Chapter II

Literature Review

LITERATURE REVIEW

2.1 Hydroprocessing:

Hydroprocessing of commercial feeds is extensively practiced in the petroleum industry, and to some extent in coal liquefaction and in upgrading of synthetic fuels.The process involves hydrotreaing of atmospheric residues and / or heavy vacuum residues in a trickle – bed reactor, or ebullating – bed reactor or in a series of fixed – bed reactors containing catalysts. The process unit, works primarily as a desulfurization unit, but also reduces the metals, asphaltenes, and nitrogen in the products, thereby, ensuring proper quality of purified feed for downstream conversion units (i.e. fluid catalytic cracking, delayed Coker).

As an addition benefit, mild hydrocracking also occurs in the hydroprocessing with the conversion of residues to distillates. The process, employing a molybdenum catalyst supported on a high surface area transition alumina and promoted by cobalt or nickel, is carried out in a trickle-bed reactor or ebulleting-bed reactor at elevated temperature and hydrogen pressure. Graded catalyst systems in the different types of reactors are used in order to achieve hydrodemetallation (HDM), hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and conversion of residues to distillates at desired levels **[Furimsky and Massoth, 1999] [Topsoe et al., 1996]**.

Beside these reactions, hydrodeoxygenation (HDO) is observed for coal – derived liquids. These reactions involve hydrogenolysis of C–heteroatom bonds; an important attendant reaction is hydrogenation of aromatics (HYD) typical classes of these reactants are shown in ***Figure (1).***

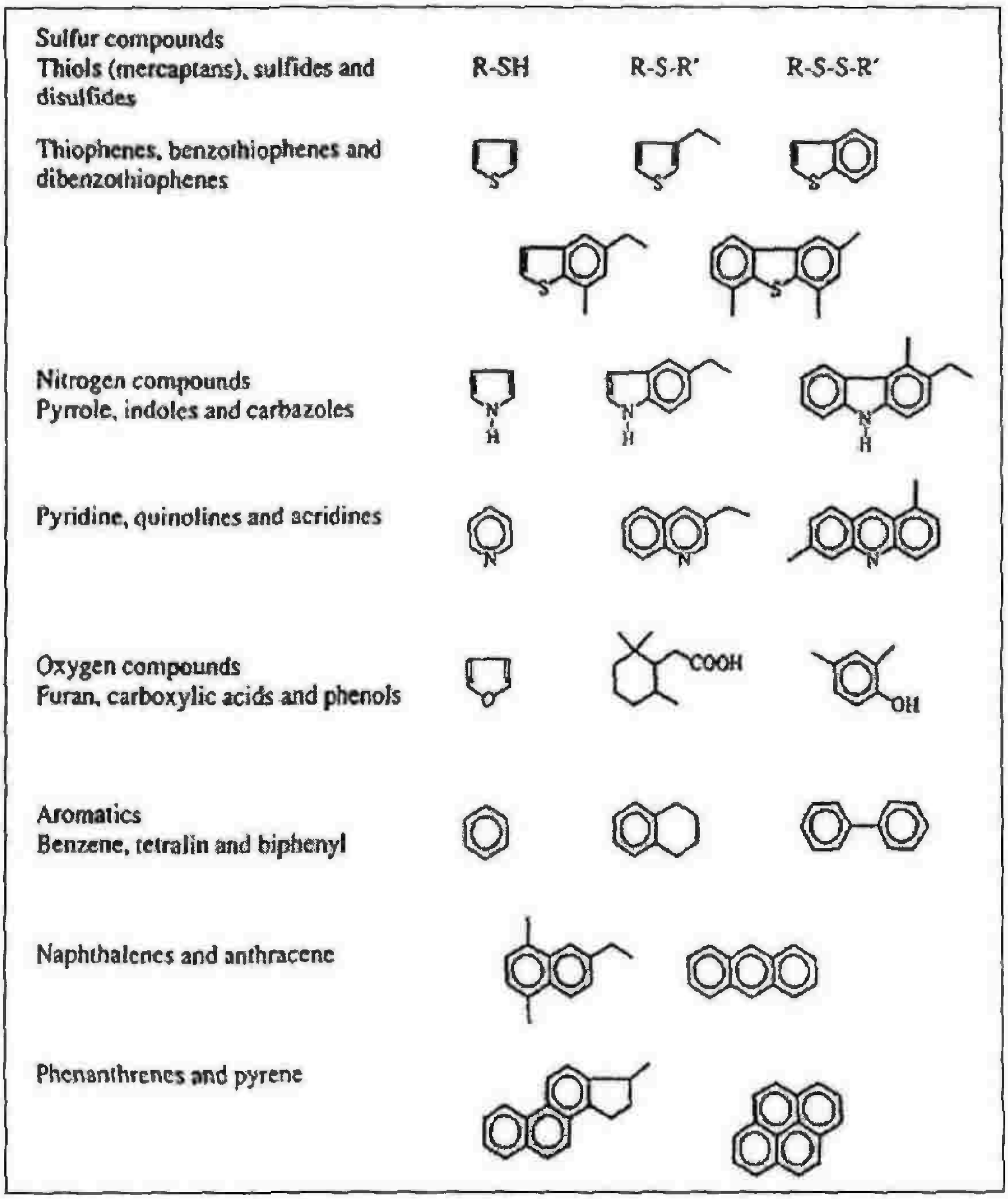

Figure (1): Typical Heteroatoms and Aromatic Compounds found in Petroleum **[Furimsky and Massoth, 1999]**

As well as C – C bond cleavage when hydrocracking of a feed is one of the objectives. Extensive information on these aspects of hydroprocessing is documented in the scientific literature **[Angelici, 1997] [Yang et al., 2008] [Perot, 2003]**.

An advanced petroleum refinery indicates the presence of several processes employing catalytic reactors **[Inomata et al., 1997]**. After distillation, some distillates require additional treatment to attain specifications of commercial fuels. For conventional distillates, this can be achieved by mild hydrorefining, whereas for the high sulfur and high nitrogen distillates, more severe conditions may be needed. Fluid catalytic cracking (FCC) is employed with the aim to increase production of liquid fuels. In this case, a gas oil fraction is cracked to lighter fractions. The FCC product has to be subjected to hydrotreatment and distillation. In some cases, the feed for FCC has to be hydrotreated to prevent poisoning of the FCC catalyst. Depending on the feed, the production of lubricants may include two steps, i.e., a dewaxing step followed by a hydrorefining step. It is evident that several catalytic processes may be part of the same petroleum refinery. A continuous change in crude oil quality and fuel specifications, the number of these processes will continue to increase. Improved and / or new catalysts will have to be developed.

An optimal match between the properties of the feed and catalyst has to be obtained to achieve high hydroprocessing conversions in a particular reactor. Both the chemical composition and physical properties of the catalyst are important **[Furimsky, 1998]**.

Hydroprocessing reactions occur on the active sites of the catalysts. Also, a suitable pore size distribution is required to ensure the access of reactant molecules to the active sites **[Furimsky and Massoth, 1999]**.

2.1.1 Hydrotreating Processes:

Hydrotreating (HDT) is essential in order to comply future legislations to clean the environment or remove of undesirable contaminants from petroleum fractions **[Rana et al., 2007]**.Catalytic hydrotreating and hydroconversion processes are extensively used in the petroleum refining industry for the upgrading of heavy oils and residues. Two types of reactor technologies, namely, fixed – bed and ebullated – bed are commonly used in these processes **[Kabe et al., 2001] [Higashi et al., 2002]**.

In the fixed – bed process, pre – heated feed and hydrogen passes in the down – flow mode over a series of reactors packed with catalysts.

In the ebullating – bed process, pre – heated feed and hydrogen enter the bottom of the reactor, and the catalyst bed is maintained in an ebullated (expanded) state by an upward flow of feed and the internal liquid recycles **[Al-Dalama and Stanislaus, 2006]**.

Hydrotreating processes are used primarily for reducing sulfur in petroleum products. In addition, the processes are used to reduce the nitrogen and oxygen content present in some crude oils, as well as to remove metals.

The hydrotreating processes are also variously known as hydrodesulfurization (HDS) which are common and commercially proven in modern day refineries.

These catalytic processes have two defined roles: desulfurization to supply low sulfur fuel oils and pretreatment of feed residue **[Oyekunle et al., 2005] [Djangkung et al., 2005]**.

Hydrodesulfurization of refractory sulfur species is the key task to achieve the tightened regulation that the sulfur content in diesel fuel must be less than 10 ppm **[Murti et al., 2005] [Marafi and Stanislaus, 2008]**.

Because of severe regulations for the emission from diesel vehicles, ultra – deep hydrodesulfurization (HDS) of gas oil currently becomes an important issue. For example, the sulfur content of gas oil in Japan is regulated below 50 mass ppm – sulfur at present and is decided to be below 10 mass ppm – sulfur in a new regulation that will be brought into operation from 2007.

Therefore, great effort has been made to develop catalyst effective for ultra – deep HDS of gas oil **[Koizumi et al., 2005] [Egorova and Prins, 2004]**.

Sulfur containing compounds such as thiophenes, dibenzothiophenes and mercaptans are removed. The removal is necessary in order to minimize the polluting effects of sulfur – containing gases such as SO_x that may be released to the atmosphere **[Al-Zeghayer et al., 2005]**.

In addition, hydrodemetallization (HDM) is other types of hydrotreating processes for removing both vanadium and nickel present in the heavy oil fractions **[Oyekunle et al., 2005]**.In recent years, hydrodemetallization catalysts have been developed to protect the more active HDS catalysts. This involves the development of new HDM catalysts for primary treatment and the production of new HDS catalysts for secondary treatment **[Speight, 2004]**.

Hydrodenitrogenation (HDN),hydrogenolysis (HDH), and

hydrodemetallization (HDM), usually dictated by the characteristics of the feedstock, although all sub processes take place to varying degrees on different hydrotreating catalysts. Hydrotreating processes are designed to minimize; cracking reactions, coke formation and hydrogen consumption.

The HDN of N-containing heterorings requires more severe conditions (high H_2 pressure) than that of other heteroring- compound **[Furimsky and Massoth, 1999] [Al – Megren et al., 2005]**.

2.1.2 Hydroprocessing Catalysts:

The catalysts of concern in hydroprocessing consist of molybdenum supported on a high surface area carrier, most commonly alumina, promoted by cobalt or nickel (Ni / Mo – Co / Mo). These catalysts are active in the sulfided state, being either presulfided or sulfided on stream with a sulfur containing feed. Sulfided catalysts containing Mo consist of essentially monolayer slabs or clusters of slabs of MoS_2 partially covering the alumina surface. The size of slabs and the amount of monolayer slabs and clusters of slabs will depend on the Mo loading relative to the alumina surface area.

The presence of Co or Ni does not affect the basic slab size of the MoS_2, being located at the edge sites of the slabs **[Furimsky and Massoth, 1999]** **[Segawa and Shokubai, 2006]**.

The support can be manufactured in a variety of shapes or may even be crushed to particles of the desired size **[Oyekunle et al., 2005]**.It is well known that presulfiding of the catalyst is very important to improve the performance of the HDT catalyst. Many reports have been published to elucidate the effect of presulfiding on the catalytic activity of a HDT catalyst **[Okamoto et al., 1980]**.

The selection of the catalysts must take into consideration the properties of the feed to be hydroprocessed. Properties of the catalysts used for hydroprocessing of light feeds may differ from those used for hydroprocessing of heavy feeds. The type of catalytic reactor chosen for the operation has also to be taken into consideration when selecting the catalyst. In the case of hydroprocessing of the light feeds, chemical and physical properties of catalysts can be readily attained. Thus, the surface area of catalysts is perhaps the main parameter, whereas porosity is less critical than in the case of heavy feeds, in general CoMo is noted for its HDS activity whereas NiMo is known for its HDN and HYD activity.

If a CoMo catalyst would be used for a high nitrogen feed, poisoning of the catalyst by nitrogen compounds could affect the operation **[Furimsky, 1998]**. Hydroprocessing catalysts are supplied in an oxidic form. During the operation, the oxidic form is converted to a sulfided form.

In this case, the sulfur present in the feed is converted to H_2S which subsequently reacts with the metal oxide to form sulfides. A significant operating time can be gained if the catalyst sulfiding is performed prior to hydroprocessing **[Blashka et al., 1998]**.

A key discovery was the identifications of the Co-Mo-S structures which were observed to be responsible for the promotion of the catalytic activity **[Clausen et al., 1981]**. Some years after the initial discovery of the Co-Mo-S structures, we observed **[Candia et al., 1984]**, that if the support interactions between the Co-Mo-S structures and the alumina support could be eliminated, the resulting structures would have an increased intrinsic activity. The Co-Mo-S and Ni-Mo-S type structures in the 1980s and 1990s showed that the building blocks of Co-Mo-S are small MoS_2- like domains or nanocrystals with the promoter atoms located at the edges of the MoS_2 layers. The Co atoms are located in the same plane as the Mo atoms, but not at perfect Mo edge sites.

In the resulting structural models, it was typically assumed that the edge structures of MoS_2 are very similar to those expected from cleaving a bulk MoS_2 crystal.

The alumina support, which is often used in hydrotreating catalysts, has the advantage that it quite easily allows a high dispersion of the Co-Mo-S structures, and the MoS_2 backbone of the Co-Mo-S structure may in fact be present as single MoS_2 layers. One of the main advantages of using alumina as a support is the quite easy formation of small stable MoS_2 nanoclusters.

Such clusters have a high concentration of MoS_2 edge sites, and this is important since it increases the amount of Co (Ni) that can be accommodated in the form of the active Co-Mo- S (Ni-Mo-S) structures. Besides stabilizing small nanoclusters, the support may also interact directly with the clusters, and this may influence the intrinsic activity of the active sites in the Co-Mo-S structures **[Topsøe, 2007] [Okamoto, 2008].**

The role of the catalysts is to promote the removal of undesired feed constituents such as sulfur, nitrogen, and metals up to specified levels **[Hauser et al., 2005].**

2.2 Deactivation of Hydroprocessing Catalysts:

The loss over time of catalytic activity and / or selectivity is a problem of great and continuing concern in the practice of industrial catalytic processes.

Costs to industry for catalyst replacement and processes shutdown total billions of dollars per year **[Bartholomew, 2001]**.

The main problem during hydroprocessing is the deactivation of catalysts, activity changes rapidly during first few hours of run and then it becomes stable.

It is generally practiced in refineries that the catalyst is allowed to deactivate to a certain level and then temperature is increased to increase reaction rate to compensate the loss of activity due to the catalyst deactivation **[Maity et al., 2004]**.

The rate of deactivation depends on the process conditions, the feed, the catalyst itself, and the deactivation mechanism for instance; increasing the hydrogen pressure will suppress coke deposition but accelerate the deposition of metals. Heavy feeds will in general cause more coke, and contain more metals **[Vogelaar et al., 2006]**.

One of the major problems related to the operation of heterogeneous catalysis is the catalyst loss of activity with time - on - stream (TOS), i.e. "deactivation". This process is both of chemical and physical nature and occurs simultaneously with the main reaction. Catalyst deactivation is defined as a phenomenon in which the structure and state of the catalyst change, leading to the loss of active sites on the catalyst's surface and thus causing a decrease in the catalyst's performance. Catalyst deactivation is a result of a number of unwanted chemical and physical changes.

Deactivation can occur by a number of different mechanisms, both chemical and physical in nature **[Forzatti and Liettil, 1999]**. Catalyst deactivation is a crucial factor in the design and operation of catalytic processes.

In hydroptocessing, the three main causes for deactivation are (1) sintering of the active phase, (2) fouling and (3) the poisoning of the catalyst's active sites **[Vogelaar et al., 2006]**.

The molecular structure of reactants in the feed has an indirect bearing on catalyst deactivation. Since rates are affected by adsorbed species, strongly adsorbed species can lower reaction rates considerably. This requires increase in temperature to maintain catalyst activity, which is usually accompanied by increased deactivation rates. Adsorbed species reduce the number of active sites via competition with the reactant **[Furimsky and Massoth, 1999]**.

2.3 Types of Deactivation:

2.3.1 Sintering:

Sintering usual refers to the loss of active surface via structural modification of the catalyst. Sintering rate has been shown to depend strongly upon time, temperature, atmosphere, support and catalyst composition, sintering being a thermally activated phenomenon is dependence on temperature **[Gudlavalleti et al., 2007}.**

Sintering occurs both in supported metal catalysts and unsupported catalysts. In the former case, reduction of the active surface area is provoked via agglomeration and coalescence of small metal crystallites into larger ones with lower surface - to - volume ratios. For sintering of supported metal catalysts, i.e. the atomic migration and the crystallite migration models.

In the first case, Sintering occurs via escape of metal atoms from a crystallite, transport of these atoms across the surface of the support (or in the gas phase), and subsequent capture of the migrating atoms on collision with another metal crystallite. Since larger crystallites are more stable (the metal-metal bond energies are often greater than the metal - support interaction), small crystallites diminish in size and the larger ones increase. The second model visualizes Sintering to occur via migration of the crystallites along the surface of the support, followed by collision and coalescence of two crystallites **[Forzatti and Liettil, 1999].**

2.3.2 Fouling:

Fouling is the physical deposition of species from the fluid phase onto the catalyst surface causing blockage of reaction sites or pores.

Extensive and severe fouling may also result in disintegration of catalyst particles, and in plugging reactor void space **[Gültekin and Hamad, 1987].**

The foulant metals are usually concentrated near the outer surface of the pellet, blocking pore mouths and reducing the active surface area available within the inner pores of the catalyst **[Marafi and Stanislaus, 2008]**.

The formation of coke is the most important example of deactivation by fouling. The definitions of carbon and coke are somewhat arbitrary and by convention related to their origin.

Carbon is a product of CO disproportionate while coke is produced by decomposition or condensation of hydrocarbons on catalyst surfaces and typically consists of polymerized heavy hydrocarbons. Nevertheless, coke forms may vary from high molecular weight hydrocarbons to primarily carbons such as graphite, depending upon the conditions under which the coke was formed and aged. The chemical structures of cokes or carbons formed in catalytic processes vary with reaction type, catalyst type, and reaction conditions **[Bartholomew, 2001]**.

2.3.3 Poisoning:

Poisoning is the loss of activity due to the strong chemisorptions on the active sites, of impurities present in the feed stream. The adsorption of a basic compound onto an acid catalyst (e.g. isomerization catalyst) is an example of poisoning.

A poison may act simply by blocking an active site (geometric effect), or may alter the adsorptive of other species essentially by an electronic effect.

Poisons can also modify the chemical nature of the active sites or result in the formation of new compounds (reconstruction) so that the catalyst performance is definitively altered. Usually, a distinction is made between poisons and inhibitors **[Haber et al., 1995]**. Poisons are usually substances whose interaction with the active sites is very strong and irreversible, whereas inhibitors generally weakly and reversibly adsorb on the catalyst surface.

Poisons can be classified as selective or non-selective. In the latter case the catalyst surface sites are uniform to the poison, and accordingly the poison chemisorptions occur in a uniform manner. As a result, the net activity of the surface is a linear function of the amount of poison chemisorbed. In the case of "selective" poisoning, on the other hand, there is some distribution of the characteristics of the active sites (e.g. the acid strength), and accordingly the strongest active sites will be poisoned first. This may lead to various relationships between catalyst activity and amount of poison chemisorbed.

Poisons can be also classified as "reversible" or "irreversible". In the first case, the poison is not too strongly adsorbed and accordingly regeneration of the catalyst usually occurs simply by poison removal from the feed **[Forzatti and Liettil, 1999]**.

2.3.3.1 Poisoning by Nitrogen Compounds:

In the case of hydroprocessing, nitrogen-containing compounds are the most common poisons by virtue of their strong adsorption on catalyst sites. Because of their basic nature, they adsorb on catalyst acidic sites, viz..............

Lewis and Brønsted sites, and may adsorb reversibly or irreversibly, depending on reaction conditions **[Furimsky and Massoth, 1999]**.

The authors **[Halabi et al., 1991] [Bartholomew, 1994] [Topsøe et al., 1996]**, explained the poisoning phenomena by two mechanisms: (1) adsorption of N - containing compounds on Lewis sites via the pair of electrons of the nitrogen atom or via the aromatic π - system and (2) interaction of N - containing compounds with protons from brønsted sites and the formation of positively charged particles **[Kogan et al., 2003]**.

Most of the nitrogen in petroleum is in the form of 5- and 6-membered heteroatom rings and anilines. It is generally accepted that 5-membered N-ring compounds are less basic (less aromatic character) than 6-membered ring compounds. Small amount of porphyrin type nitrogen (in the asphaltenes) is also present in heavy feeds **[Furimsky and Massoth, 1999]**.

2.3.3.2 Poisoning by Coke:

In hydroprocessing of petroleum products, catalyst deactivation by coke deposition is one of the major concerns in petroleum and petrochemical industries, both from economic and technological perspectives **[Bartholomew, 2002] [Ancheyta et al., 2002]**.

The coke deposition occurs in the pores and / or on the surface of the catalyst, and always leads to loss of activity and product selectivity **[Sahoo et al., 2004] [Bhatia et al., 1990]**.

During the start- up phase in hydro processing, initial coking is one of the most significant factors influencing catalyst deactivation **[Marafi and Stanislaus, 1997]**.

Particularly, in residual oil hydrotreating, coke deposition is believed to be rapid in the initial period **[Callejas et al., 2001]**, and initial coke is reported to cause a large loss in surface area and rapid deactivation of the catalyst **[Marafi and Stanislaus, 2001]**.

The soft coke which is formed at the initial stage of reaction is the principle cause of a loss of micro pores and consequently surface area. It approximately reduces one - third of the porosity **[Newson, 1975]**, whereas the hard coke which is formed in a later stage of reaction and metal sulfides take up the remaining porosity. At the initial stage, coke is mostly deposited on the surface area. Its interaction with the surface is much stronger when the feed contains more aromatic hydrocarbons.

Heavy oil generally contains oils, resins, and asphaltene. Therefore, asphaltenes are precipitated on the catalyst surface and block the catalyst pore.

When the catalyst pore is small, coke is deposited on the pore mouth **[Maity et al., 2007]**. The strength of the interaction of coke precursors with the catalyst depends on the properties of the catalyst surface and the structure of the coke precursor. It was established by **[Appleby et al., 1962]**, that coking increases with increasing acidity of the surface and / or increasing basicity of the precursors **[Furimsky and Massoth, 1999]**.

The principal causes of the catalyst deactivation are deposition of carbonaceous particle (coke). Coke is deposited very rapidly within a few hours of run and then it gets a steady - state, to control the coke formation, special attention has to be paid on pore size, pore volume and pore size distribution of the catalysts. The pore not only gives the paths for reactant and products molecules, but also sites for deactivation.

The pore diameter of the catalyst is more critical when the size of reactant molecules is bigger. The coke deposition has an adverse effect on the catalyst porosity. The mode of catalyst deactivation depends on pore diameter. For small pore diameter, catalyst deactivation occurs due to pore mouth plugging, whereas for large pore diameter, it happens due to core poisoning **[Furimsky, 1998]** **[Baltus, 1993]** **[Maity et al., 2003]**.

The major part of the coke is covering the support rather than the active phase, suggesting that there may not be any correlation between the amount of coke on the catalyst and catalytic activity. However, it was shown by **[Chu et al., 1996]**, that a correlation may be obtained after the extractable portion of the deposit blocking the micro pores, is removed.

The support is almost entirely covered with coke, whereas the slabs of active phase are not covered. It is believed that coke on the support consists of several layers. In the case of the CoMo / Al_2O_3 catalyst, almost 96 % of the surface was covered by the coke. The calculated layer thickness corresponded to three to four layers of coke. On the Mo / Al_2O_3 catalyst, only about 50 % of the surface was covered with the coke. Apparently, with this catalyst, the coke tends to agglomerate near the active phase **[Furimsky and Massoth, 1999]**.

Generally, most hydroprocessing units are operated in such a way that constant sulfur content of the product is ensured, so the reactor temperature has to be raised to offset catalyst deactivation.

At higher operating temperatures, coke formation seems to be accelerated, and the catalyst deactivates even more rapidly for not only coke but also metal deposition [**[Furimsky and Massoth, 1999]**.

Studies on initial coke formation during the early hours of the residue hydrotreating process are scarce **[Richardson et al., 1996]**.

In particular, the factors influencing the initial coking, its nature and its role in catalyst functionality and properties have not received much attention **[Matsushita et al., 2004]**.

2.3.3.3 Poisoning by Metals:

During hydroprocessing, part of the metals present in the feed will deposit on the catalyst surface and cause deactivation.

The nature of the metals deposited depends on the origin of the feed; vanadium (V) and nickel (Ni) are the predominant metals in petroleum crudes, heavy oils and oil shale - derived liquids, while iron (Fe) and titanium (Ti) are the main metals in coal-derived liquids.

Deactivation by metals is irreversible. The rate of metal deposition varies from metal to metal. For example, in the case of V and Ni, the initial deposition occurs at much higher rate for V than for Ni, and increases with increasing pore diameter **[Kabayashi et al., 1987]**. This suggests that the formation of V deposits may have an adverse effect on the rate of Ni deposit formation. While the initial coke deposition is rapid before the pseudo-equilibrium level is reached, metal deposits continually increase with time **[Myers et al., 1989]**. Then, during the entire period, metals deposition occurs on the catalyst, which has already lost a substantial portion of its original porosity and surface area **[Fonseca et al., 1996] [Ancheta et al., 2002]**.

This is generally true for petroleum-derived feeds and coal derived feeds as well as other feeds. In order to maintain design activity, temperature is raised to offset deactivation. Hence, the deposition of metals affects the lifetime of the catalyst. Some metals tend to deposit on the external surface of the catalyst particles, whereas others are more evenly distributed. This leads to diffusion limitations which affect access to the active sites in the particle interior. It is evident that coke and metals plug the pores and eventually may lead to a complete loss of the activity **[Newson, 1975]**.

[Jacobsen et al., 1987], have suggested that metal sulfides gradually narrow the pores and thus slow down the diffusion of reactant molecules into the undeactivated interior of the catalyst particles [**[Furimsky and Massoth, 1999]**. Among the cause of catalyst deactivation in HDS is the accumulation of metals such as nickel (Ni) and vanadium (V) as metal sulfides and coke deposition on the catalyst. Deposition of metals on the catalyst results in the blocking of access to the active sites of the catalyst, and it is the major cause of reduced activity of the original catalyst **[Oyekunle and Ikpekri, 2004]** **[Speight, 2000]**.

The presence of vanadium and nickel is of particular concern because of the deactivation effect during hydrotreating. The metals are commonly distributed between porphyrin and non - porphyrin types of structures **[Agralwal and Wel, 1984]**.

2.4 Regeneration of the Hydrotreating Catalysts:

Regenerated catalysts beneficiate from the growth of the hydroprocessing market segment, thanks to stricter environmental regulations on fuels **[Dufresne, 2007]**. Regeneration can restore activity more or less efficiently for various refining or petrochemistry catalysts. By using an oxidizing atmosphere at a temperature of 450-550°C, carbonaceous species can be eliminated.

Regeneration has the benefit of eliminating the first cause of deactivation, coke deposit, but it can do more, in the case of hydroprocessing catalysts, regeneration converts a sulfide phase, which could have partially sintered, back to an oxide phase quite similar to the original one of the fresh catalyst **[Eijsbouts, 1999]**.

In a general study of the regeneration of cobalt-molybdenum/alumina catalysts **[Arteaga et al., 1987a]**, showed that catalysts deactivated by carbon deposition using a butadiene/argon mixture can lead, after carbon burn off and sulfiding of the catalyst, to a better activity in both HDS (hydrodesulfurization) of thiophene and HYD (hydrogenation) of cyclohexane than the freshly sulfided catalyst.

A simulation of the regeneration process using the freshly sulfided catalyst, free of carbon deposits, also led to a catalyst more active than the starting sulfided material. However, most of the regenerations performed on catalysts submitted to a forced deactivation in laboratory are not representative of industrial catalysts **[Delmon, 1985]**.

Industrial catalysts are submitted to more severe conditions than laboratory catalysts, and several operational factors such as the time scale, temperature of reaction, and nature of the feed stock can lead to coke formation, sintering, and adsorption of metals and poisons, the latter being difficult to remove **[Silva et al., 1994]**. The avoidance of high - temperature excursions is especially important in fixed bed reactors, where the combustion gives rise to a high - temperature reaction front that moves along the bed as the coke deposits. Thus for instance **[Blasco et al., 1992]**, have shown that increasing temperature during regeneration may cause irreversible loss of catalytic activity by sintering in catalysts. In this case, the extent of the deactivation was related to time- temperature history in a series of operation- regeneration cycles.

High - temperature excursions can be avoided if a careful monitoring of the temperature along the bed is carried out during regeneration and the amount of oxygen fed to the reactor is adjusted to keep the temperature within acceptable limits. A 2.3% oxygen concentration in the feed is usually low enough to start regeneration, and this level can be progressively stepped up as the regeneration progresses **[Fulton, 1988]**. Given the importance of avoiding excessive temperature rises, a great deal of effort has been spent on the simulation of catalyst regeneration in fixed bed reactors, with the aim of studying the influence of operating conditions upon the dynamics of propagation and upon the magnitude of the high- temperature fronts generated within the bed **[Royo et al., 1994]**.

Regenerated catalysts also beneficiate from the growth of the hydroprocessing market. Besides the growing fresh catalyst market, the regenerated HDT catalyst usage is also increasing. It is estimated at

25,000 - 30,000 t/year worldwide, only for the distillates hydrotreaters as the reside catalysts are usually not regenerable. So, in distillate hydrotreating, the ratio between the regenerated and the fresh catalyst market is thus below 50 % **[Dufresne, 2007].**

Regeneration and deactivation were already extensively studied with respect to the nature of coke deposits **[Kern and Jess, 2005]**