals. Since it is known that noble metal catalysts are easily deactivated by sulfur compounds, a two-stage processing strategy is being adopted. The first stage involves deep desulfurization of the fuels using metal sulfide catalysts, and the second stage deals with hydrogenation over noble metal catalysts. Some representative polyaromatic structures are shown below.
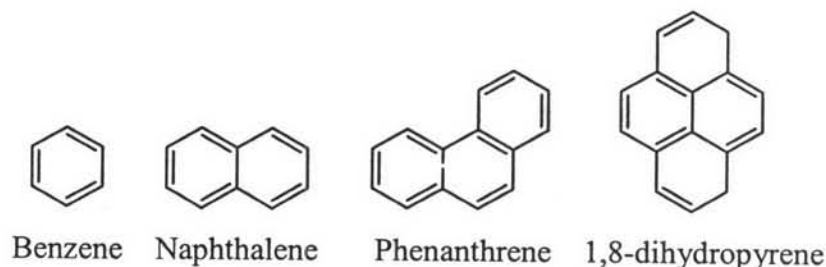
Benzene   Naphthalene   Phenanthrene   1,8-dihydropyrene

Figure 2.1   Ring-structures of representative polycyclic aromatic compounds in diesel fuels.

The hydrotreating is typically carried out by a two-stage process. The first-stage hydrotreating process, which uses bimetallic catalysts (CoMo, NiMo, and NiW on Al_2O_3), can only work under severe operating conditions, such as higher hydrogen pressure and higher temperature. The other is the second-stage hydrotreating process using monometallic or bimetallic catalysts (Ni, Pd, Pt and Pt-Pd) in the second stage; it can achieve deep levels of aromatics hydrogenation under mild operating conditions, such as moderate hydrogen pressure and lower temperature. However, noble metal catalysts are easily poisoned by small amounts of sulfur. The hydrodesulfurization unit in the first-stage reactor, then, has to reduce the level of sulfur in a few ppm.

A revolution of the refining process started since the discovery in 1950 of alumina-supported NiMo and CoMo catalysts used in a wide range of crude oils. The concern in desulfurization became a major issue, whereas dearomatisation was only of minor importance at that time. Sulfur content in diesel fuel is an environmental concern because during combustion, sulfur is converted to SOx, which not only contributes to acid rain but also poisons the catalytic converter for exhaust emission treatment.

The removal of aromatic hydrocarbon has received considerable attention because it is related to the improvement of combustion efficiency, and lower particulate and NOx emission (Cooper and Donnis, 1996). In addition, the decreasing of aromatics content is also closely related to the increase of cetane number.

Cetane number is one of the very important properties of diesel fuel oil. It is the measurement of a diesel fuel's ignition quality. Ignition quality is measured by ignition delay, the time between the start of fuel injection and the start of fuel combustion. Fuels with good ignition quality give short ignition delays and are assigned high cetane number. Cetane number should not be considered alone when evaluating diesel fuel quality. Viscosity, API gravity, BTU content, distillation range, sulfur content, stability and flash point are also very important.

Recently, a lot of research has studied the ring opening of the last ring of the naphthenic ring which is a promising reaction to obtain a high cetane number. The figure below (2.2) is the proposed aromatics saturation (ASAT) plus selective ring opening (SRO) naphthenic upgrading chemistries (McVicker *et al.*, 2002). The saturation of naphthalene to decalin, requiring the addition of 5 mol of hydrogen, improves both density and cetane number. However, the lowest density achievement by the complete saturation of naphthalene is near 0.9 and the maximum cetane number is about 38. To comply with anticipated diesel specifications of densities < 0.85 and cetane number > 40, product improvements are needed.
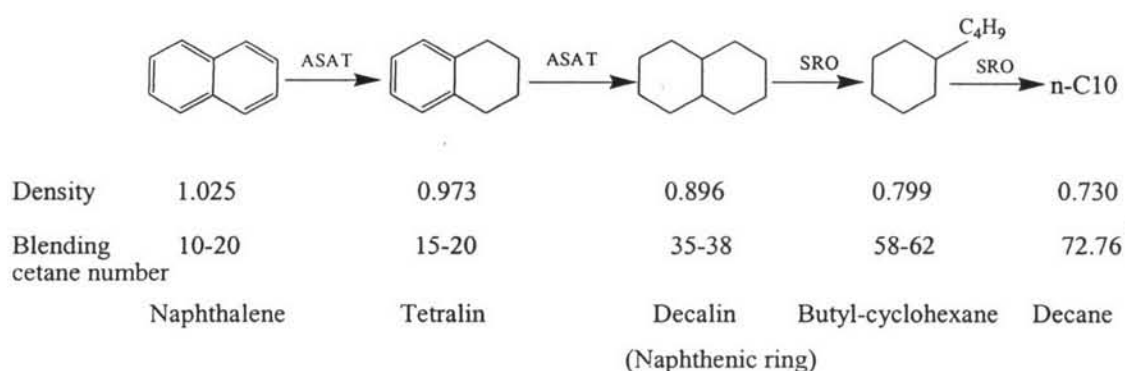
	Naphthalene	Tetralin	Decalin (Naphthenic ring)	Butyl-cyclohexane	Decane
Density	1.025	0.973	0.896	0.799	0.730
Blending cetane number	10-20	15-20	35-38	58-62	72.76

Figure 2.2 Aromatic saturation of multi-ring aromatics followed by selective ring opening which provides density and cetane number benefits.

In order to achieve the ring opening, naphthalene can be hydrogenated to tetralin, and further to decalin. And then, decalin becomes the ring opening product. Selective ring opening can be carried out on certain noble metals by hydrogenolysis.

Alumina is the most widely used support because it is inexpensive, structurally stable and because it can be prepared with a wide variety of pore sizes and pore size distributions. Commercial materials are available with surface areas in the range of 100 to 600 m^2/g and down to essentially nonporous alumina. A number of different crystalline phases can exist. The most important aluminas for use as carriers are the transition aluminas. γ-Al_2O_3 is of greatest interest since it has a high area and is relatively stable over the temperature range of interest for most catalytic reactions.

γ-Alumina has a high surface area (typically about 250 to 350 m^2/g). Further heating to about 850°C, either in use or in regeneration, converts this to δ-alumina. Above 1,100°C, this is converted to the θ form, which then goes to α-alumina with the collapse of the structure and the formation of the dense, low-area material. The θ form can be stabilized by the addition of rare earth oxides or other additives. The nature of various additives and impurities present, as well as the environment, can have a marked effect on high temperature stability. Thermodynamically, hexagonal α-alumina is the stable form at all temperatures, and structures such as γ, η, etc., are frequently referred to as transition aluminas. These are not hydrated structures, and they are more or less crystalline (Satterfield, 1991).

The aluminas formed at temperatures of about 300°C or more are not hydrated but contain small amounts of water, which is gradually evolved on heating to higher temperatures. The conversion of OH groups to water on heating leaves behind a structure, with exposed aluminum atoms, which behaves like a Lewis acid. In addition, Bronsted-type acidity exists, steaming from the OH groups. Strong acidity may be produced by deliberately incorporating halogens such as chlorides or fluorides in the structure to catalyze reactions of various hydrocarbons as in catalytic reforming. The halide may be introduced inadvertently if a metal halogen compound, such as $PdCl_2$ or H_2PtCl_6, is used in the catalyst preparation.

The hydrogenation of tetralin over sulfided NiW/Al_2O_3 and $NiMo/Al_2O_3$ catalysts has been studied by Yasuda $et\ al.$ (1997). The sulfided NiW/Al_2O_3 catalyst could only work in tetralin hydrogenation under low H_2S partial pressure, and the structure of the sulfide phases was quite stable in the reducing atmosphere. On the

other hand, the sulfided $NiMo/Al_2O_3$ catalyst was advantageous in tetralin hydrogenation under high H_2S partial pressure, where the hydrogenation activity of both catalysts were inhibited by H_2S. The sulfided $NiMo/Al_2O_3$ catalyst under low H_2S was less stable than the sulfide NiW/Al_2O_3 catalyst due to the structural changes of the active phases.

After Yasuda's study, Rodriguez *et al.* (2003) studied the Ni-impregnated-Zr-doped mesoporous molecular sieves as catalysts for the hydrogenation and ring-opening of tetralin. They found the zirconium-doped mesoporous silica is a suitable support for the high metal loading of nickel where the metal support interaction is moderate. Moreover, the high metal loading leads to large metallic particles mainly located on the external surface of the support. These catalysts are very active in the hydrogenation of tetralin at 350°C, especially those with high nickel content, which causes no deactivation by coke deposition.

A variety of noble metals (Pt, Pd) on alumina support were examined for competitive hydrogenation of poly-aromatic hydrocarbons on sulfur resistant bimetallic Pt-Pd catalysts by Jongpatiwut *et al.* (2004). It was found that platinum-palladium bimetallic catalysts perform better than either of the monometallic catalysts. Catalyst preparation affected catalyst property activities, like calcinations temperatures and order of impregnation.

The noble metal catalysts (Pt, Pd, and Pt-Pd) on βZ and silica-alumina supported have been compared in the simultaneous hydrogenation of toluene and naphthalene in the presence of dibenzothiophene. From the experiment, Pawelec *et al.* (2002) presented that the Pt-Pd/βZ catalyst at a high metal content gave higher activity for the hydrogenation of toluene than the one with a low metal content. The only way to enhance the activity and stability of the βZ catalyst for the hydrogenation of aromatics is by increasing the noble metal content and by neutralizing the support after calcining the acidic sample.

Yasuda and Yoshimura (1997) reported that the coexistence of Pt with Pd on USY zeolite (SiO_2/Al_2O_3 = 680) greatly enhanced the tetralin hydrogenation activity and improved sulfur tolerance, which depended on the Pt/Pd ratio and reached a maximum at a Pd:Pt mole ratio of 4:1. The reaction was carried out at a

hydrogen pressure of 3.9 MPa at 553 K in the presence of dibenzothiophene at a sulfur concentration of 500 wtppm. After that, Yasuda *et al.* (1999) studied the sulfur-tolerance of a Pd-Pt/Al$_2$O$_3$-B$_2$O$_3$ catalyst for aromatic hydrogenation. They found that the Pd-Pt/Al$_2$O$_3$-B$_2$O$_3$ catalyst had higher sulfur tolerance than the catalyst supported on SiO$_2$-Al$_2$O$_3$, γ-Al$_2$O$_3$, SiO$_2$ and USY zeolites for the hydrogenation of tetralin in the presence of DBT and excellent hydrogenation selectivity.

The addition of a second metal (e.g. Pt-Pd or Pt-Ge) was found to enhance the sulfur tolerance. This promotion has also been ascribed to a change in the electronic properties. It has been shown that the addition of germanium to platinum decreases the rate of aromatic hydrogenation, whereas the addition of palladium to platinum gives higher hydrogenation activity. It was concluded that the decrease in metal-S bond strength is not a sufficient condition to obtain high aromatic hydrogenation activity in the presence of H$_2$S (Guillon *et al.*, 2001).

Pawelec *et al.* (2004) studied deep aromatic hydrogenation over Au-Pd/γ-Al$_2$O$_3$ catalysts under a hydrogen pressure of 5.0 MPa and temperatures of 498, 523, 548 K; they found that the bimetallic Au-Pd on γ-alumina showed the highest activity in the hydrogenation of naphthalene, but without a synergistic effect between the Au and Pd particles.

Monometallic Pt catalysts are usually not used for hydrotreating because of their sensitivities to sulfur compounds in the feedstock. However, the bimetallic Pt-Pd catalyst has shown much higher sulfur resistance. The hydrodesulfurization (HDS) of dibenzothiophene activity on several catalysts decreased in the order : Co(5)-Mo(16) ≈ Pt(3)-Pd(10) ≥ Pt(3) > Pd(10) and the hydrogenation (HYD) of phenanthrene activity decreased in the order : Pt(3)-Pd(10) ≥ Pd(10) > Pt(3) ≥ Co(5)-Mo(16). The noble metal catalyst, Pt(2)-Pd(10), showed a comparable HDS result and excellent HYD promotion when compared with the conventional Co-Mo catalyst (Qian *et al.*, 1999).

Rousset *et al.* (2001) found that Pt is the most active catalyst at low sulfur concentration. In contrast, Pd became slightly more active than Pt for high sulfur content.

Augusto *et al.* (2001) found that the addition of potassium decreases the number and strength of acidic sites presenting in the Pt/Y catalyst, and that the change in acidity is associated with the support, since the acidity of metal/zeolite catalysts originates from the zeolite rather than from the metal. Both nitrogen and sulfur poisons influenced the cis/trans selectivity of tetralin hydrogenation. In 2002, Arribas and Martinez found that the presence of Bronsted acid sites is required to achieve some reactions, for example, isomerization, ring opening, cracking and dealkylation. Furthermore, because zeolite is somewhat expensive, the use of zeolites as a support is economically less attractive.

Zeolite-supported noble metal catalysts have also been receiving more attention as aromatics hydrogenation catalysts. Fujikawa *et al.* (2001) suggested that the lower apparent activation energy for the hydrogenation of aromatics over Pt/HY catalyst is probably responsible for a stronger adsorption of the aromatics on the Bronsted acid sites of the HY zeolite. They concluded that the acidic properties of the catalyst play an important role in the kinetic behavior of aromatics hydrogenation. However, zeolites drastically increase undesirable cracking activity, which accelerates the rate of coke deposition and enhances the yields of naphtha and gas. These circumstances are caused by the acidity of zeolite being too high.

It has been recognized for some time that the incorporation of fluorine in oxide catalysts enhances their activity for acid-catalyzed reactions such as cracking, isomerization, alkylation, polymerization, and disproportionation. The incorporation of fluorine increases the activity by enhancing the acidic properties of the catalyst. The enhancement of catalytic properties in fluorinated metal oxide catalysts is associated with a change in the surface chemistry of the catalyst. The addition of fluorine can cause lower metal dispersion and the orders of impregnation affect metal dispersion. Since fluorine is an electronegative atom, the replacement of OH groups by fluorine made the metal electron deficient on the surface of the catalyst. As a result, it enhanced the sulfur tolerance of the catalyst (Jongpatiwut *et al.*, 2004). Recently, the effect of promoter by using fluorine and chlorine in the hydroconversion of cyclohexene was found by Aboul-Fotouh and Aboul-Gheit, (2001) using platinum-containing catalysts with other noble metals. They found that metal fluorides are more significantly produced than the metal chlorides in

monometallic catalysts, which may decrease the promoting effect of fluorine. In bimetallics, clusters of the metals are formed, which may protect them from excessive halide formation. Thus, F acts as a more efficient promoter for bimetallics for enhancing hydrogen spillover due to its higher electronegativity and stronger inductive effect.

In 2003, Eliche-Quesada *et al.* studied the effects of preparation method and sulfur poisoning on the hydrogenation and ring opening of tetralin on NiW/zirconium-doped mesoporous silica catalysts. They found that Nickel-tungsten impregnated mesoporous silica with a Ni loading of 20 wt% and a W loading of 5 wt% is an excellent catalyst for the hydrogenation and ring opening of tetralin subjected to high hydrogenation pressure, with a good thiotolerance. The order of impregnation affects the dispersion and the nature of the active phases and, as a consequence, the performance of the catalysts. The consecutive impregnation of nickel and tungsten seems to be the best procedure for obtaining a catalyst with an improved ring opening activity and thiotolerance.

The support is also important for the development of aromatic hydrogenation catalysts. It is well-known that the sulfur tolerance of noble metals increases when they are supported on acidic supports. However, strong acid sites on the supports cause undesirable reactions, such as hydrocracking and coke formation. Olsbye *et al.* (1997) studied Pt/alumina catalysts preparation. They reported that hexachloroplatina complex anions were specifically adsorbed on the surface of aluminas at pH >4. At pH <4 the alumina was highly soluble. A maximum adsorption of Pt was achieved at a pH around 4 with contact times of 24 h or more. γ-alumina and θ-alumina were found to exhibit similar adsorption properties towards the hexachloroplatinic complex.

In 2003, Hedoire *et al.* presented that the Bronsted acidity of the zeolite used to disperse molybdenum sulfide had a marked influence on the catalytic and electronic properties of the active phase. This means that the concept of changing the properties of metal particles is by changing the acid/base properties of the support interaction.

Platinum, supported on alumina catalysts, was prepared by impregnation methods under various conditions. Matsuhashi *et al.* (2004) presented that (1) high dispersion of platinum was achieved without extra modification of the catalyst preparation method, (2) an attentive pretreatment brought a highly reproducible result in the platinum dispersion measurement, (3) the catalytic activities for the combustion of propane, the hydrodesulfurization of thiophene and hydrogenation of naphthalene were affected by the starting materials of platinum, and (4) the relation between the turnover frequency and platinum dispersion was negative in the combustion of propane, the oxidation of CO, the hydrogenations of ethylene and naphthalene, hydrodechlorination of trichloroethane (CH_3CCl_3), and the hydrodesulfurization of thiophene.