

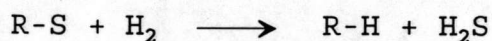
CHAPTER II

LITERATURE REVIEWS

Hydrodesulfurization Reaction

In petroleum industry, long-term trend will be to process heavier feedstocks containing large percentages of sulfur and nitrogen. As the crudes become heavier, percentage of condensed sulfur heterocyclics increases faster than simpler compounds such as mercaptans and sulfides which are relatively easy to desulfurize. In middle distillates most of sulfur compounds are present in form of heterocyclic compounds such as thiophenes, benzothiophenes and dibenzothiophenes. The presence of sulfur compounds in the crudes not only lead to the problems of air pollution but also cause major problems the hydroprocessing operations. Therefore, it is important to remove the sulfur from the crude petroleum.

Catalytic hydrodesulfurization is economically a very important process because of the increasing demand for fuels containing the smallest possible quantities of sulfur. In this reaction, sulfur-containing petroleum react catalytically with hydrogen to convert into hydrogen sulfide and hydrocarbon products.



The hydrodesulfurization reaction is virtually irreversible at temperatures and pressures ordinarily applied, roughly 300°C to 450°C and up to 200 atm (2,940 psig). The reaction is exothermic with heat of reaction of the order of 10 to 20 kcal/mol of hydrogen consumed, or roughly 50 to 100 Btu per standard cubic foot of hydrogen consumed [Gates et al., 1979].

The great variety of materials treated in HDS processes led to the development of a number of technological procedures. The experimental conditions depend on boiling range and character of feedstock, degree of desulfurization required and catalyst employed. Industrial HDS is generally carried out between 300 and 425°C and pressures from 10 to 200 atm (147-2,940 psig) [Vrinat, 1983].

Nevertheless, although industrial HDS is a middle or high pressure process, most of laboratory kinetic studies have been made at atmospheric pressure. However, the newly recognized importance of heavy petroleum fractions and alternative fossil fuel sources 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 effort has recently been made in the construction of new laboratory reactors able to provide reaction data free from mass and heat transfer effects. New laboratory high pressure flow microreactors have been described by Eliezer et al. [1977].

The order of reactivity of HDS is about mercaptans (RSH) > disulfides (R-S-S-R') > sulfides (R-S-R') > thiophenes. Reactivity decreases with increased molecular size and varies depending upon whether R is an aliphatic or aromatic group.

The current technological emphasis on HDS of petroleum residua and of coal-derived liquids points to the need for understanding the chemistry of HDS of the heterocyclic compounds, which are expected to be among the least reactive compounds in these feedstocks. Thiophene, the simplest compound in this class, has often been chosen for kinetics studies, and thiophene has often been assumed to be representative of the whole class of sulfur-containing aromatic compounds.

Hydrodesulfurization of Thiophene

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].

The HDS of thiophene has received considerable attention in the past, partly because this reaction is a simple model of the reactions that take place when sulfur-containing petroleum fractions are catalytically desulfurized. However, in spite of the large amount of research in the HDS of this compound, the reaction mechanism and kinetics are not completely understood and the results from different laboratories are not always in agreement.

Early thiophene HDS investigations, the great majority of which have been performed at atmospheric pressure, have been reviewed [Gates et al., 1979; Vrinat, 1983]. The general reaction network of thiophene is given in Figure 2.1. It appears that HDS of thiophene may proceed by two independent routes: i) adsorption of thiophene through S and the cleavage of the C-S bonds (hydrogenolysis), resulting in loss of sulfur or ii) flat adsorption of thiophene as a π -complex to the catalyst surface, followed by hydrogenation of thiophene to tetrahydrothiophene (THT) and a subsequent C-S bond cleavage.

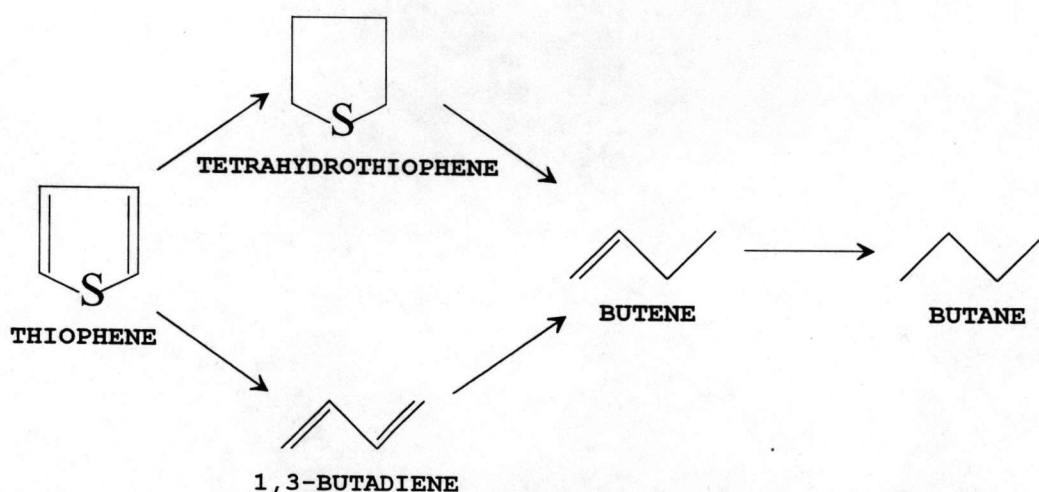
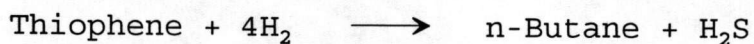


Figure 2.1 Pathways for Thiophene Hydrodesulfurization
[From Massoth and Murali Dhar, 1982]

HDS of thiophene occurs either with or without hydrogenation of heterocyclic ring. Pathways involving prior hydrogenation of the ring can be affected by thermodynamics because hydrogenation of sulfur-containing

rings of organosulfur compounds is equilibrium-limited at practical HDS temperatures. If the hydrogenolysis reaction resulting in C-S bond cleavage is not limited thermodynamically, hydrogenation is favoured only at low temperatures and at high pressures. An example is reported in Figure 2.2 in which temperature dependence of equilibrium constants for the various reactions involved in thiophene desulfurization is shown. It can be seen that the formation of tetrahydrothiophene (reaction 2) is only favoured for temperatures below 350°C. Thus, sulfur removal pathways via hydrogenated sulfur intermediates may be inhibited at low pressures and high temperatures because of the low equilibrium concentrations of the latter species.

The gas-phase HDS equilibrium constants of thiophene at different temperatures are listed by Speight [1981] with the corresponding standard enthalpy of reaction ($\Delta H^\circ = -68$ kcal/mol).



$$\log K \quad \text{at } 227^\circ\text{C} \quad = \quad 12.07$$

$$\quad \quad \quad \text{at } 427^\circ\text{C} \quad = \quad 3.85$$

The reactivity of thiophene was determined by Nag et al. [1979] in batch reactor packed with CoMo/Al₂O₃ catalyst at a temperature of 300°C and a pressure of 71 atm. It showed that thiophene has pseudo-first order rate constant equal 1.38×10^{-3} L/g of catalyst·S.

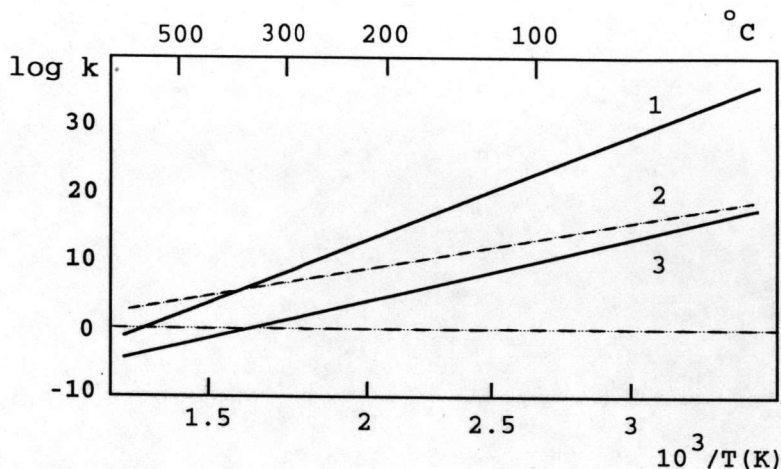
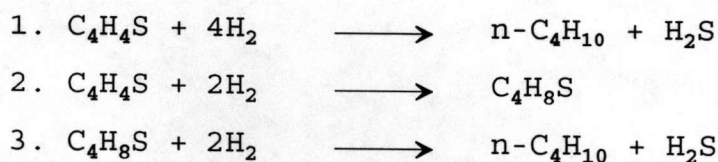
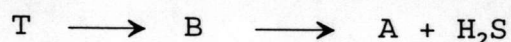


Figure 2.2 Equilibrium Constants (K) of Reactions Involved During Thiophene HDS [From Weisser and Landa, 1973]



In a thorough set of experiments characterizing HDS of thiophene in vapor phase [Van Parijs and Froment, 1986], the experimental conditions were varied over a wide range (total pressure, 2-30 bar; temperature, 260-350°C; molar hydrogen to hydrocarbon ratios, 4-9) on CoMo/Al₂O₃ catalyst. They showed that, since no 1,3-butadiene and tetrahydrothiophene were detected in the effluent stream, the following consecutive reaction scheme was adopted for the hydrogenolysis of thiophene (T) into hydrogen sulfide, butene (B), and butane (A):

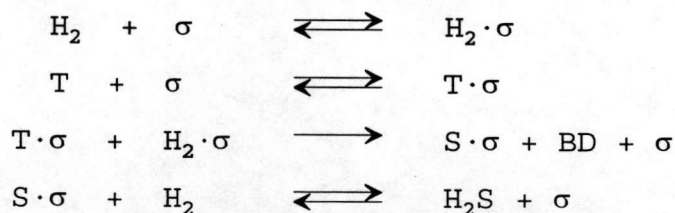


A reaction network was proposed in which thiophene was hydrodesulfurized to give butenes, followed

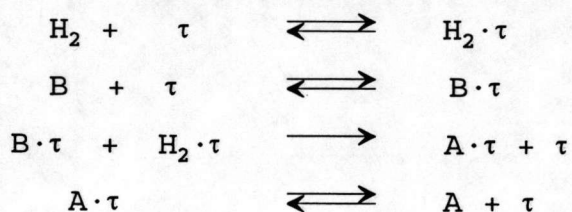
by hydrogenation of the butenes to give butane. Two different kinds of catalytic sites were assumed, one for thiophene hydrogenolysis (hydrogenolysis site, σ) and one for butene hydrogenation (hydrogenation site, τ). The existence of two different types of sites in CoMo catalyst under HDS conditions has been evidenced by Owens and Amberg [1962], Zdrzil [1975], Delmon [1979], and Vrinat [1983]. Since it was not detected in the effluent, 1,3-butadiene must be a highly reactive intermediate. On both types of active sites the surface reaction between the reactants and competitively adsorbed hydrogen are rate-determining step. Hydrogen can be also 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 σ -sites.

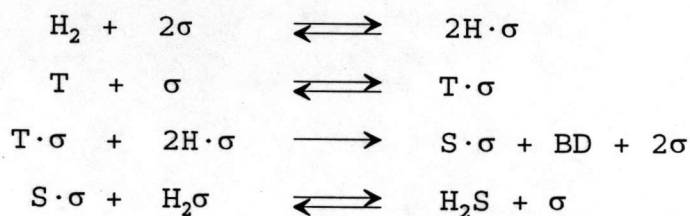


b. For the formation of butane through hydrogenation of butene on the τ -sites.

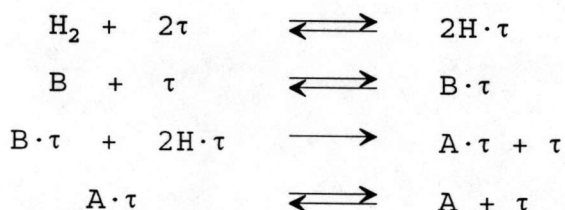


II. Kinetic model via hydrogen atomically (dissociatively) adsorption

a. For the hydrogenolysis of thiophene on the σ -sites.



b. For the formation of butane through hydrogenation of butene on the τ -sites.



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

S = sulfur; BD = 1,3-butadiene;

σ = hydrogenolysis sites

τ = hydrogenation sites

The suggestion that the first reaction of thiophene in primary reaction path is C-S bond cleavage to form 1,3-butadiene, rather than hydrogenation of C=C bond, is supported by further data of Desikan and Amberg [1964]. Their results show that hydrogenated compound with C-S bonds intact (tetrahydrothiophene) gives products in HDS different from those observed for thiophene. This indicated that the C-S bond cleavage

takes place before the hydrogenation step.

Satterfield and Roberts [1968] reported the first extensive determination of kinetics of thiophene HDS, in a steady state recirculation flow reactor on CoMo/Al₂O₃ catalyst at atmospheric pressure and temperatures between 235-265°C. The thiophene disappearance was represented by the following Langmuir-Hinshelwood rate equation:

$$r_{HDS} = k \frac{K_T P_T K_H P_H}{(1 + K_T P_T + K_S P_S)^2}$$

(k, rate constant; K, equilibrium constant; P, partial pressure; subscripts: T, thiophene; H, hydrogen; S, hydrogen sulfide). The form of the kinetic expression implies a two-point thiophene adsorption in competition with H₂S on one type of active sites and hydrogen adsorption on a second type of active sites.

Rate equations similar to the above have been applied in other kinetic studies of thiophene HDS on CoMo/Al₂O₃ catalysts and NiMo/Al₂O₃ catalysts; they were summarized in Table 2.1. Rate equations from the low pressure experiments indicated that thiophene inhibits its own HDS; in some investigations, hydrogen sulfide has been found to inhibit HDS reaction. Hydrogenation and hydrogenolysis are inferred to occur on two different kinds of sites since hydrogen sulfide affects rate of thiophene hydrogenolysis and olefin hydrogenation differently [Gates et al., 1979].

Table 2.1 Kinetic Equations for Thiophene
Hydrodesulfurization [From Vrinat, 1983]

Reference	Data	Solvent Temp. (°C) Press. (atm)	Catalyst Used	Ea (kcal/mol)	Rate Expression $r = r_{HDS}$ $r^{\circ} = \text{initial rate}$
Satterfield	1968	- 235-538 1	CoMo/Al ₂ O ₃	3.7	$r = k \frac{K_T P_T}{(1 + K_T P_T + K_S P_S)^2} P_H$
Ozimek	1975	- 307-400 1	CoMo/Al ₂ O ₃	21.6	$r = k \frac{K_T P_T^{\circ}}{(1 + K_T P_T^{\circ})^2} P_H^{\circ}$
Massoth	1977	- 400 1	Mo/Al ₂ O ₃	-	$r = k \frac{K_T P_T}{(1 + K_T P_T + K_S P_S)^2} P_H^m$
Morooka	1977	benzene 250-350 1	CoMo/Al ₂ O ₃	20	$r = k \frac{K_T P_T}{(1 + K_T P_T + K_S P_S)^2} P_H$
Chakraborty	1978	naphtha 237-290 1	NiMo/Al ₂ O ₃	3	$r = k \frac{K_T P_T}{(1 + K_T P_T)^2} P_H$
Kawaguchi	1978	n-hexane 270-350 1	NiMo/Al ₂ O ₃	16	$r = k \frac{K_T P_T}{(1 + K_T P_T + K_S P_S)} \cdot \frac{K_H P_H}{(1 + \sqrt{K_H P_H})^2}$
Vyskocil	1979	- 350 1	CoMo/Al ₂ O ₃	-	$r^{\circ} = k \frac{K_T P_T^{\circ}}{(1 + K_T P_T^{\circ})^2} P_H^{\circ}$
Lee	1977	- 250-313 1	CoMo/Al ₂ O ₃	-	$r = k \frac{K_T P_T K_H P_H}{(1 + K_T P_T + K_S P_S)} \cdot \left\{ \frac{1}{1 + K_H P_H} + k' \right\}$

Hydrodesulfurization Catalysts

Alumina Support: Hydrodesulfurization catalysts most often contain alumina as a support, typically having a surface area of the order of 2 to 3×10^5 m²/kg, a pore volume of about 5×10^{-4} m³/kg, and an average pore diameter of about 10 nm. Of various types of alumina available, γ -Al₂O₃ appears to be the one generally applied. Since the chemical nature of this support may be important to the surface chemistry of HDS [Schuit and Gates, 1973].

The most commonly used hydrodesulfurization catalysts consist of cobalt oxide and molybdenum oxide (CoMo), or nickel oxide and molybdenum oxide (NiMo), dispersed on high surface area alumina supports. Molybdenum is generally regarded as the active desulfurization component, 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 composition being 3 wt% CoO and 12 wt% MoO₃. An alternate catalyst composition is NiMo/Al₂O₃, used especially if hydrodenitrogenation or hydrogenation reactions are to be emphasized. As with CoMo, the ratio Mo/Ni exceeds 1 [Satterfield, 1980].

CoMo catalysts are by far the most popular choice for desulfurization, particularly for straight-run petroleum fractions. NiMo catalyst is often chosen instead of CoMo catalyst when higher activity for polyaromatics saturation or nitrogen removal is required, or when more refractory sulfur compounds such as those in

cracked stocks must be desulfurized. Nickel-tungsten (NiW) catalyst is usually chosen only when very high activity for aromatics saturation is required along with activity for sulfur and nitrogen removal but more costly [Schuit and Gates, 1973].

The catalysts are manufactured with the metals in an oxide state. In the active form they are in the sulfide 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/Al₂O₃ catalysts than with CoMo/Al₂O₃ catalysts. If not presulfided before use, NiO may be reduced to metallic Ni by the reducing environment in reactor, and this may then be difficult to convert to the sulfide. Metallic Ni may cause undesirable 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 as yet. With a CoMo catalyst the sulfided forms may be represented as MoS₂ and Co₉S₈, but their compositions actually are complex. MoS₂ by itself is considerably more active than Co₉S₈, but a mixture of the two is more active than either alone. The mechanism of their interaction is still speculative. These species may also react with the alumina support, but the main weight of evidence is that such compounds formed with alumina contribute little, if any, catalytic activity. Their role, as well as that of

alumina itself, is essentially that of a support. The sulfided catalyst is quite different in structure from the oxide precursors. MoS_2 and WS_2 form 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, atom of Ni (or Co) might intercalate into the MoS_2 or WS_2 structure, forming the active sites [Schuit and Gates, 1973; Weisser and Landa, 1973].

There has been much work done in the field of MoS_2 -based HDS catalysis trying to establish what phase is responsible for catalytic activity. Much of this research has focused on the effect of the Co promoter and whether its predominant contribution is of the electronic or structural nature. Recently Topsoe et al. [1990] has reviewed some of the recent literature regarding the state of the active hydrotreating catalyst. The active phases in promoted CoMo (NiMo) catalysts are the so-called Co-Mo-S (Ni-Mo-S) structures. It is proposed that the Co edge atoms in Co-Mo-S are present in two types of sites having square and tetragonal pyramidal coordination, respectively. These represent the free and occupied sites which interconvert during a catalytic cycle.

Effects of Temperature on Hydrodesulfurization

The factors which are considered to influence the rate of HDS reaction are: i) liquid hourly space velocity (LHSV), ii) chemical and physical properties of crude

oil, iii) reaction temperature, iv) reaction pressure, v) H₂/oil ratio, vi) size of the reactor, and vii) partial pressure of hydrogen. However, the effects of these factors are interrelated in such a complicated way that the individual effects are very difficult to construe. Only the effects of temperature will be discussed in more detail. An increase in temperature increases the rate constant and, hence, the rate of reaction. Experimental confirmation is abundant [Kim and Choi, 1987]. Not only does a higher temperature increase the rate of reaction of the crude oil on the surface of catalyst, it also increases the rate of diffusion by vaporizing the crude oil. On the other hand, a higher temperature also brings about the decomposition of the hydrocarbons, which can be avoided by operating below 430°C.

Satterfield and Roberts [1968] had studied a cobalt molybdate catalyst at atmospheric pressure, using thiophene feed in a differential reactor with recirculation. They reported that variation of temperatures had some effect on the rate of reaction. Reaction rate of thiophene increased from 0.156×10^{-8} to 0.180×10^{-8} as the results of the increasing temperature from 235°C to 265°C. Furthermore, they indicated that the hydrodesulfurization and subsequent hydrogenation reactions proceed on separate sites. As the same reaction, Lipsch and Schuit [1969] concluded that no thiophene conversion was found below 210°C on cobalt molybdate catalyst because no hydrogen adsorption. The

increase of thiophene conversion from 3% to 65% as the results of the increasing temperature from 250°C to 460°C. Above 400°C the thiophene conversion increased suddenly but at temperatures between 250-360°C it increased slightly. Morooka and Hamrin [1977] purposed to compare quantitatively the catalytic activity of a commercial HDS catalyst that has been used in coal liquefaction. The reaction chosen was the HDS of thiophene, which serves as a model coal-sulfur compound. Thiophene diluted in benzene to the volume ratio 1/1. The experiment was conducted with a continuous-flow differential reactor and a cobalt molybdate catalyst at a total pressure of 104 kN/m² (15 psig) and temperature ranges from 250°C to 350°C to obtain overall activation energy. In this study, conversions were in the range of 4-16% and the overall activation energy for thiophene HDS decreased gradually with an increase of temperature. At lower temperatures (250-270°C) the activation energy (84 kJ/mole) using catalyst was twice as high temperatures (40 kJ/mole for 300-350°C). Further experiment was carried out in bench-scale tubular reactor at total pressure of 2-30 bar (29-435 psig) for the same reaction on a cobalt molybdate catalyst with 1.8 wt% S as thiophene. Van Parijs and Froment [1986] indicated that thiophene conversion increased in the range of 15-88% with increasing temperature from 260°C to 350°C at a pressure of 75 psig.

Daly [1978] indicated that the effects of temperature on reaction rate of HDS of benzothiophene

were the same results performed on HDS of thiophene. Most of the previous work on the HDS has been performed at atmospheric pressure. Since coal liquefaction HDS processes operate at pressure greater than 1000 psig it was interest to study the HDS of benzothiophene at elevated hydrogen pressure (1250 psig) in a stirred-batch reactor over a $\text{CoO-MoO}_3\text{-Al}_2\text{O}_3$. He showed that the rate constant and conversion increased with an increase of temperature. Rate constant increased from 1.21×10^{-5} to $1.83 \times 10^{-3} \text{ sec}^{-1}$ and conversion increased in the range of 5-92% with increasing temperature from 200°C to 400°C . Above 350°C conversion increased rapidly it was twice as lower temperature.

The most commonly used catalyst on HDS is a cobalt molybdate catalyst but most of the time nickel molybdate catalyst is widely used in petroleum industry for hydrotreatment of petroleum feedstocks. Mohammed et al. [1985] indicated that nickel molybdate catalyst was effective not only for sulfur model compounds but also for sulfur removal of crude oil which has many types of sulfur compounds. The hydrotreatment was carried out in trickle-bed reactor over $\text{NiMo/Al}_2\text{O}_3$ catalyst at a pressure of 6.1 MPa (885 psig) and reaction temperatures varied from 320°C to 420°C with LHSV ranging from 0.37 to 2.6 h^{-1} . Bai-Hassan reduced crude, which containing 4.2 wt% sulfur, was used as feedstock. This study revealed that desulfurization activity increased with increasing temperature. The sulfur removal varied from 23% to 67%

at temperatures ranging from 320°C to 420°C at a LHSV of 2.0 h⁻¹.

From the literature reviews in this section showed that the temperature strongly influenced the reaction rate of HDS of sulfur model compounds such as thiophene and benzothiophene, or HDS of crude oil with various of sulfur compounds. HDS reaction over cobalt molybdate catalyst and nickel molybdate catalyst was the same affected by reaction temperature.

Composite sulfides, like Co-Mo, Ni-Mo, and Ni-W, are more active for hydrorefining of petroleum fractions than simple sulfides of molybdenum or tungsten. Cobalt and nickel are usually described as promoters of molybdenum or tungsten in spite of the fact that cobalt and nickel sulfides possess their own activities. Upon their mixing with group VI metal sulfides the resulting activity is more than additive. Therefore, the attention has been paid to the influence of catalyst composition on HDS of crude oil and model sulfur compounds such as thiophene, benzothiophene, and dibenzothiophene.

The first approach was made by Cerreny [1986] for 2-methylthiophene HDS over CoMoS/Al₂O₃, NiMoS/Al₂O₃, and NiWS/Al₂O₃ catalysts at a total pressure of 100 bar (1470 psig) and a temperature of 250°C. The results showed that CoMoS/Al₂O₃ catalyst gave more than twice conversion (51%) during the same space time than the two other catalysts (22% and 20% for NiMoS/Al₂O₃ and NiWS/Al₂O₃ catalyst,

respectively). Obviously CoMoS/Al₂O₃ catalyst was the most active HDS catalyst. The results was also confirmed by Vit [1993] for thiophene HDS over Mo/Al₂O₃, CoMo/Al₂O₃, and NiMo/Al₂O₃ catalysts. The effect of promoter (Co, Ni) on activity of Mo catalysts was compared in HDS of thiophene at temperature of 320°C and a hydrogen pressure of 2 MPa (290 psig) in fixed-bed reactor. The results showed that the presence of Co or Ni accelerated the HDS reaction. Thiophene activity of CoMo/Al₂O₃ catalyst [3.00 mol h⁻¹ mol(Mo)⁻¹] possessed slightly higher than NiMo/Al₂O₃ catalyst [2.75 mol h⁻¹ mol(Mo)⁻¹].

On the contrary, the results from many researchers were not in agreement with the results as indicated above. Lindner et al. [1989] demonstrated that NiMo catalyst (60% thiophene conversion) was more active for HDS of thiophene than CoMo catalyst (50% thiophene conversion) at temperature of 250°C and at atmospheric pressure in a continuous-flow reactor. More recently, Ihm et al. [1990] reported the effects of different kinds of active metals on thiophene HDS kinetics, in a fixed-bed reactor. Three commercial catalytic systems, CoMo/Al₂O₃, NiMo/Al₂O₃, and NiW/Al₂O₃, were used for this study. The three catalytic systems showed the same type of rate equations under the reaction condition of atmospheric pressure and temperatures between 275-325°C, irrespective of the kinds of active metals. The reaction rate of HDS of thiophene decreased in the order NiMo > CoMo > NiW. It was also found that the reaction rate

increased with increasing temperature. CoMo system showed the rate constant was closely to NiMo system at higher temperature (325°C).

HDS of heavy gas oil has been one of the major refining processes. Recently, the demand for low-sulfur diesel fuel below 0.05 wt% of sulfur is increasing to minimize the emission of sulfur oxides from diesel engines. On the other hand, heavier feed which contains more unreactive sulfur compounds has to be refined to increase the supply for diesel fuel. Therefore, more severe reaction conditions and/or catalysts of higher activity are some ways to improve the sulfur removal. Mann et al. [1987] reported the results obtained in the hydrotreatment of heavy oil over alumina-supported Co-Mo, Ni-Mo, and Ni-W in a trickle-bed reactor. The effects of temperature on the catalytic hydrotreatment of heavy oil were studied at temperatures between 300-450°C, a pressure of 6.99 MPa (1000 psig) and a LHSV of 2. HDS activities increased with increasing temperature for all three catalysts, the values of HDS activity were 20.1-82%, 35-82%, and 19-83% for Co-Mo, Ni-Mo, and Ni-W catalysts, respectively. While Ni-W catalyst showed the best HDS activity at temperatures greater than 350°C, Ni-Mo catalyst showed the best performance at temperatures less than 350°C. Ni-Mo catalyst gave higher HDS activity than Co-Mo catalyst at temperatures less than 350°C, while Co-Mo catalyst gave slightly higher HDS activity than Ni-Mo catalyst at temperatures greater than 350°C.

Recently Ma et al. [1995] indicated that the different sulfur compounds existing in different fractions were desulfurized by different reaction mechanisms. In this study, an autoclave was used to observe HDS reactivity of the fractions derived from a gas oil at a temperature 360°C under a total pressure of 2.9 MPa (400 psig). CoMo catalyst showed slightly but definitely higher catalytic activity (91% conversion) than that of NiMo catalyst (90% conversion) for HDS of lighter fractions. In contrast, NiMo catalyst showed significantly higher catalytic activity (58% conversion) than that of CoMo catalyst (46% conversion) for HDS of heavier fractions. The gas oil contains more than 60 kinds of sulfur compounds which appear to have very different HDS reactivities. The benzothiophenes, more reactive sulfur compounds than dibenzothiophenes, are predominantly in lighter fractions. In contrast, the alkyldibenzothiophenes, which are recognized as the most unreactive, are dominant in heavier fractions. It was reported that NiMo catalyst was more active for hydrogenation of aromatics than CoMo catalyst. Hence, the superiority of NiMo catalyst over CoMo catalyst for HDS of heavier fractions can be also attributed to its higher hydrogenation activity which is very essential for HDS of such alkyldibenzothiophenes.

Deactivation of Catalysts

Most catalysts used in heterogeneous catalytic processes are subjected to a decrease in initial activity

over a period of time. The selectivity associated with the activity change may improve or become worse. The time required for the activity to fall to an undesirable level varied with the severity of the process conditions and type of reaction. The reason why this happens is often very complicated but is usually due to four basic mechanisms: poisoning, fouling, sintering or thermal degradation, and loss of catalyst material through formation and escape of vapors [Satterfield, 1980; Bartholomew, 1984 and Hughes, 1984].

The poisoning may be due to a side reaction involving the same reactants as a main reaction (a parallel poisoning process). Alternately, the deposited material may be the result of further reaction of the primary product (a series poisoning process). Still another possibility is deactivation due to an independent reaction involving a different reactant, e.g., impurity in the feed to the reactor. A poison blocks the active catalytic metal site and may also induce changes in the surface or result in formation of compounds.

Catalyst poisons can be classified in various ways, such as by their degree of affinity for the surface, as temporary or permanent, or as selective or nonselective. In particular, we will make a distinction between temporary and permanent poison, a point which rests upon 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 active sites in a uniform manner, such that the net activity of the surface is a direct function of the quantity 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 quantity of poison chemisorbed.

Fouling is a physical deposition of species from the fluid phase onto the catalyst surface. This results in blockage of reaction sites or pores with consequent loss of active catalyst area, and in extreme cases, it may even lead to blockage of the interparticle void spaces and complete blockage of the reactor. 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. If reaction occurs, coke deposits must also necessarily occur according to the chemistry of the process. The distribution of coke deposits is a

function of reaction process occurring and operating conditions. After a prolonged period of coke deposition and activity decline, the coke is removed by oxidative regeneration at a temperature up to a maximum of 550°C. Activity is often only partially restored by this process.

Sintering or thermal degradation is an irreversible physical process associated with the loss of catalyst area due to crystal growth in catalyst phase, or with the loss of catalyst support area due to support collapse which occurs when catalyst is operated above the normal temperature range. Another thermal effect is the transformation of a catalytic phase to a non-catalytic one.

The loss of catalytic metal through the formation of compounds such as metal carbonyls, oxides, sulfides, and halides in environments containing CO, NO, O₂, H₂S, and halogens is the fourth mechanism of catalyst decay. A somewhat amorphous catalyst may crystallize, or a compound active on crystal habit may be converted into a less active crystalline form. A supported metal catalyst may be reduced in activity or selectivity by becoming alloyed with a metallic impurity or by reaction with the support; for example, a nickel/alumina catalyst may be converted to a nickel aluminate.

As stated previously, a catalyst poison is an impurity present in the feed stream that reduces catalyst

activity. A poison which acts by chemisorption generally does so by being more strongly adsorbed than reactant. The effect may be substantially reversible or irreversible, depending on the strength of adsorption and other factors, although many cases will be intermediate. The rate of catalyst recovery after a poison has been eliminated from a feed stream may be conveniently formulated in terms of a rate of desorption. Therefore, the study of the effects of impurities in the petroleum on HDS reaction is necessary. HDS networks include hydrogenation as well as hydrogenolysis reactions, which evidently occur on different kinds of catalytic sites [Desikan and Amberg, 1964; Satterfield and Roberts, 1968; Broderick and Gates, 1981]. The effects of impurities have been determined for both types of reactions, with the results interpreted in terms of their competitive adsorption on the two kinds of sites. The investigation of the effects of various impurities on reactivities of HDS of dibenzothiophene was reported by Nagai and Kabe [1983]. This study was carried out in a fixed-bed reactor at a temperature of 300°C and a total pressure of 100 atm (1470 psig) on a molybdena-alumina catalyst. The mechanism discussed is based on selective poisoning studies, using various nitrogen, aromatic hydrocarbon, low-molecular weight sulfur, and oxygen compounds. They concluded that nitrogen compounds were the strong inhibitors of HDS and the other impurities were the weak inhibitors. Nitrogen compounds decreased rate of

dibenzothiophene HDS at all temperatures. They inhibited hydrogenation activity but did not affect desulfurization activity because they adsorbed more strongly than did dibenzothiophene at lower temperatures. At higher temperatures (above 320°C) nitrogen compounds also hinder desulfurization together with hydrogenation of dibenzothiophene. The degree of inhibition reaction of nitrogen compounds decreased in the order of acridine > carbazole > phenothiazine > dicyclohexylamine. Sulfur and oxygen compounds retarded all reactions of HDS of dibenzothiophene. Moreover, they concluded that the reactions of desulfurization, denitrogenation, and deoxygenation proceed on one type of site and hydrogenation reactions proceed on another site.

Due to the effect of deactivation by nitrogen poisoning is the strong inhibitor of HDS and the most widely investigated, the following literature will be focused only on nitrogen poisoning in the HDS process.

Effects of Nitrogen Compounds on Hydrodesulfurization

For many years, nitrogen compounds are said to be inhibit HDS reaction through competitive adsorption. Although the significance of competitive adsorption in HDS has been recognized since the 1950s [Kirsch et al., 1959], but only recently have quantitative inhibition effects been reported. Variable in each studied are catalysts, sulfur model compounds used, nitrogen model compounds used, type of reactor and operating conditions.

The studies on inhibition effects of nitrogen compounds on HDS reaction also showed that HDS catalysts have two active sites, one for hydrogenation which occurs on Bronsted acid sites and the other for hydrogenolysis which occurs on Lewis acid sites.

One of the earliest reported works on thiophene poisoning is that of Kirsch et al. [1959]. They revealed that olefin hydrogenation was more strongly inhibited by nitrogen compound than hydrodesulfurization. Their experiments were carried out over CoMo/Al₂O₃ at a temperature of 370°C and a pressure of 300 psig with a synthetic gasoline blended from heptane-heptene feed containing 0.4 wt% sulfur as thiophene. With their experimental conditions, sulfur removal from this feedstock was 79%, while addition of pyridine (0.2 wt% nitrogen in feed) reduced this to 59%.

Two studies using pure compounds have also shown the detrimental effect of nitrogen compounds on HDS reaction. Desikan and Amberg [1964] observed that pyridine poisoned thiophene HDS on a presulfided CoMo/Al₂O₃ catalyst at a temperature of 367°C in a manner indicating that there are two sites which have HDS activity, one very strongly acidic and the other having low affinity for electrons. The strong acid sites are sufficiently electrophilic to interact with olefins and to hydrogenate them. Hydrogen sulfide, thiophene, and pyridine can be strongly adsorbed on them. The weaker acid sites can be poisoned irreversibly only by a

sufficiently strong base such as ammonia, or alkaline. These sites can be expected to desulfurize. Pyridine apparently poisons these sites to different extents. Lipsch and Schuit [1969] also reported that pyridine poisons thiophene HDS, using a CoMo/Al₂O₃ catalyst that was prereduced but not presulfided, but the effect was not great as that of Desikan and Amberg. Both these studies utilized an atmospheric pressure pulsed reactors, so the results are mainly qualitative.

Further studied of the pyridine poisoning on thiophene hydrogenolysis was examined by Sheikhezai et al. [1977] on Mo/Al₂O₃, Co/Al₂O₃, and CoMo/Al₂O₃ catalysts in a pressurized continuous flow reactor at a temperature of 300°C and a pressure of 30 atm (440 psig). The pyridine poisoning experiment was also in agreement with the above literatures. The relative activities of three catalysts, Mo/Al₂O₃, Co/Al₂O₃, and CoMo/Al₂O₃ for thiophene desulfurization were 100%, 44.4%, and 91.0%, respectively, while addition of pyridine reduced these to 52%, 23.3%, and 91.0%, respectively. These results illustrated that Mo/Al₂O₃ catalyst seemed to be a more active HDS catalyst than the commercial CoMo/Al₂O₃ catalyst but, contrary to the former, the latter maintained its HDS activity in the presence of pyridine.

HDS and HDN occur simultaneously but in both cases the least reactive compounds are those containing heterocyclic rings. The reactions of heterocyclic compounds are the greatest industrial interest. In an

earlier study using mixtures of thiophene and pyridine as model compounds for the two groups of reactions, Satterfield et al. [1975] demonstrated that pyridine severely inhibited HDS of thiophene on sulfided CoMo/Al₂O₃ catalyst at a pressure of 50 psig with a flow microreactor. The increase of thiophene conversion from 37% to 88% and 3% to 12% were the results of the increasing temperature from 280°C to 320°C for thiophene alone and addition of pyridine, respectively. In addition, small additions of pyridine caused a major inhibition of HDS of thiophene but larger additions had little effect. The pattern of this inhibition suggested there are two types of HDS sites involved. The first are postulated to be very active for HDS but very sensitive to nitrogen bases. Sufficient quantities of these bases will completely block these sites and render them inactive for HDS. The second type of sites are much less active for HDS, but they are also less susceptible to pyridine poisoning. These latter sites are responsible for HDS activity after the first type of sites have been blocked. On the other hand sulfur compounds were found to have dual effects on catalytic nitrogen removal. At temperatures lower than 325°C, thiophene inhibited the conversion of pyridine by competing with pyridine for hydrogenation sites on the catalyst. At higher temperatures (325-400°C), thiophene enhanced HDN rate, apparently by interaction of HDS reaction product, H₂S, with the catalyst to improve its hydrogenolysis activity.

Later, Satterfield et al. [1980] reported further studied of pyridine inhibition of thiophene HDS over NiMo/Al₂O₃ catalyst at higher pressure ranging from 1 to 7 MPa (145-1000 psig) and temperatures of 200°C to 400°C in a plug-flow microreactor. The increasing the reaction temperature (230-270°C) caused a significant increase in thiophene conversion from 35% to 95% at a pressure of 500 psig. While the addition of pyridine caused significant decreases in thiophene conversion from 3% to 22%. These results indicated that in qualitative the effect of temperature on thiophene conversion was about the same for thiophene alone as for thiophene and pyridine mixtures. In conclusion, thiophene HDS was inhibited by the presence of pyridine at all temperatures and pressures studied. Complete conversion was still possible under inhibited conditions but required higher reaction temperatures than for the reaction of thiophene alone.

In the series of investigations involving benzothiophene, as well as thiophene, Cowley and Massoth [1978] also found that pyridine inhibited benzothiophene HDS over a sulfided Mo/Al₂O₃ catalyst at a temperature of 345°C in a stirred-flow microbalance. The increase in pyridine concentration resulted in an increase in catalyst weight and a corresponding decrease in catalyst activity. Neither the weight nor catalyst activity returned to its original value when pyridine was removed from reaction stream, indicating a permanent poisoning of

some sites. It is evident pyridine adsorbs on active desulfurization sites.

A thorough analysis of the inhibition by quinoline of the reactions in dibenzothiophene network was carried out by Bhide [1979]. Studies used a NiMo/Al₂O₃ catalyst in a batch reactor at a temperature of 350°C and a pressure of 3.4 MPa (500 psig). Quinoline strongly inhibited all the reactions of dibenzothiophene network. Hydrogenation reactions were inhibited more than hydrogenolysis reactions, and the approximate 2-fold difference in the decrease of the rate constants was interpreted as evidence of separate sites for hydrogenation and hydrogenolysis reactions. Using Bhide's data, Lo [1981] developed a model based on Langmuir-Hinshelwood rate expressions for each reaction of the dibenzothiophene network; an advantage 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-site model proposed years earlier by Desikan and Amberg [1964].

Investigations of inhibition of the HDS of some sulfur compounds by various nitrogen compounds have also been reported. These results are useful for correlating molecular structure with inhibition, and they provide

insights into inhibition mechanisms.

Miciukewicz et al. [1984] studied the inhibiting effects of several nitrogen compounds on thiophene HDS on a CoMo/Al₂O₃ catalyst at a temperature of 350°C and at atmospheric pressure in a stirred balance microreactor and compared them to inhibition of hexene hydrogenation. For a given nitrogen compound deactivation of HDS was greater than that of hydrogenation in the absence of steric effects and deactivation was generally greater for those nitrogen compounds having higher pK_a values. But the sterically hindered nitrogen compounds were weakly adsorbed than the others and inhibited the thiophene HDS less. Surprisingly, the hindered nitrogen compounds inhibited 1-hexene hydrogenation more than thiophene HDS. The further experiments of the same reaction were reported by Massoth and Miciukewicz [1986]. The kinetics of deactivation of thiophene HDS and hexene hydrogenation by pyridine poisoning were studied in a flow microbalance reactor on CoMo/Al₂O₃ catalyst at a temperature of 350°C and at atmospheric pressure. Under the reaction conditions employed, pyridine did not undergo reaction. The relative hydrogenation of hexene activities were less depressed at a given amount of pyridine adsorbed as compared with HDS activities. The deactivation kinetics could not be correlated with a reversible (rapid) pyridine adsorption model. A quasiirreversible model correlated the data very well. In this model, the rates of adsorption and desorption of

pyridine are relatively slow compared to reaction rates. Thus, its effect on catalytic activity is reflected in a quasipermanent poisoning of active sites, lowering the reaction rate constant, rather than in a reversible competitive adsorption for active sites. Furthermore, it is deduced that the number of catalytically active sites is small compared to the total adsorption sites.

The foregoing results suggest relations between the basicity of unhindered organonitrogen compounds and the strength of their inhibition for conversion of sulfur compounds. Such relations were sought by LaVopa and Satterfield [1988] for thiophene HDS and by Nagai et al. [1986] for dibenzothiophene HDS. LaVopa and Satterfield studied the poisoning effect experiments of 14 nitrogen compounds in a vapor-phase flow reactor over a NiMo/Al₂O₃ catalyst at a pressure of 7.0 MPa (1000 psig) and temperature ranges from 300°C to 400°C. The pseudo-first-order rate constant k' for thiophene disappearance in the presence of several inhibitors was correlated by the following equation:

$$k' = k / (1 + K_I P_I)$$

where the subscript I denotes an inhibitor. They calculated adsorption constants, pK_a values, and proton affinities for nitrogen compounds as shown in Table 2.2, these data obtained at 360°C. The two measures of basicity: pK_a values measured in aqueous solution at 25°C proton affinity values. Adsorption strength of the

Table 2.2 Calculated Adsorption Constants, pK_a Values, and Proton Affinities (PA) for Nitrogen Compounds Studied [From LaVopa and Satterfield, 1988]

Compound	K (kPa^{-1})	pK_a	PA (kcal/mol)
Naphthalene	0.011		199.8
Ammonia	0.048	9.24	207
Phenanthrene	0.064		209 ^b
Aniline	0.094	4.63	213.5
2-Ethylaniline	0.10	4.42	
2,6-Dimethylpyridine ^a	0.11	6.71	231.5
1-Methylpiperidine ^a	0.26	10.19	233.2
Pyridine	0.43	5.29	222
1,2,3,4-Tetrahydroquinoline	0.46		225 ^b
Carbazole	0.51		
Piperidine	0.58	11.12	229.7
4-Methylpyridine	0.68	6.02	229
Quinoline	0.98	4.80	227.6
5,6,7,8-Tetrahydroquinoline	2.0		
Decahydroquinoline	2.0		
1,8-Bis(<i>N,N</i> -dimethylamino)naphthalene	3.1		246.2

^a Sterically hindered;

^b Estimated

inhibitors increased with increasing of basicity in the order ammonia < aniline < pyridine < quinoline. The same order was observed at temperature of 300°C and 400°C. Adsorption equilibrium constants for nonsterically hindered species correlated with gas-phase basicity in the form

$$\ln K \propto (\text{proton affinity}).$$

This relation hold over the entire range of temperatures studied (300-400°C). Furthermore, they indicated that HDS activity decreased with increasing partial pressure of nitrogen compounds, but HDS activity could be increased with increasing temperature because the strength of adsorption of nitrogen compounds decreased with increasing temperature. Nagai et al. [1986] examined the nature of HDS sites of NiMo/Al₂O₃ catalyst in a flow microreactor at temperatures between 220-340°C and a total pressure of 10.1 MPa (1460 psig). At the relatively low temperature of 260°C, they observed that nitrogen compounds inhibited hydrogenation but not hydrogenolysis of dibenzothiophene. In addition, they concluded that the degree of inhibition of nitrogen compounds was due to the strength of their basicities which revealed intrinsic basicity. Adsorption constant increased uniformly with increasing basicities and proton affinities measured in the gas phase. Higher basicity is indicated by higher pK_a values or higher of nitrogen compounds. Adsorption constant values of acridine, quinoline, pyridine, piperidine, cyclohexylamine, γ-picoline, dicyclohexylamine and aniline were 200, 131, 107, 85, 77, 63, 45, and 19 kPa⁻¹, respectively. In both studies, the estimated adsorption parameters correlated poorly with basicities of nitrogen compounds in aqueous solution (i.e., pK_a values). Instead, these parameters generally correlated well with gas-phase proton affinities, which evidently better represent 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 hydrogenation sites poisoned by nitrogen compounds were Bronsted acid sites.

From the literature reviews, the presence of nitrogen compounds in feed stream greatly decreased catalytic HDS activity and did not improve selectivity of a catalyst. On the other hand, under some conditions heterocyclic nitrogen compounds actually increased the rate of reaction of HDS, an effect that had confirmed by Nagai [1985]. He reported that the HDS of dibenzothiophene at temperatures between 220-300°C and a total pressure of 10.1 MPa (1460 psig) on NiMo/Al₂O₃ catalyst in a continuous-flow microreactor was increased by addition of acridine with high selectivity for desulfurization reaction. Dibenzothiophene conversion with addition of acridine was about 2 times greater than that for reaction of dibenzothiophene alone at all reaction temperatures. In the initial stage of the addition (a small amount of a nitrogen compounds on the surface of the catalyst), poisoning effect on catalyst suggested that the poisons block active sites and thus prevent hydrogenation of dibenzothiophene. 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 structures on the edge of MoS₂,

Topsoe et al., 1981; Topsoe, N. and Topsoe, H., 1983] to become more active for desulfurization of dibenzothiophene. In addition, the poisons might help in the desorption of sulfur adsorbed on desulfurization sites of the catalyst. This phenomenon was also observed for a sulfided NiW/Al₂O₃ catalyst under the same conditions of his previous experiment, but not for a sulfided CoMo/Al₂O₃ catalyst [Nagai, 1987]. He concluded that the addition of acridine highly increased the selectivity for desulfurization while decreasing the concentration of hydrogenated compounds.

LaVopa and Satterfield [1988] also found that the addition of quinoline showed the same effect as acridine. The rate of HDS at a pressure of 7.0 MPa (1000 psig) on a presulfided NiMo/Al₂O₃ catalyst was markedly increased by the presence of quinoline at a temperature of 260°C, the conversion of dibenzothiophene raised from approximately 55% to 97% at a space time of 580 hr g.of cat/mol of dibenzothiophene. The addition of quinoline suppressed hydrogenation functionality, but it enhanced desulfurization. However, at temperature of 360°C it moderately decreased the HDS reaction from approximately 60% to 50% conversion of dibenzothiophene at a space time of 8 hr g.of cat/mol of dibenzothiophene.

Chantalakka [1993] investigated the influence of nitrogen compounds on HDS of thiophene over a CoMo/Al₂O₃ catalyst in a fixed-bed reactor at temperature of 210°C and a total pressure of 2.73 MPa (400 psig). Substances

used to represent nitrogen compounds were pyridine, quinoline, 1,2,3,4-tetrahydroquinoline, 2,6-lutidine, and pyrrole. Data from Table 2.3 showed that the addition of nitrogen compounds even at low concentration (0.5 wt% N as nitrogen compounds) to the feedstock inhibited thiophene conversion due to competitive adsorption of nitrogen compounds on active sites. Inhibition strength depended upon type and structure of nitrogen compounds. Basic nitrogen compound (pyridine) inhibited more than non-basic nitrogen compound (pyrrole). Increasing saturation to ring (1,2,3,4-tetrahydroquinoline) and steric hindrance in structure (2,6-lutidine) of nitrogen compounds decreased their inhibition.

Table 2.3 Thiophene Conversion in the Presence of Nitrogen Compounds

Nitrogen Compounds	Conversion of Thiophene (%)		
	Thiophene alone at 48 hrs.	Addition of Nitrogen Compounds at 96 hrs.	Thiophene alone at 120 hrs.
Pyridine	57.33	19.2	67.06
Quinoline	59.44	20.71	23.44
1,2,3,4-Tetrahydroquinoline	62.63	23.92	33.53
2,6-Lutidine	58.12	51.23	67.19
Pyrrole	53.63	30.74	59.14

Literature Summary

1. Operating conditions for hydrodesulfurization reaction depend on the boiling range and character of feedstock, the degree of desulfurization required and the catalyst employed. In general, the temperatures range from 300°C to 450°C and the pressures range from 147 psig to 2,940 psig.

2. The most commonly used hydrodesulfurization catalysts consist of cobalt oxide and molybdenum oxide (CoMo), or nickel oxide and molybdenum oxide (NiMo), dispersed on high surface area alumina (Al_2O_3) supports.

3. Operating temperature strongly influences the reaction rate of hydrodesulfurization. When increasing temperature, the rate of hydrodesulfurization increased.

4. Catalyst used in hydrodesulfurization can be deactivated by impurity poisoning (such as aromatic hydrocarbon, sulfur, nitrogen, and oxygen compounds) contained in feedstocks. Nitrogen compounds are the strong inhibitors of hydrodesulfurization reaction and the other impurities are the weak inhibitors.

5. The presence of nitrogen compounds in the feed stream greatly decreases the reaction rate of catalytic hydrodesulfurization and does not improve the selectivity of catalyst. On the other hand, under some conditions heterocyclic nitrogen compounds actually increase the rate of hydrodesulfurization reaction.

Notation

R	aliphatic or aromatic hydrocarbon
S	sulfur or hydrogen sulfide
T	thiophene
B	butene
A	butane
BD	1,3-butadiene
r_{HDS}	rate of hydrodesulfurization reaction
k	rate constant for thiophene disappearance
k'	rate constant for thiophene disappearance in the presence of inhibitor
K	adsorption constant
K_T	equilibrium constant of thiophene
K_H	equilibrium constant of hydrogen
K_S	equilibrium constant of hydrogen sulfide
P_T	partial pressure of thiophene
P_H	partial pressure of hydrogen
P_S	partial pressure of hydrogen sulfide
pK_a	basicity in aqueous solution
PA	proton affinity

Greek symbols

σ	hydrogenolysis site
τ	hydrogenation site