# CHAPTER II

# LITERATURE REVIEWS

## 2.1 Hydrodesulfurization Reaction.

Petroleum as well as coal derived liquids contain a wide variety of sulfur containing compounds. Sulfur compounds must be removed to improve qualities of both feedstocks and products and to protect the performance of catalyst in downstream processes. The most important method to remove sulfur compounds is catalytic HDS process.

In this process, the sulfur containing compounds react with hydrogen and produce hydrogensulfide, resulting in a reduction of sulfur content in feedstocks.

$$R\text{-}S \quad + \quad H_2 \quad \text{------>} \quad R\text{-}H \quad + \quad H_2S$$

Different sulfur compounds have different reactivities and can be removed with different extents in HDS process. The different in the extent of removal of sulfur compounds depends on its basicity and structure.

Hydrodesulfurization reaction is exothermic and irreversible under the reaction conditions employed in industries (e.g. 340-425°C and 55-170 atm) (Gates et al., 1979; Speight, 1981, and Vrinat, 1983). Hydrodesulfurization reaction consists of two types of reactions, thermal decomposition reaction and hydrogenolysis reaction. Thermal decomposition reaction occured by thermal

at preheater or vaporizer section. The products from thermal decomposition reaction are hydrogen sulfide and olefins. Hydrogenolysis reaction is exothermic and occured over suitable catalyst under hydrogen ambient. The products from hydrogenolysis reaction consist of hydrogen sulfide and saturated hydrocarbons.

Recent researches in HDS reaction have been directed at the chemistry of thiophenic compounds, because these are the least reactive organosulfur compounds in petroleum and other fossil fuels (Gates et al. ,1971).

Mechanism in HDS of heterocyclic sulfur compounds consists of two pathways. First pathway occured via ring hydrogenation prior C-S bond scission while second pathway occured directly on C-S bond scission. The pathway involving prior hydrogenation of ring can be affected by thermodynamics because hydrogenation of sulfur containing rings of organosulfur compounds is in equilibrium at practical HDS temperature (Vrinat, 1983).

## 2.2 Hydrodesulfurization of Thiophene.

The removal of sulfur compounds from hydrocarbon streams by HDS on CoMo catalysts has been extensively studied (Parijs and Froment, 1986; Daly, 1978; Geneste, 1980, etc.). Many researchers (Satterfield and La Vopa, 1988; Massoth and Miciukiewicz, 1986, etc.) in HDS reaction has been directed at the chemistry of thiophenic compounds because these are the least reactive organosulfur compounds in petroleum. In this study, thiophene was chosen to study the influence of nitrogen compounds

on its HDS reaction.

Thiophene, $C_4H_4S$ as a heterocyclic sulfur compound, is a volatile, colorless liquid with a slight aromatic odor resembling that of benzene (Drew, 1982).

Hydrodesulfurization of thiophene is exothermic and essentially irreversible under wide range of conditions employed industrially at the temperature ranges between 340 and 425°C and the pressure between 55 and 170 atm (Gates et al., 1979; Speight, 1981 and Vrinat, 1983). In ICI research (Phillipson, 1971), there is a report which showed that the exothermic reaction of thiophene HDS had heat of reaction of -66.98 kcal/mol at 700 K.

There are many conditions in studying HDS of thiophene. The experimental conditions depend on the boiling point range and characteristics of the feedstocks, the degree of desulfurization required, type of reactors used, and the catalyst employed. Industrial HDS is generally carried out at temperature between 573 and 698 K and pressure between 10 and 200 atm. (Gates et al., 1979 ; Speight, 1981 and Vrinat, 1983).

Nevertheless, although industrial HDS is a middle or high pressure process, most of laboratory kinetics studies have been made at atmospheric pressure. However, the newly recognized importance of heavy petroleum fractions and alternative fossil fuel source have shown the need for kinetic data for the hydrotreatment of thiophenic sulfur compounds under conditions similar to those used in industry. Thus an important effect has recently been made in the construction of new laboratory reactors able to provide reaction data free from mass and heat

transfer effects. Gradientless reactors for vapor phase
or multiphase systems have been reported by Mahony et al.
(1978) and new laboratory high pressure flow microreac-
tors have been described by Elizer et al. (1977) and by
Vrinat and De Mourgues (1980).

Product distribution and reaction intermediates
during thiophene HDS have been thoroughly reviewed in
some papers (Tanaka and Okhura, 1977; Massoth and Murali
Dhar, 1982; Weisser and Landa, 1973; Gates et al., 1979
and Ohtsuka, 1977) and the general reaction network of
thiophene by Massoth and Murali Dhar (1982) is given in
Figure 2.1.

There are two pathways in this reaction. The
first pathway is called hydrogenolysis and the second
pathway is called hydrogenation. The second path is not
rapid compared with the first path, so that $C_4$ products
obtained consists of butane and mixture of butene
isomers. Two intermediates, 1,3-butadiene and tetra-
hydrothiophene, are generally observed in trace amount.
Because, they are rapidly hydrogenated to butene isomers.
It appears that HDS of thiophene may proceed by two inde-
pendent routes: i) adsorption of thiophene through sulfur
followed by loss of sulfur or ii) adsorption of thiophene
parallel to the catalyst surface followed by hydrogena-
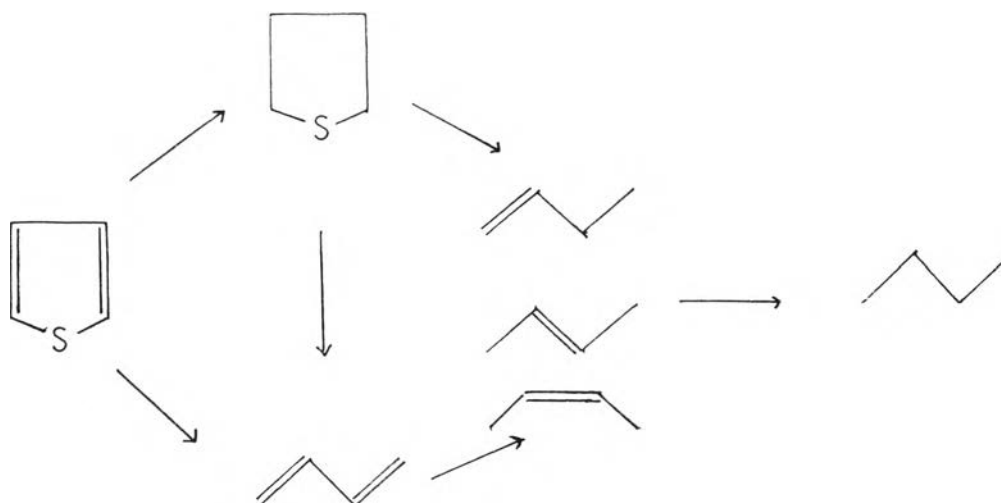tion and further C-S bond rupture.

Figure 2.1 Pathways for thiophene hydrodesulfurization
(from Massoth and Maruli Dhar, 1982)

HDS of thiophene occured either with or without
hydrogenation of heterocyclic ring.  Hydrogenation path-
way could be affected by thermodynamic, and favoured only
at low temperatures and high pressures.  An example is
reported in Figure 2.2 in which the temperature depend-
ence of the equilibrium constants for the various reac-
tions involved in thiophene is shown.  It can be seen
that the formation of tetrahydrothiophene (reaction 2) is
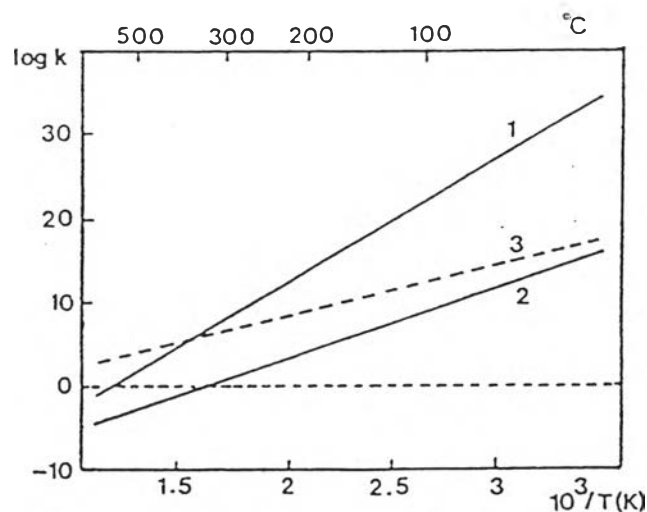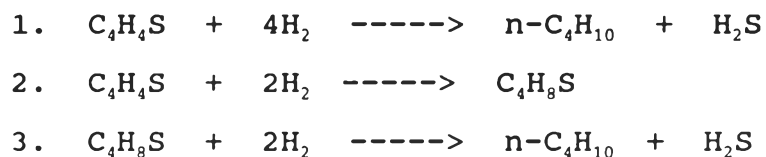only favoured for temperature below 623 K.

Figure 2.2 Equilibrium constants (K) of reactions
          involved during thiophene hydrodesulfurization
          (From Weisser and Landa, 1973)

1.  $C_4H_4S$  +  $4H_2$  -----> n-$C_4H_{10}$  +  $H_2S$

2.  $C_4H_4S$  +  $2H_2$  -----> $C_4H_8S$

3.  $C_4H_8S$  +  $2H_2$  -----> n-$C_4H_{10}$  +  $H_2S$

     Products distribution and amount of each product
depending upon conditions, type of reactor used, and
catalysts employed.  Tables 2.1 and 2.2 show effect of
pressure and temperature on the yield of tetrahydrothio-
phene and butenes in thiophene HDS on CoMo/$Al_2O_3$ cata-
lysts.

TABLE 2.1   Effect of Pressure and Temperature on The Yield of Tetrahydrothiophene in Thiophene Hydrodesulfurization on Co-Mo/$Al_2O_3$ Catalysts

| Pressure (MPa) | Temperature ($^{\circ}$C) | conversion (%) | | Reference |
|---|---|---|---|---|
| | | Overall | to THT | |
| 0.1 | 400 | 40 | 0.03 | Kraus and Zdrazil,1977 |
| 0.1 | 350 | 20 | 0.10 | Kraus and Zdrazil,1977 |
| 0.1 | 300 | 22 | 0.40 | Kraus and Zdrazil,1977 |
| 0.1 | 260-360 | 3-10 | not found | Morooka and Hamrin,1977 |
| 0.1 | 250-310 | 0-10 | max. 3 | Lee and Butt,1977 |
| 0.9 | 200 | 0-100 | max. 9 | Devanneux and Maurin,1981 |
| 1.75 | 220 | 0-100 | max. 12 | Devanneux and Maurin,1981 |
| 1.5 | 250 | 17 | 10 | Kraus and Zdrazil,1977 |
| 2.1 | 260 | 0-100 | max. 4 | Pokorny and Zdrazil,1977 |
| 2.8 | 290 | 0-100 | max. 10 | Pazos and Andreu,1977 |

TABLE 2.2   Effect of Pressure and Temperature on The Yield of Butenes
in Thiophene Hydrodesulfurization on Co-Mo/Al$_2$O$_3$ Catalysts

| Pressure (MPa) | Temperature (°C) | 100 x mol butenes / mol hydrocarbon | Reference |
|---|---|---|---|
| | | At 20% thiophene conversion | |
| 0.1 | 350 | 95 | Massoth and Chung, 1981 |
| 0.1-0.3 | 320-430 | 93 | Blake, 1981 |
| 0.1 | 350 | 90 | Wakabayashi and Orito, 1971 |
| 0.1 | 400 | 88 | Bladuri and Mitchell, 1980 |
| 2.8 | 290 | 50 | Pazos and Andreu, 1984 |
| | | At 40% thiophene conversion | |
| 0.1 | 350 | 93 | Mitchell and Scott, 1984 |
| 0.2 | 305 | 87 | Van Parys, 1984 |
| 0.8 | 282 | 75 | Van Parys, 1984 |
| 1.8 | 282 | 66 | Van Parys, 1984 |

The gas-phase HDS equilibrium constants of thiophene at different temperature are listed by Speight (1981).

Thiophene + 4H$_2$ -----> n-butane + H$_2$S

logK at 227°C = 12.07

at 427°C = 3.85
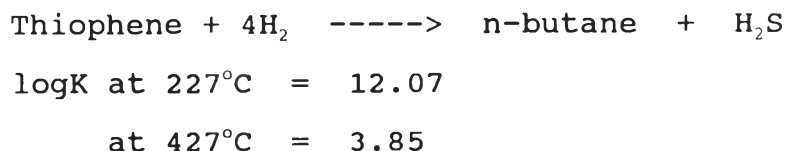
The standard enthalpy of reaction (H ) = -68 kcal/mol, H (300K) = -62 kcal/mole, H (700 K) = -66.98 kcal/mol.

The reactivity of thiophene was determined by Nag et al. (1979). It showed that thiophene has pseudo-first order rate constant equal $1.38*10^{-3}$ l/g of catalysts.
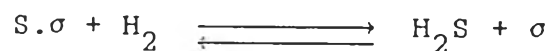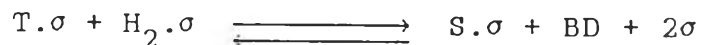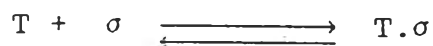
Van Parijs and Froment (1986) had studied the kinetics of HDS of thiophene in vapor-phase flow reactor. They studied in a wide range of conditions (Temperature between 260 and 350°C, Pressure between 2 and 30 atm, and molar H$_2$/thiophene ratio of 4-9) on CoMo/Al$_2$O$_3$ catalyst. They showed that, since amount of 1,3-butadiene and tetrahydrothiophene are less than butene in the effluent stream, the following consecutive scheme was adopted for the hydrogenolysis of thiophene (T) into hydrogen sulfide (S), butene (B), and butane (A).

The hydrogenolysis of thiophene to butenes and the hydrogenation of butenes to butane are considered to take place on different kinds of active sites; (Hydrogenolysis sites and Hydrogenation sites). The existence of two different types of sites in CoMo catalysts under HDS conditions has been evidenced by Owens and Amberg (1961), Zdrazil (1975), and Delmon (1977). On both types of
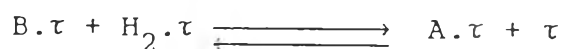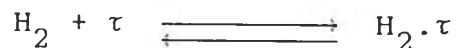
active sites the surface reactions between the reactions and competitively adsorbed hydrogen are rate determining step.  Hydrogen can be adsorbed in both molecular and atomic form which gave different kinds of rate equation as follows.

I. Kinetic Model via hydrogen Molecularly adsorption.

a.   For the hydrogenolysis of thiophene on the $\sigma$- sites.

$$H_2 + 2\sigma \rightleftharpoons H\ 2.\sigma$$

$$T +\ \sigma \rightleftharpoons T.\sigma$$

$$T.\sigma + H_2.\sigma \rightleftharpoons S.\sigma + BD + 2\sigma$$

$$S.\sigma + H_2 \rightleftharpoons H_2S + \sigma$$

b.   For the formation of butane through hydrogenation of butene on the $\tau$ sites.

$$H_2 + \tau \rightleftharpoons H_2.\tau$$

$$B + \tau \rightleftharpoons B.\tau$$

$$B.\tau + H_2.\tau \rightleftharpoons A.\tau + \tau$$

$$A.\tau \rightleftharpoons A + \tau$$

II. Kinetic model via hydrogen atomically(dissociatively) adsorption.

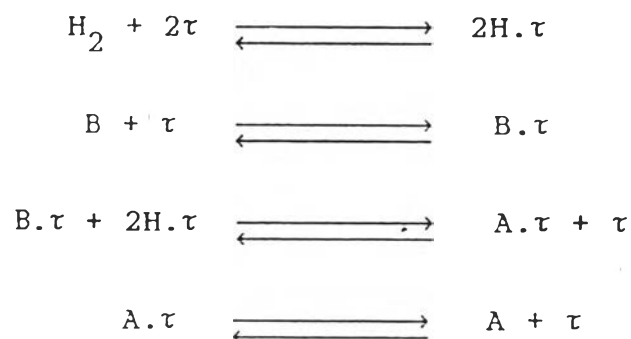a. For the hydrogenolysis of thiophene on the $\sigma$-sites.
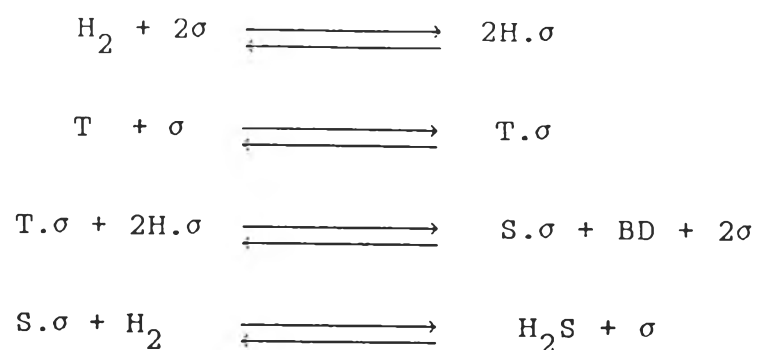
$$H_2 + 2\sigma \rightleftharpoons 2H.\sigma$$

$$T + \sigma \rightleftharpoons T.\sigma$$

$$T.\sigma + 2H.\sigma \rightleftharpoons S.\sigma + BD + 2\sigma$$

$$S.\sigma + H_2 \rightleftharpoons H_2S + \sigma$$

b. For the formation of butane through hydrogenation of butene on the $\tau$-sites.

$$H_2 + 2\tau \rightleftharpoons 2H.\tau$$

$$B + \tau \rightleftharpoons B.\tau$$

$$B.\tau + 2H.\tau \rightleftharpoons A.\tau + \tau$$

$$A.\tau \rightleftharpoons A + \tau$$

where   T = thiopene ; B = butene ; A= butane ;

S = $H_2S$ ; BD = 1,3-butadiene ;

= hydrogenolysis sites

= hydrogenation sites

There are many investigators who studied kinetic equations of thiophene HDS as shown in Table 2.3.

TABLE 2.3  Kinetic Equations for Thiophene Hydrodesulfurization

| Reference | Date | Solvent Temp./K Press./atm | Catalyst Used | Ea/ kcal mol$^{-1}$ | Rate Expression $r = r_{HDS}$ $r° = $ initial rate |
|-----------|------|----------------------------|---------------|---------------------|-----------------------------------------------------|
| Satterfield | 1968 | – 508-538 1 | Co-Mo/Al$_2$O$_3$ | 3.7 | $r = k \dfrac{K_T P_T}{(1+K_T P_T + K_S P_S)^2} P_H$ |
| Ozimek | 1975 | – 580-673 1 | Co-Mo/Al$_2$O$_3$ | 21.6 | $r = k \dfrac{K_T P_T°}{(1+K_T P_T°)^2} P_H°$ |
| Massoth | 1977 | – 673 1 | Mo/Al$_2$O$_3$ | – | $r = k \dfrac{K_T P_T}{(1+K_T P_T + K_S P_S)^n} P_H^m$ |
| Morooka | 1977 | benzene 523-623 1 | Co-Mo/Al$_2$O$_3$ | 20 | $r = k \dfrac{K_T P_T}{(1+K_T P_T + K_S P_S)^2} P_H$ |
| Chakraborty | 1978 | naphtha 510-563 1 | Ni-Mo/Al$_2$O$_3$ | 3 | $r = k \dfrac{K_T P_T}{(1+K_S P_S)^2} P_H$ |
| Kawaguchi | 1978 | n-hexane 543-623 1 | Ni-Mo/Al$_2$O$_3$ | 16 | $r = k \dfrac{K_T P_T}{(1+K_T P_T + K_S P_S)} \cdot \dfrac{K_H P_H}{(1+\sqrt{K_H P_H})}$ |
| Vyskocil | 1979 | – 623 1 | Co-Mo/Al$_2$O$_3$ | – | $r = k \dfrac{K_T P_T}{(1+K_T P_T°)^2} P_H°$ |
| Lee | 1977 | – 523-586 1 | Co-Mo/Al$_2$O$_3$ | – | $r = k \dfrac{K_T P_T\, K_H P_H}{(1+K_T P_T + K_H P_H)} \left\{ \dfrac{1}{1+K_H P_H} + k \right\}$ |

Rate equations from kinetic studies as shown in
Table 2.3 indicated that thiophene inhibits its own HDS
at low pressure experiment. Hydrogen sulfide also inhib-
ited HDS reaction. Hydrogenation and hydrogenolysis
reaction are infered to occur on two different kinds of
active sites since hydrogen sulfide affected rates of
thiophene hydrogenolysis and olefin hydrogenation, dif-
 fererently.

2.3 Hydrodesulfurization Catalysts.

The most commonly used HDS catalysts consist of
cobalt oxide and molybdenum oxide(CoMo) or nickel oxide
and molybdenum oxide (NiMo), dispersed on high surface
area alumina supports (McKinley, 1957). Molybdenum is
generally regarded as the active desulfurization com-
ponent, with cobalt or nickel acting as a promoter which
increases catalytic activity. The ratio of Mo/Co is
always considerably greater than 1, a representative com-
position being 3 wt% CoO and 12 wt% $MoO_3$. An alternate
catalyst composition is $NiMo/Al_2O_3$, used especially if HDN
or hydrogenation reactions are to be emphasized. As with
CoMo, the ratio Mo/Ni exceeds 1, less widely used are
$NiW/Al_2O_3$ catalysts, which are quite active but more
costly. So, CoMo catalysts are by far the most popular
choice for desulfurization, particularly for straight run
petroleum fractions, (Drew, 1982).

The catalysts are manufactured with the metals in
an oxide state. In the active form they are in the sul-
fide state, which is obtained by sulfiding the catalyst
either prior to use or with the feed during actual use,

the method of presulfiding the catalyst is considerably more important in the case of NiMo/Al$_2$O$_3$ than with CoMo/Al$_2$O$_3$ catalysts. If not presulfided before use, NiO may be reduced to metallic Ni by the reducing environment in the reactor, and this may then be difficult to convert to the sulfide. Metallic Ni may cause undersiderable reactions and probably sinters more rapidly than a nickel sulfide. The structure of the active catalysts has been subjected to much discussion, but there is no consensus yet. With a CoMo catalyst the sulfided forms may be represented as MoS$_2$ and Co$_9$S$_8$, but their compositions actually are complex. MoS$_2$ by itself is considerably more active than Co$_9$S$_8$, but a mixture of the two is more active than either alone. The mechanism of their interaction is still speculative. The sulfided catalyst is quite different in structure from the oxide precursors. MoS$_2$ forms layered type structures in which layers of S atoms alternate with layers of metal atoms. It has been suggested that at the edges of such a structure, atoms of Co might intercalate into the MoS$_2$ structure, forming the active sites (Weisser and Landa, 1973). In comparision of CoMoS/Al$_2$O$_3$, NiMoS/Al$_2$O$_3$ and NiWS/Al$_2$O$_3$ with respect to their specific acitvity for hydrogenation and C-S bond splitting during conversion of 2-methylthiophene was observed by Duchet (1983) and Daly (1987). The results showed that CoMoS/Al$_2$O$_3$ give more than twice conversion during the same space time than the two other catalysts. Obviously CoMoS/Al$_2$O$_3$ was the most active HDS catalyst and was confirmed by many researchers (Owens and Amberg, 1961 ; Satterfield, 1981 and Firmsky, 1983).

## 2.4 Deactivation of catalysts

In catalytic process, catalysts usually lose their activities while in operation over a period of time. The time required for the activity to fall to an undesirable level varied with the severity of the process conditions and the type of reaction. Three kinds of catalyst deactivation may occur: a) sintering or thermal deactivation, b) fouling or coking and c) poisoning. These phenomena may occur singly or in combination but the overall result is the removal of active sites from the catalyst surface. (Huges, 1984; Petersen and Bell, 1987 and Butt et al., 1988).

### 2.4.1. Deactivation by sintering

Sintering or thermal deactivation of the catalyst is a physical process rather than a chemical process. Normally, the term sintering is applied in describing the loss of active surface area of the catalyst which occur throughout the catalyst or may be localized at the individual areas where reaction occurs. Sintering can occur in the support which cause to change the pore structure or agglomerate the active metal which cause to lose the dispersion of the metal crystallites. The other was the incorporation of the active metal into the support that the new form is inert for the reaction. Sintering can be avoided by working at operating temperature below the normal range of temperature.

### 2.4.2. Deactivation by fouling or coking

Fouling is a process of catalyst deactivation that may be either physical or chemical in nature. In general, much larger amounts of material are responsible for deactivation in fouling processes than in poisoning. The most typical of fouling processes is that of the carbonaceous deposit of coke that forms on most catalysts used in the processing of petroleum fractions or other organic chemical feedstocks. The formation of carbonaceous or coke deposits (containing in addition to carbon, significant amounts of hydrogen plus traces of oxygen, sulfur, and nitrogen) on the catalyst surface during the processing of organic based chemical feedstocks is the usual example of fouling. It is important to recognize that the coke deposit in this originates from the reactions occuring, is not an impurity. Because of this intrinsic association with the main chemical reactions, fouling by coke cannot be eliminated by purification of the feed or use of a guard catalyst. If reaction occurs, coke deposition must also necessarily occur according to the chemistry of the process. However, coke formation can be minimized by appropriate choice of reactor and operating conditions, and in some cases by modification of the catalyst (Thomas, 1978).

### 2.4.3. Deactivation by poisoning.

Poisoning is the catalytic deactivation due to small amounts of material, specific to a specific catalyst and associated with the adsorption of the poison on the active sites of catalyst. Poison is often associated

with contaminants such as sulfur compounds in the feed
stream of petroleum fraction which is then termed impuri-
ty poisoning.  Though, there are many well documented and
best identified of poisoning processes, it is important
to recognize that other forms of poisoning may occur.
These include poisoning by a product of the desired and
undesired reaction which may be preferentially adsorbed
on the active sites of the catalyst, thus retarding the
adsorption of reactant.

Catalyst poisons can be classified in various
ways, such as by their degree of affinity for the sur-
face, as temporary or permanent, or as selective or non-
selective.  In particular, we will make a distinction
between temporary and permanent poison, a point which
rests upon the degree of reversibility of chemisorption
on the surface, and inhibitors of reaction rate which are
either reactants or products of the main reaction being
carried out.  The description of a poison as selective or
nonselective is related to the nature of the surface and
the degree of interaction of poison with the surface.  A
nonselective case is the chemisorption of poison on the
surface which removes actives sites in a uniform manner,
such that the net activty of the surface is a direct
function of the amount of poison chemisorbed.  In
essence, every active sites looks like every other active
sites to the poison molecule.  Conversely, in selective
poisoning there will be some distribution of properties
of the active sites, such as acid strength which can be
the result of any member of factors but which results in
nonuniform deactivation of the surface. Often these will

appear as exponential or hyperbolic relationships between the net activity of the surface and the amount of poison chemisorbed.

Most poisoning processes are effectively irreversible, but there is an important class of poisons that are reversible in activity (Massoth and Miciukiewicz, 1986).

Since the effects of deactivation by nitrogen poisoning is recieved more attention than the structural changes, the folowing literature will be focused only on nitrogen poisoning in HDS process.

## 2.5 Effect of nitrogen compounds on hydrodesulfurization reactions.

Many investigators studied effects of nitrogen compounds on HDS reactions (Bhinde, 1979; Lo, 1981; Satterfield, 1975, 1980. etc.). Only recently quantitative inhibition effects have been reported. Variable in each studied are catalysts, sulfur model compounds used, nitrogen model compounds used, catalysts, type of reactor and condition.

Studies on inhibition effects of nitrogen compounds on HDS reaction also showed that HDS catalysts have two active sites, o..e for hydrogenation which occur on bronsted acid sites and the other for hydrogenolysis which occur on lewis acid sites, because nitrogen poisoned each active site differently. Nitrogen compounds inhibited HDS reaction by competitive adsorption to active sites (Krisch, 1959). Degree in inhibition of nitrogen compounds depends on it's type and molecular

structure.  The following literature will be supported
this reason.

Bhinde (1979) analyzed inhibition of quinoline on
dibenzothiophene HDS by kinetic treating each reaction in
dibenzothiophene network.  The network of dibenzothio-
phene consists of both hydrogenation and hydrogenaolysis
reactions.  He concluded that hydrogenation reactions
were inhibited more than hydrogenolysis reaction, and
approximately 2-fold difference in the degree of the rate
constants was interpreted evidence of separate sites of
hydrogenation and hydrogenaolysis.  Using Bhinde's data,
Lo (1981) developed a model based on Langmuir-Hinshelwood
rate expressions for each reaction of the dibenzothio-
phene network ; an advantange of this approach was the
simultaneous modeling of HDS and HDN.  It was found that
a single-site model for the hydrogenolysis reactions in
the dibenzothiophene network (such as the one used to
model naphthalene hydrogenation) gave a poor fit to the
data.  A two-site model, with more parameters, gave a
better fit.  The form of the equations is suggestive of
the two sites model also proposed earlier by Desikan and
Amberg (1964).

In 1983, the course of poisoning study, Nagai and
Kabe noticed selective poisoning patterns for HDS
dibenzothiophene on a $Mo/Al_2O_3$ catalyst based on the
kinetics of the poisoning effect on this reactions.
Studies were carried out in a high pressure flow micro-
reactor and used various poisoning agents, such as
nitrogen, polyaromatic, sulfur, and oxygen compounds.
They found that nitrogen compounds also inhibited the

hydrogenation of dibenzothiophene more strongly at lower
temperatures.  At higher temperatures, the nitrogen
compounds also hindered the desulfurization together with
the hydrogenation of dibenzothiophene.  The reactions of
the desulfurization, the denitrogenation, and deoxygen-
ation proceeded on one type of sites and the hydrogen-
ation reactions proceeded on another type of sites.  In
the studies about selective poisoning of nitrogen com-
pounds on HDS reaction were developed at differential in
catalyst, type of reactor and condition.  In 1986, Nagai
and Aiba studied selective poisoning on various nitrogen
compounds on hydrodesulfurization sites of $NiMo/Al_2O_3$ in a
flow microreactor at 220-340°C and 10.1 MPa total pres-
sure.  They concluded that nitrogen compounds were effec-
tive poisons for dibenzothiophene hydrogenation but not
for the desulfurization reaction at lower temperatures.
They also suggested that the poisoning effect of nitrogen
compounds was not correlated with their solution basic-
ities but with their gas phase basicities.  Gas phase
basicity, which called proton affinity, was obtained by
measuring the equilibrium constants for the proton tran-
sfer reactions.  This value defined from direct measure
of the bronsted base strength of the molecule.  These
results indicated that hydrogenation occured on bronsted
sites that appeared on sulfided $NiMo/Al_2O_3$ catalysts.
Hence, it appeared that a nitrogen compounds adsorbed
strongly on Bronsted acid sites rather than Lewis acid
sites or coordinatively unsaturated sites.  In this
conditions range, nitrogen compounds decreased the
concentration of unreactred dibenzothiophene slightly.

The increase in the conversion was not observed for the sulfided Mo/Al$_2$O$_3$ catalyst (Nagai and Kabe, 1983). It seemed that nitrogen compounds enhanced the desulfurization on the NiMo/Al$_2$O$_3$ catalyst. Nitrogen compounds decreased hydrogenated products in the following order acridine > quinoline > Pyridine > piperidine > cyclohexylamine > picoline > dicyclohexylamine > aniline. The increase in desulfurization product was also in the same order.

Investigatiions of inhibition of the HDS of some sulfur compounds by various nitrogen compounds have also been reported (Gutberlet and Bertolacini, 1983; Miciukiewicz, 1984; La Vopa and Satterfield, 1988, etc.). These results are useful for correlating moleclar structure with inhibition, and they provided insights into inhibition mechanisms. The degree of inhibition by organonitrogen compounds as a function of stearic hindrance around the nitrogen atom was investigated by Gutberlet and Bertolacini (1983), who measured inhibition of the HDS of a petroleum naptha by various methyl- and ethyl-substituted pyridines. In this work, distinction between sulfur removal via direct hydrogenolysis of the organo-sulfur species or by its prior hydrogenation was not possible. Under the conditions employed, the organo-nitrogen compounds added to the naptha underwent little HDN. The naptha HDS data were fitted to the following equation:

$$r = \frac{k P_S}{(1 + K_{H_2S} P_{H_2S})(1 + K_A P_A^{0.5} + K_B P_B^{0.5} + K_C P_C^{0.5})} \qquad (2.1)$$

where S, A, B, and C denoted sulfur components of
the naptha, ammonia, nitrogen components of the naptha,
and nitrogen added to the naptha, respectively.  Data
from Table 2.4 showed that the inhibition parameter
correlated well with the degree of steric hindrance about
the nitrogen atom ; the hindered nitrogen compounds were
characterized by relatively low values of the inhibition
parameters.  The weak inhibition by the unhindered
4-methylaniline (Table 2.4 ) was attributed to the part-
ial delocalization of its lone-pair electrons associated
with resonance interactions.  Inhibition of hydrodesul-
furization by ammonia (produced by rapid hydrodesulfur-
ization of benzylamine) was comparable to that character-
izing the unhindered heterocyclics, in qualitative agree-
ment with Lo's results (1981).

The relatively weak inhibition by sterically hin-
dered species has also been reported for thiophene HDS by
La Vopa and Satterfield (1988).  As with the work of
Gutberlet and Bertolacini (1983), it is not clear whether
the HDS here involves hydrogenolysis of the thiophene
directly or desulfurization of a hydrogenated thiophene.
The pseudo-first-order rate constant  k' for thiophene
disappearance in the presence of several inhibitors was
correlated by the following equation:

$$k' \quad = \quad k \; / \; (1 + K_I P_I) \qquad\qquad (2.2)$$

where the subscript I denoted an inhibitor.  At 360°C, the
values of $K_I$ for pyridine, 1-methylpyridine, and 2,6-
dimethylpyridine were 430, 263, and 110 atm$^{-1}$,

TABLE 2.4  Calculated Adsorption Constants, pKa Values and
Proton Affinities for Nitrogen Compounds Studied.

| Compounds | K (KPa ) | pKa | PA (kcal/mol) | Reference |
|---|---|---|---|---|
| Napthalene | 0.011 | | 199.8 | Lau et al.,1978 |
| Ammonia | 0.048 | 9.24 | 207 | Meot-ner,1979 |
| Phenanthrene | 0.064 | | 209 (b) | Meot-ner,1979 |
| Aniline | 0.094 | 4.63 | 213.5 | Meot-ner,1979 |
| 2-Ethylaniline | 0.10 | 4.42 | | |
| 2,6-Dimethylpyridine (a) | 0.11 | 6.71 | 231.5 | Aue et al.,1976 |
| 1-Methylpiperidine (a) | 0.26 | 10.19 | 233.2 | Aue et al.,1976 |
| Pyridine | 0.43 | 5.29 | 222 | Meot-ner,1979 |
| 1,2,3,4-Tetrahydroquinoline | 0.46 | | 225 (b) | Lau et al.,1978 |
| Carbazole | 0.51 | | | |
| Piperidine | 0.58 | 11.12 | 229.7 | Aue et al.,1976 |
| 4-Methylpyridine | 0.68 | 6.02 | 229 | Brown and Tse, 1980 |
| Quinoline | 0.98 | 4.80 | 227.6 | Meot-ner,1979 |
| 5,6,7,8-Tetrahydroquinoline | 2.0 | | | |
| Decahydroquinoline | 2.0 | | | |
| 1,8-Bis(N,N-dimethylamino)n | 3.1 | | 246.2 | Lau et al.,1978 |

(a) = Sterarically hindered
(b) = Estimated sponge

respectively, in qualitative agreement with the data of
Gutberlet and Bertolacini (1983). There is apparently a
lack of quantitative agreement between the two sets of
results, however.

A relatively weak inhibition by sterically hin-
dered organonitrogen compounds had even been reported for
low-pressure experiments (Miciukiewicz et al., 1984. The
adsorption of nitrogen compounds on the catalyst at
steady state was determined with feeds containing a
nitrogen compounds and either thiophene or 1-hexene. The
inhibition was expressed in terms of ratios of pseudo-
first-order rate constants for disappearance of thiophene
(or 1- hexene) with and without nitrogen compounds. The
hindered nitrogen compounds were more weakly adsorbed
than the others (as measured gravimetrically) and inhi-
bited the thiophene hydrdesulfurization less. Surpris-
ingly, the hindered nitrogen compounds inhibited 1-hexene
hydrogenation more than thiophene hydrodeulsurization.

The correlation of the degree of steric hindrance
with the inhibition parameter (identified with the
adsorption equilibrium coonstant of the inhibition) for
sulfur removal suggested that the nitrogen compounds
inhibited reaction by adsorption through the $sp^2$ lone-pair
electrons of the nitrogen atom. This proposal at first
might appear to contradict the hypothesis of Mathur et
al. (1982) that heterocyclic nitrogen compounds were
adsorbed flat through their  electrons. However, in the
inhibition experiments just described, hydrogenation of
the nitrogen compounds did not occur to a significant
extent, and the adsorption leading to inhibition might

well had been different from that leading to catalytic hydrogenatiion of the inhibitors. Moreover, as Kwart et al. (1982) had pointed out that, 2,6-dimethyl-pyridine was hydrogenated at higher temperatures and pressure than those of the inhibition experiments, and the 2,6-dimethylpiperidine thus formed was a strong inhibitor of hydrodesulfurization because its $sp^3$ lone pair electrons were not hindered owing to the puckered nature of the piperidine ring.

A few studies had also attempted to measure the relative poisoning effects of a vareity of nitrogen compounds upon a specific reaction. Lo (1981) studied mutual inhibiting effects that occured in binary reaction systems consisting of pairs of hydrogenation of napthalene, HDS of dibenzothiophene, or HDN of quinoline and indole. Studies used a NiMo/$Al_2O_3$ catalyst in a batch reactor at 350°C and 3.4 MPa. For napthalene hydrogenation inhibition effects increased in the order of dibenzothiophene < ammonia < indole and intermediates < quinoline and intermediates. The degree of inhibition was expressed in term of an apparent adsorption constant derived from the kinetics. These varied over two orders of magnitude.

Miciukiewicz et al. (1984) studied the inhibiting effects of several nitrogen compounds on thiophene HDS on a CoMo/$Al_2O_3$ catalyst at 350°C and 1 atm and compared them to inhibition of 1-hexene hydrogenation.

For a given nitrogen compounds deactivation of HDS was greater than of hydrogenation in absence of stearic effects and deactivation was generally greater

for those nitrogen compounds having higher pKa values.

Nagai and co-workers, (1983 and 1986) have reported studies of HDS of dibenzothiophene in the presence of various nitrogen compounds. Under some conditions heterocylic nitrogen compounds actually increased the rate of reaction of dibenzothiophene. In the Nagai studies, whether the dibenzothiophene disappearance rate increased or decreased, the nitrogen compounds consistently inhibited the formation of partially hydrogenated products. Thus, the ratio of biphenyl to cyclohexylbenzene, the principal products isolated, increased, and the amounts of hexahydrodibenzothiophene, isolated in small amounts, decreased. In one study with Mo/AlO$_3$ at 300°C and 10 MPa the effect of nitrogen compounds in reducing the hydrogenation functionality increased in the order phenanthrene < carbazole < acridine. In a latter study using a NiMo/Al$_2$O$_3$ catalyst at 260°C and 10 MPa the effect increased in the order aniline < pyridine < quinoline < acridine. Apparent adsorption constants were measured from the inhibition of the secondary reaction of tetrahydrodibenzothiophene to form hexahydrodibenzothiophene, both intermediates being present at relatively low concentrations. These adsorption constants increased linearly with gas-phase basicity (proton affinity), but did not correlate well with solution basicity (pKa). They observed that cyclohexylamine and piperidine did not fit the correlation and suggested that they might had decomposed.

The foregoing results suggested relations between the basicity of unhindered organonitrogen compounds and the strength of their inhibition for conversion of organosulfur compounds. Such relations were sought by LaVopa and Satterfield (1988) for thiophene HDS and by Nagai et al. (1986) for dibenzothiophene hydrogenation to give hexahydrodibenzothiophene LaVopa and Satterfield represented the inhibition with with equation 2.2; parameters are listed in Table 2.4. At the relatively low temperature of 260°C, Nagai et al. (1986) observed that nitrogen compounds inhibited hydrogenation but not hydrogenolysis of dibenzothiophene.

In both studies, the estimated adsorption parameters correlated poorly with basicities of the nitrogen compounds in aqueous solution (i.e., pKa values). Instead, these parameters generally correlated well with gas-phase proton affinities, which evidently better represent the interaction between an organic base and a surface catalytic site. Data characterizing hindered species did not follow the correlation, as expected. As the gas-phase proton affinities are enthalpy changes for proton-transfer reactions, it was speculated that the hydrogenation sites poisoned by the nitrogen compounds were Bronsted acid sites.

The inhibition effect of the nonbasic corbazole appeared unexpectedly strong. Table 2.4, for example, indicated that the adsorption parameter charaterizing carbazole was comparable to that charaterizing much more basic species (e.g., piperidine). Strong inhibition by carbazole had also been observed, for dibenzothiophene

hydrogenation, by Nagai and Kabe (1983).

Inhibition of dibenzothiophene hydrogenation to give tetrahydrodibenzothiophene was represented with a Langmuir-Hinshelwoood rate expression. The inhibition parameters were determined to be 690, 650, 62, and 41 atm$^{-1}$ for acridine, carbazole, phenothiazine, and dicyclohexylamine, respectively. The high value of the adsorption characterizing carbazole was attributed to products of a rapid hydrogenation converting it to basic compounds, although the identities of the basic compounds and the kinetics of their formation were not determined. This hypothesis appeared reasonable in light of the networks of nonbasic nitrogen compounds. Thus, the distinction between nonbasic and basic organonitrogen compounds, as far as inhibition was concerned was lost after hydrogenation of the nonbasic species to give basic ones.

Additional results of Nagai and Kabe's study were in agreement with other investigations including (a) the much weaker inhibition of dibenzothiophene hydrogenation by phenanthrene (adsorption parameter equal to 10 atm$^{-1}$) compared to nitrogen inhibitors and (b) the weaker inhibition by dicyclohexylamine consistent with steric hindrance about its nitrogen atom. LaVopa and Satterfield (1988) demonstrated that the approach of representing the inhibition by eq. 2.2 had some generality. Using the inhibition terms for quinoline and its nitrogen containing products determined in the HDS experiments, they were able to generate concentration profiles for dibenzofuran conversion that matched well data from dibenzofuran conversion with quinoline in the feed.

For selective poisoning of nitrogen compounds on HDS reaction has been studied by many investigators. (Fu, 1989; Nagai et al., 1983, 1986).

Fu and Schaffer, 1989 studied the effects on conversion and selectivety of about 30 different nitrogen compounds on cracking catalysts. The experiment was conducted in a micro-confined fluid bed unit (MCBU) in reaction temperature ranged from 950 to 1050°F. Three catalysts used were all zeolitic cracking catalysts with a silica-alumina binder. They found that the effect of nitrogen compound on cracking yields strongly depends on its molecular structure. Six-member heterocyclic nitrogen compounds inhibit reaction conversion more than five-member heterocyclic nitrogen compounds. The addition of one or more two fused rings to pyridine substantially increases the poisoning effect. They confirmed that the nitrogen-containing heterocyclics were stronger poisons than the pure aromatic compounds. It should be noted that the substitution of a second carbon with nitrogen in the aromatic ring actually decreased the poisoning effect. In cracking conditions nitrogen compounds may be hydrogenated to other forms which generate slightly more potent poisons for cracking catalysts. Alkyl side chains contain in nitrogen compounds increase poisoning. Moreover, conversion decreases in a fairly regular fashion with the size of side chain. They also found that the nitrogen bases poison only the acid sites and not the metal sites responsible for hydrogenation production. The extent of poisoning should depend on the average residence time of the nitrogen molecules on the

catalyst surface. In varying temperatures , nitrogen adsorption (the number of acid sites covered by nitrogen) decrease at higher temperature. In varying concentration, both coke and hydrogen increased significantly when the concentration of multi-ring nitrogen compounds was increased. It should be pointed out that these studies were not designed to determine the effect of diffusion on the poisoning behavier between single ring and multi-ring nitrogen compounds. They concluded that there were at least three independent parameters that could determine the extent of nitrogen poisoning: the strength of nitrogen bases; the nature of the catalyst; and the inherent properties of a feedstock. They also prooved that the proton affinity, which was determined by measuring the gas-phase proton transfer reaction between a base and the $NH_4^+$ ion, should be a better indicator for a catalyst poisoning than solution basicity ($K_b$). The poor correlation with $K_b$ was not unexpected if one considers the strong influence that ion-solvent interaction had on the basicity determined in aqueous solution.

In 1985, Nagai studied activity and selectivity of a poisoned $NiMo/Al_2O_3$ for HDS of dibenzothiophene. The experiments were carried out in a continuous-flow micro-reactor at a high pressure within the temperature range of 220-300°C with a 30 L/h hydrogen flow rate , 10.1 total pressure, and a weight hourly space velocity of 7.5. A solution containing 5 wt% of dibenzothiophene in xylene was introduced into the reactor. The solution was replaced by a solution containing 5 wt% of dibenzothiophene and 0.5 wt% of acridine after 3 h. From the

results showed that in the initial stage of addition (a
small amount of a nitrogen compound on the surface of the
catalyst), the poisoning effect on the catalyst suggests
that the poisons block the active sites and thus prevent
the hydrogenation of dibenzothiophene (Nagai et al.,
1986).  As the amount of nitrogen compounds increased
over the surface, it appeared that the poisons rearrange
the surface structure [active sites Ni-Mo-S type struc-
ture on the edge of $MoS_2$ (Topse et al., 1984 and Topse,
1986) to become more active for the desulfurization of
dibenzothiophene.  In addition, the poisons might help in
the desorption of sulfur adsorbed on ths desulfurization
sites of the catalyst.  This phenomenon was also observed
for a  sulfided $NiW/Al_2O_3$ catalyst but not for $CoMo/Al_2O_3$
catalyst (Nagai et al., 1986).  They concluded that the
addition of nitrogen compounds improved desulfurization
activity with high selectivity to a biphenyl from diben-
zothiophene.

Nagai et al.,1986 studied the selectivity of sul-
fided $NiW/Al_2O_3$ catalyst in desulfurization of dibenzo-
thiophene in the presence of nitrogen compounds in a
continous-flow microreactor at 260 to 360°C and 10.1 MPa
total pressure.  The results showed that addition of
nitrogen compounds such as acridine, pyridine, piperidine
and quinoline on sulfided $NiW/Al_2O_3$ catalyst highly
increase the selectivity for desulfurization while
decreasing the concentration of decomposed and hydrogen-
ated compounds.  The strong acid sites on the catalyst
surface were diminished after the addition of nitrogen
compounds.  In 1988, Lavopa and Satterfield studied

response of dibenzothiophene hydrodeulsulfurization to presence of nitrogen compounds on sulfided NiMo/Al$_2$O$_3$ at 260°C and 7 MPa. They found that at the same total pressure 7.0 MPa, the addition of quinoline at 260°C indeed markedly increased the hydrodeulsulfurization of dibenzothiophene. However, at 360°C it moderately decrease the hydrodesulfurization reaction. They conclude that inhibition effects from compettitive adsorption would be expected to diminish with increase temperature. Addition of ammonia at 360°C and partial pressure up to 96 KPa had no effect on the rate of dissappearance of dibenzothiophene. They showed that both nitrogen compounds suppressed formation of partially hydrogenated products. The accelerating effect of quinoline may be caused by its reducing the competitive adsorption of strongly adsorbed products.