CHAPTER II

LITERATURE REVIEWS

2.1 Hydrodesulfurization Reaction [6, 7]

Hydrodesulfurization is a reaction between organosulfur compounds and hydrogen gas resulting on formation of hydrogen sulfide and hydrocarbon without sulfur element as major products. Hydrodesulfurization process is used for removal a sulfur compounds from petroleum feedstocks which will improve the quality of the downstream products and protect the performance of the catalyst used in downstream operations. Many researches were conducted to study hydrodesulfurization reaction and its applications in petroleum industries. Ramirez and Guardia [8] studied hydrodesulfurization of kerosene fraction of Romashkine crude. Initial contents of compounds in the kerosine fraction were 5.6 % mercaptans, 24.0 % aliphatics and alicyclic sulfides, 44.0 % thiophene and alkylthiophenes, 0.8 % disulfides, and 0.1 % elemental sulfur. These compounds were removed 98.0 %, 96.7 %, 95.7 %, 67.2 %, and 20.2 % respectively by hydrodesulfurization process. Mamaeva, et al. [9] improved the quality of diesel fuel by hydrodesulfurization of thiophene in diesel fraction. They suggested that the additions of olefin improved its hydrodesulfurization activity.

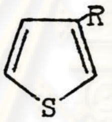
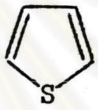
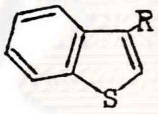
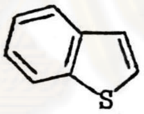
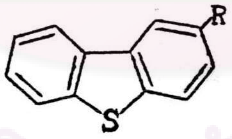
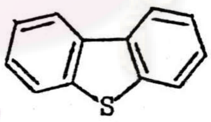
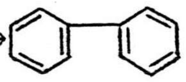
Many types of sulfur compounds are presented in petroleum feedstocks. Examples of these sulfur compounds are shown in Table 2.1. It is necessary to reduce the sulfur content of petroluem fractions for a variety of reasons; (1) The maximum acceptable sulfur content in the feed to a catalytic reformer is determined by the nature of the catalyst. Bimetallic reforming catalysts are especially sensitive, and the sulfur content must be limited to the vicinity of 1 ppm or less. (2) Air-pollution control standards require removal of, in some cases, 80 percents or more of the sulfur otherwise present in various fuel oils. (3) Much of the sulfur in a gas oil fed to a catalytic cracker may be deposited in the form of coke, the sulfur content of which is converted to sulfur dioxide in the regenerator and emitted to the atmosphere in the combustion gases. To limit air pollution from this source the sulfur content of the gas oil may be reduced before being fed to the catalytic cracking unit. (4) The organosulfur content of feed to a hydrocracker must be reduced to avoid poisoning of the hydrocracking catalyst. (5) Reduction of sulfur content reduces corrosion during refining and handing and improves the odor of the product.

A summary of the most important classes of reactions occurring in hydrodesulfurization process is given here, The desired reactions are hydrogenolysis resulting in cleavage of a C-S bond; e.g.,

$$\text{R-SH} + H_2 \longrightarrow \text{RH} + H_2S \qquad \text{(i)}$$

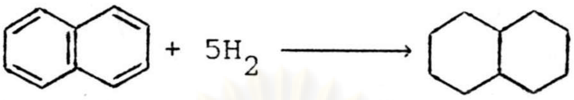
Under industrial reaction conditions, hydrogenolysis reactions resulting in breaking of C-C bonds also occur, e.g.,the hydrocracking reaction.

TABLE 2.1 Examples of Sulfur-Containing Hydrocarbons in Petroleum Crude oil

Name	Structure	Typical Reaction
Thiols (mercaptans)	R-SH	$R\text{-}SH + H_2 \longrightarrow RH + H_2S$
Disulfides	R-S-S-R′	$R\text{-}S\text{-}S\text{-}R' + 3H_2 \longrightarrow RH + R'H + 2H_2S$
Sulfides	R-S-R′	$R\text{-}S\text{-}R' + 2H_2 \longrightarrow RH + R'H + H_2S$
Thiophenes		 $+ 4H_2 \longrightarrow n\text{-}C_4H_{10} + H_2S$
Benzothiophenes		 $+ 2H_2 \longrightarrow CH_3CH_2$-  $+ H_2S$
Dibenzothiophenes		 $+ 2H_2 \longrightarrow$  $+ H_2S$

$$RCH_2CH_2R' + H_2 \longrightarrow RCH_3 + R'CH_3 \qquad (ii)$$

Hydrogenation of unsaturated compounds also occurs during hydrodesulfurization, and the reaction rates are sinificant compared with those of hydrodesulfurization; e.g.,


(iii)

The last three classes of reactions take on economic importance in the processes by consuming expensive hydrogen without removing sulfur.

Thermal cracking reactions can also take place at relatively high temperatures to produce molecular-weight reduction.

The hydrodesulfurization reactions are virtually irreversible at temperature and pressures ordinarily applied, roughly 300 to 450°C and up to 200 atm. The reactions are exothermic with heats 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.

2.2 Typical organic sulfur-containing compounds in feed [10, 11]

Many researches have been conducted using several kinds of organic sulfur-containing compounds to study hydrodesulfurization reaction. Nagai and Kabe [12] studied the selectivity for hydrodesulfurization and hydrogenation of dibenzothiophene on a presulfided MoO_3-Al_2O_3 catalyst. The major products of this reaction were cyclohexylbenzene and biphenyl. Dibenzothiophene hydrogenation was inhibited by a small addition of N compounds and was completely suppress by H_2S. They suggested that hydrogenation and hydrodesulfurization occurred on different sites. Shin, et al. [13] also studied hydrodesulfurization of dibenzothiophene dissolved in n-heptane on sulfided Co-Mo/Al_2O_3 catalyst in a fixed bed flow reactor at reaction temperature between 533 and 537 K, and total reaction pressure from 2 to 6 MPa. The reactions was first order with respect to dibenzothiophene concentration. Most of the products were biphenyl and cyclohexylbenzene.

Hydrodesulfurization of benzothiophene was investigated over a CoO-MoO_3 -Al_2O_3 catalyst by Daly [14]. Studies ratures of 200 to 400°C and a pressure of 1250 psig. The hydrodesulfurization of benzothiophene proceeded by two separate mechanisms, both pseudo-first order in benzothiophene. Pokorny and Zdrazil [15] studied the reaction of benzothiophene and thiophene on sulfided Co-Mo/Al_2O_3 and MoS_2 catalysts at the temperature ranges from 543 to 623 K and at the hydrogen partial pressures from 0.5 to 2.0 MPa in a tubular flow reactor. They found that benzothiophene was more reactive than thiophene, and difference in their reactivitied in a competitive reactions exceeded that in simple reactions.

Maternova and Zdrazil [16] studied hydrodesulfurization of diethylsulfide and thiophene on a Co-Mo/Al_2O_3 catalyst at a temperature of 573 K and a hydrogen partial pressure of 2 MPa. In the reaction, diethylsulfide reacted faster than thiophene. The kinetic data showed that the ring of thiophene was hydrogenated in the first step and the

C-S bond was eliminated.

2.3 Hydrodesulfurization Catalyst [17-19]

Hydrodesulfurization is a catalytic reaction. The nature of the catalytic process is proceeded without severe condition by reducing activated energy. Therefore the reaction may be accomplished at a lower temperature and a lower pressure than that required for the homogeneous reaction. Catalysts used in hydrodesulfurization consist of transition metal group VIII, Ni or Co, as promoter to improve catalyst activity [20]. These matals were impregnated on the support such as γ-alumina, active carbon or silica. Vissers, et al. [21] evaluated first, second and third row transition metal sulfided ranging from Group VIB to VIII, supported on actived carbon for their ability to catalyze the hydrodesulfurization of thiophene at atmospheric pressure. They suggested that second and third row elements had the catalytic activity varying over more than an order of magnitude and maximum occuring at Rh in the second and Ir in the third row. First row elements showed a twin-shaped pattern with maximum activity located at Cr and Co. Superior catalysts had low binding energy shifts and preserve a high degree of metal character under sulfiding conditions. Whereas Harris and Chianelli [22] studied electronic factors of first and second row transition metal sulfides that related to their hydrodesulfurization catalyst activity, which were combined to form an activity parameter for each sulfide. A model for the binding of molecule thiophene to the catalyst surface was consistent both with the relation between bulk electronic structure and sulfide catalytic activity, and with ligand properties of thiophene in transition metal complexes.

The most common catalyst used in industry is a mixture of active metals on a γ-alumina support, which must be sulfided before used. Since metal sulfide is the active form for hydrodesulfurization. Osei-Owusen and Aharoni [23] studied adsorption of sulfur compounds by hydrodesulfurization catalysts. They found that the adsorption of sulfur compounds from liquid phase hydrodesulfurization reaction was too slow to be measurable when the catalyst was in oxidic state but proceeded at a measurable rate on the sulfided catalysts. Gissy, et al. [24] studied hydrodesulfurization activation procedure of Co-Mo/alumina catalyst. They treated catalysts with sulfiding agent before benzothiophene dissolved in n-dodecane was used in hydrodesulfurization reaction. They suggested that presulfiding with hydrogensulfide gave better hydrodesulfurization activity than presulfiding with thiophene, owing to the coke precursor which was formed in the hydrogenolysis of thiophene. The method of presulfiding the catalyst is considerably more important in the case of Ni-Mo/Al_2O_3 than with Co-Mo/Al_2O_3 catalysts. If not presulfided before use, NiO may be reduced to metallic Ni by reducing environment in the reactor, and then this may be difficult to convert to the sulfide. Metallic Ni may cause undesirable and probably sinters more rapidly than a nickel sulfide.

Toulhoat and Berrebi [25] studied supported metal oxide catalysts for heavy petroleum fraction. The catalysts were sulfided and activated in 3 steps by (i) introduction of a polysulfide into the catalyst pores in the absence of hydrogen at 0-50 °C, (ii) sulfidation of the metal oxide at 65-275 °C and 0.5-70 bar for approximately 5 minutes, and (iii) activation of the catalyst at above 275 °C for more than 1 minute. They suggested that a suitable catalyst was $NiO-MoO_3$ and a suitable sulfiding agent was TPS containing 37 wt% sulfur. In the hydrorefining of coker gas oil over a presulfided 3:14 (wt%) $NiO-MoO_3/Al_2O_3$ at the temperature of 300 °C, the catalyst had a 97.3 % hydrodesulfurization activity and 82.7 % hydrodenitrogenation activity. The sulfided catalysts were also useful in toluene hydrogenation and cyclohexane isomerization.

The support of hydrodesulfurization was developed and distinguished which was the most suitable for each transition metal of hydrodesulfurization catalyst. Rao and Dhar [26] studied the catalytic functionalities of Al_2O_3 and SiO_2-supported WS_2 catalyst in thiophene hydrodesulfurization and cyclohexene hydrogenation. They found that hydrogenation decreased linearly with increasing SiO_2 content of the support. Hydrodesulfurization decreased sharply at low SiO_2 contents and more slowly at higher SiO_2 contents of the support. They suggested that the active metal was well dispersed on Al_2O_3 whereas the dispersity decreased gradually as the SiO_2 content of the support increased. This case was the same as Muralidhar, et al. [27] who suggested that the catalytic activity of zation of thiophene and hydrogenation of 1-hexene model compounds was decreased when the SiO_2 content in the support was increased. Co and Mo formed bonds with Al_2O_3 which persisted after the sulfiding while the bonding with SiO_2 was weak. Co and Mo crytallites on SiO_2 had lower activity than on Al_2O_3. Moore, et al. [28] studied the effect of an acidic support of the hydrotreating catalyst on simultaneous hydrodesulfurization and hydrodenitrogenation of heterocyclic sulfur and nitrogen at the temperature ranges from 200 to 400 °C and at the pressure ranges form 0.27 to 1.4 MPa. They suggested that SiO_2-Al_2O_3 support was more effective support for hydrodenitrogenation of pure pyridine, whereas Al_2O_3 was a more effective support for hydrodesulfurization of pure thiophene and for hydrodesulfurization of thiophene and hydrodenitrogenation of pyridine in mixed feed. Moon and Ihm [29] studied the activities of Mo and Co catalysts supported on activated carbon or Al_2O_3 in thiophene hydrodesulfurization and C_2H_4 hydrogenation by using NO chemisorption and temperature programmed desorption. They found that the carbon-supported catalysts showed higher hydrogenation and hydrodesulfurization activities than the Al_2O_3-supported catalysts, especially when the metal loading was small.

Spozhakina, et al. [30] studied thiophene hydrodesulfurization on supporting phosphorus-, silicon-, and titanium-molybdenum heteropoly acids (HPA). They suggested that the presence of HPA in the initial catalysts promoted the formation of the Mo state ensuring high reaction rates. A possibility for HPA synthesis when supporting paramolybdate on TiO_2 accounted for the great effect of the support on the catalyst properties. Ng and Gulari [31] studied the effects of preparation conditions on MoO_3-TiO_3 catalyst activity /selectivity. They suggested that these catalysts were more active than Al_2O_3-supported catalysts at low MoO_3 loading (less than 4%). Promotion by Co increased catalyst activity only by a modest amount. Later, Daly [32] used TiO_2-CoO_2 and TiO_2-MnO as support materials of 5 wt% CoO-16 wt% MoO_3 catalyst for hydrodesulfurization and hydrodenitrogenation. They concluded that the initial hydrodesulfurization and hydrodenitrogenation rates of these catalysts were higher than the standard supported on Al_2O_3, but the catalyst deactivated rapidly due to carbon deposition.

Okamoto, et al.[33] studied a comparative characterization of sulfided MoO_3/Al_2O_3 and MoO_3/TiO_2 catalysts for hydrodesulfurization of thiophene and hydrogenation of butadiene. They found that sulfided MoO_3/Al_2O catalysts consisted of MoS_2-like phases and Mo(V) species, while sulfided MoO_3/TiO_2 catalyst was fully sulfided to MoS_2-like phases. There were α-sites and β-sites on MoS_2-like phases. They suggested that α-sites were responsible for the hydrogenation at low and high reaction temperatures and in the presence and absence of H_2S, while dual sites were as the hydrodesulfurization active centers in the hydrodesulfurization reaction.

Hydrodesulfurization of thiophene over zirconia and alumina supported cobalt-molybdenum catalysts at the temperature of 280 °C and at the pressure of 1 MPa was studied by

Sedlacek, and Vit, [34]. The activity and selectivity of Mo/ZrO and Co-Mo/ZrO catalysts in thiophene hydrodesulfurization were compared with those of a commercial Co-Mo/Al_2O_3 catalyst. They found that the activity of the former was lower than that of the latter. The S/Mo ratio for the ZrO_2-supported catalysts was 1:2, and that for the commercial catalyst was 2.2.

Pratt and Sanders, [35] studied the structure and hydrodesulfurization activity for thiophene of MoS_2 catalysts supported on Al_2O_3, SiO_2, TiO 2, and ZrO_2. They suggested that the dominant surface species on Al_2O_3 and SiO_2 consisted of MoS_2 oriented vertically on the support. On TiO_2 and ZrO_2, the MoS_2 formed islands lying flat on the support, which expanded at higher loading to encapsulate the support particles. The specific activity for the TiO_2-and ZrO_2-supported systems were significantly higher than for the Al_2O_3- and SiO_2- supported systems.

Bridgewater, et. al. [36] studied the activity of a series of charcoal-supported Co-Mo catalysts in the hydrodesulfurization of thiophene at the temperature of 350 °C and at the atmospheric pressure. They concluded that butane formation was much higher over these charcoal-supported catalysts than over Al_2O_3-or graphite-supported catalysts and charcoal-supported catalysts had a higher hydrogenation activity. Duchet, et al. [37] studied the activity of varying transition metal sulfided catalysts over carbon supported for thiophene hydrodesulfurization and butene hydrogenation in a flow microreactor at atmospheric pressure. They found that sulfur species were supposedly connected with the catalytic activity for hydrodesulfurization. The Co/C gave the highest activity for hydrodesulfurization. Therefore Co and Ni were considered as the promoters for the MoS_2 and WS_2 phase.

Topsoee, et al. [38] studied the role of promoter atoms in cobalt-molybdenum and nickel-molybdenum catalysts. The Co-Mo-S structure responsible for the promotion of the hydrodesulfurization activity was shown to be MoS_2 with the Co atoms located in edge positions. They suggested that Co or Ni edge sites played a more important role than Mo edge sites in both hydrodesulfurization and hydrogenation. Corelation between surface characteristics and hydrodesulfurization activity of MoO_3-Al_2O_3 catalysts was studied by Houalla, et al. [39]. They found that thiophene conversion rates was higher for these same catalysts when they used higher Mo/Al ratios. The MoO_3-Al_2O_3 catalysts were promoted by addition of Ni or Ni and Ti. These promoted catalysts increased both thiophene conversion ratio and the surface Mo/Al ratios. Both promoters diminished the importance of pH. Lahiri and Nandi [40] studied thiophene hydrodesulfurization in heptane over Co-MoO_4/Al_2O_3 promoted with WO_3, Fe_2O_3, or NiO at the temperature of 400 °C and a contact time of 120 gm-hr/gm-mole. The composition of CoO, FeO_3, MoO_3, and Al_2O_3 were 3, 1, 16, and 80% respectively. This composition was optimum for 95% hydrodesulfurization of thiophene in heptane and it was used to desulfurize stright-run naphtha, kerosine and gas oil from petroleum feedstock.

Mitchell, et al. [41] studied the activity and product distribution for the thiophene hydrodesulfurization over Mo/Al_2O_3 catalysts, promoted by Ru, Co, Ni or Co-Nb/Al_2O_3 catalysts at the temperature ranges from 523 to 673 K and atmospheric pressure. They suggested that the promoters enhanced the desulfurization activity, excepts for uncalcined Ru, and diminished the hydrogenation activity of the catalysts. The Co-Nb catalysts were inactive. The promotion of V catalysts by Ni showed that an MoS_2-type layer was not essential for synergy. The catalyst structure in which all or some parameters were dispersed by binding to unsaturated sulfur atoms at the edge of MoS 2 patches.

McCarty [42] studied the catalytic activity of reduced tenary Mo sulfides, known as Chevrel phase compounds, for thiophene hydrodesulfurization and for 1-butene hydrogenation at the temperature of 400 °C. Chvrel phase compounds of the general composition $M_xMo_6S_8$, with M being Ho, Pb, Sn, Ag, In, Cu, Fe, Ni, or Co had hydrodesulfurization activities comperable to modle unpromoted and Co-promoted MoS_2 catalysts. They suggested that the most active catalysts were the large cation componnds (Ho, Pb, Sn) and the least active catalysts were the small cation compounds (Cu, Fe, Ni, Co). Except for the Ni phase $Ni_{1.6}Mo_6S_8$, all Chevrel phase catalysts had hydrogenation activitie which were much lower than the model MoS_2 catalysts. They found that the oxidation state of the surface Mo atoms of the large action compounds was unchanged after 10 hours of thiophene reaction whereas some oxidation was apparent for the small cations compounds.

Fu, et al. [43] studied the promotion effect of titanium dioxide on Mo-Co/γ-Al_2O_3 catalyst. They suggested that hydrodesulfurization activity of TiO_2-containing catalyst showed a maximum with increasing Tio_2 content. The promotion effect of TiO_2 upon the catalyst was realized through the coordinated action between TiO_2 and CoO which increased the formation probability of Co-Mo-S phase in the catalyst. Therefore both the active center number and the intrinsic activity of Mo-Co/γ-Al_2O_3 catalyst increased. Lindner, et al. [44] studied thiophene hydrodesulfurization by treatment of Fe-, Co-,or Ni- promoted Mo powders with S at the temperature ranges from 473 to 673 K. They found that the Ni-, Co-,and Fe- promoted catalysts gave more than 60, 50 and more than 40% , thiophene conversion, respectively, which 30 and less than 1% thiophene conversions were obtained for $MoS_{1.95}$ and MoS respectively. They suggested that the promoters not only increased the activity of these Mo catalysts but they also changed the product distributions.

Researches have been conducted to investigate the suitable active metals for hydrodesulfurization catalyst. Carbon-supported Fe-Mo sulfided catalyst in thiophene hydrodesulfurization at the temperature of 673 K in a flow microreactor operaing at atmospheric pressure was characterized by Raselaar, et al. [45]. The Mo content was 9.5 wt% while the Fe content was 0.6-9.0 wt%. They suggested that sulfided Fe-Mo/C catalysts contained a mixed "Fe-Mo-S" phase and "Fe-sulfide". The former was responsible for the promoting effect toward thiophene hydrodesulfurization. They concluded that the Fe atoms in the "Fe-Mo-S" phase were located at surface of MoS_2 microcrystals. The amount of "Fe-sulfide" present in the catalyst increased with increasing Fe content. This "Fe-sulfide" might partly covered "Fe-Mo-S" phase, thus causing a decrease in the promoting effect. Villa Garcia, et al. [46] suggested that general stoichiometry of Fe-Mo sulfide was $Fe_{2x}Mo_{1-x}S_2$ with x=0.025-0.3.

Thakur [47] studied the role of Fe-promoted MoS_2 catalysts by varying Fe/(Fe+Mo) from 0 to 1.0 ratios. They compared the steady-state specific activity (conversion/g) of iron-molybdenum sulfide catalysts and their ratio/unit surface area of catalyst in hydrogenation of cyclohexene and hydrodesulfurization of thiophene with those from other Group VIII metal (Ni,Co)-promoted catalysts. They suggested that Fe behaved like Ni in promoting hydrogenation and hydrodesulfurization activities.

Groot, et al. [48] compared Fe-sulfided catalysts supported on various C materials, on Al_2O_3 and on SiO_2 in thiophene hydrodesulfurization activity. The Fe content was 0.2-5.0 atoms per nm^2 support surface area. They suggested That C-supported Fe-sulfided catalysts was much more active for thiophene hydrodesulfurization than the Al_2O_3- and SiO_2-supported ones within the surface loading range studied. The activity of sulfided Fe on Al_2O_3 catalyst was lower than other supported transition metal sulfides cause by an incomplete sulfidation. Groot, et al. [49] studied the characteristic of C-supported Fe-sulfided catalysts on hydrodesulfurization of thiophene and hydrogenation of butene in a flow microreactor at atmospheric pressure. The Fe content was varied from 0.03-1.9 Fe atoms per nm^2 support surface area. C-support Fe sulfide catalyst had a much higher hydrodesulfurization activity than Al_2O_3-supported Fe-sulfided catalysts. They were also more active and less sensitive to deactivation than C-supported MoS_2 catalysts, which were the better hydrogenation catalysts.

Beyond above documents, there are many researches concerning with investigation and improvement by using several transition metal which are suitable for hydrodesulfurization reaction. Vit and Zdrazil [50] studied hydrodenitrogenation and hydrodesulfurization of C-supported sulfides of Ru, Rh, Pd, Ir and Pt by using activity and selectivity of a mixture of pyridine and thiophene of 280 °C and 2 MPa. The properties of these sulfides were also compared with those of commercial Ni-Mo/Al_2O_3 and Co-Mo/Al_2O_3 Shell catalysts. They found that the C-supported sulfides of Pt were better hydrodesulfurization and much better hydrogenation catalysts than commecial bimetallic catalysts.

Afanas'ev, et al. [51] studied phase composition and properties of catalysts based on oxidized and sulfidized Zirconium nickel tungsten hydride ($ZrNiW_nH_x$) alloys. They found that sulfidation of oxidized $ZrNiW_nH_x$ (n=0.01-0.70) alloys were more active than an industrial Ni-W-S catalyst in the hydrogenolysis of thiophene. $NiWO_4$ was the precursor of centers active in the hydrogenolysis of thiophene. The activity of the catalysts depended on the temperatures of oxidation and sulfidation.

Kuo, et al. [52] studied hydrodesulfulization of thiophene with submonolayers of surface S on ruthenium catalysts. They suggested that these catalysts promoted hexene isomerization, poisoned H adsorption sites, hampened hexene hydrogenation, increse stretching frequencies of adsorbed CO_2 in a crystal-size-dependent mode, and incresed the selectivity toward the hydrodesulfurization vs.hydrogenation of thiophene 100 fold. A multilayer of Sulfur promoted irreversible H adsorption, thiophene hydrogenation, and hexene isomerization. Later on Kuo, and Tatarchuk, [53] studied thiophene hydrodesulfurization over sulfided Ru/γ-Al_2O_3 and Co-Mo/γ-Al_2O_3 catalysts at the temperature ranges from 548 to 623 K and at the pressure of 101 KPa. They found that thiophene hydrodesulfurization over sulfided ruthenium catalysts proceeded direct hydrogenolysis in the absence of tetrahydrothiophene formation. Sulfided Ru/Al_2O_3 catalysts provided a 2-fold higher thiophene hydrodesulfurization ratio than Co-Mo/Al_2O_3 catalysts when they were compared per square meter of active area, while specific thiophene hydrodesulfurization rates were 7 fold higher over Co-Mo/Al_2O_3 catalysts than over Ru/Al_2O_3 when compare per oxygen titratable site. They suggested that mild presulfidization provided surface (i) retaining partial monolayers of absorbed surface as evidence by microgravimeter and oxygen adsorption and (ii) catalizing direct hydrogenolysis to C_4 products and H_2S [54]. The improvement of ruthenium sulfide catalyst was studied by Vrinat, et al. [55]. They studied catalytic properties in hydrogenation and hydrodesulfulization reaction of ruthenium sulfide solid solution containing iron, cobalt or nickle. These sulfide catalysts were used in hydrogen ation biphenyl and hydrodesulfurization of thiophene. They found that the Co-Ru catalysts showed good activity for hydrodesulfurization but very low activity for hydrogenation, and Fe-Ru catalyst had low activity for both reactions. Ni-Ru catalysts had twice the activity of Ru_2S.

Bussell and Somorjai [56] stuidied thiophene hydrodesulfurization over rhenium single crystals and polycrystal foids. They found that rhenium single crystals were 1-6 times more active than molybdenum single crystals, which was in agreement with previous studies using rhenium disulfide and molybdenum disulfide catalysts. The progress document of Bussell and Somorjai [57] was concerned with thiophene hydro-desulfurization over polycrystalline metal foids of Co,Mo and Re. They found that hydrodesulfurization activities of the 3 metal foids over unsupported and supported metal sulfides were in the order Co<Mo<Re. They suggested that Co was the most suitible as a promotor of Mo in Co-Mo catalysts.

Thiophene hydrodesulfurization over transition metal single crystal (Mo,Re) and polycrystal foid (Co,Mo,Re) surfaces was studied by Bussell [58]. They suggested that thiophene hydrodesulfurization was a structure-insensitive reaction over Mo surface, but a structure-sensitive reaction over Rh surface. The hydrodesulfurization reaction over Mo occurred on a strongly bonded adsorbate overlayer composed primarily of carbidic carbon. In contrast, hydrodesulfurization of thiophene over Rh surface occured directly on the metal surface. The ability of the Rh surface to remain free of strongly bonded deposits of carbon and/or sulfur made them more active than Mo surface.

Frety, et al. [59] prepared supported Iridium catalyst by deposited Ir particles on carriers of varying activity. They suggested that activity of the support and the surface tolurance of the catalysts increased but the hydrodesulfurization ability for dibenzothiophene decreased.

Agostini, et al. [60] used Ni-U/Al_2O_3 and Ni-Mo-U/Al_2O_3 catalyst for hydrodesulfurization and hydrodenitrogenation. They concluded that the U in these catalysts blocked the formation of Ni aluminate, increased the dispersity of the active phase, and promoted the hydrogenation of the reaction products.

Guillard, et al. [61] studied the catalytic properties of unsupported vanadium sulfides (V_2S_3) in hydrotreatment reactions. The comparison of the catalytic properties of this chalcogenide with those of Mo or W sulfides showed the superiority of V_2S_3 for perfroming hydrogenation reaction of various cyclic molecules. The hydrodesulfurization properties of V_2S_3 catalysts were the same order as with those of Mo or W sulfides.

Candia, et al. [62] studied the nature of the hydrodesulfurization and hydrogenation sites in Co-Mo/Al_2O_3 and

Ni-Mo/Al_2O_3 catalysts. They suggested that there were two types of catalyst sites. These sites were unpromoted site associated with the Mo atoms and promoted site associated with Co or Ni atoms presented as Co-Mo-S or Ni-Mo-S. Both promoted and unpromoted site was much higher than that of the unpromoted site and the promoted effect of Co or Ni with respect to hydrodesulfurization was much smaller than that observed for the hydrodesulfurization reaction. Mo disulfide layers in hydrotreat catalysts were studied by Kemp, et al. [63]. They found that the tendency of Ni occupied octahedral sites between the MoS_2 layers, while the Co prefers a tetrahedral configulation. In the later research, Alias and Srimivasan [64] studied the activity of Ni-MoO_3 hydrodesulfurization catalysts. They suggested that octahedral sites were responsible for promoting hydrodesulfurization of thiophene. The higher active catalysts were relatively more susceptible to change in paramagnetic nature occurring during reduction by hydrogen. Ihm, et al. [65] studied hydrodesulfurization of thiophene over Co-Mo, Ni-Mo and Ni-W/Al_2O_3 catalysts. They found that the Ni-W system showed the possibility of higher hydrodesufurization funtionality through the relatively weaker adsorption of thiophene and H_2S than did the Co-Mo or Ni-Mo system. The adsorption constants of thiophene, H_2S and 1-butane decreased in the order Co-Mo>Ni-W , whereas H showed the reserved order.

The most common hydrodesulfurization catalyst is a mixture of cobalt and molybdenum oxides on a γ-alumina support. An alternate catalyst composition is Ni-Mo/Al_2O_3 that used especially in hydrodesulfurization, hydrodenitrogenation, and hydrogenation reaction. This conclusion was encouraged by Krichko [66]. Ni-Mo/Al_2O_3 catalysts was used in hydrorefining of coal distillates (b. 120-230 °C). The catalyst containing 10.5 wt% MoO_3 and 2.6 wt% NiO with surface area 130 m^2 and the volume of pores (more than 1000 Å) 0.3 cm^3/g had the best activity for sulfur, nitrogen, and oxygen removement and hydrogenation. The optimal conditions were 380 °C, 6 MPa, and space velocity 1 h^{-1}. Under these condition, phenals, nitrogen compounds, unsaturated hydrocarbons, and sulfur compounds were 100, 100, 98.4, and 98.5 % removed, respectively. This investigation was agreed with the following. Teruo, et al. [67] studied hydrotreating of coal derived middle distillate over Co-Mo/Al_2O_3 and Ni-Mo/Al_2O_3 catalysts. They suggested that the activity of Ni-Mo/Al_2O_3 for desulfurization, denitrogenation, and hydrogenation of the aromatic rings was higher than that of Co-Mo/Al_2O_3. The order of removal in the present of the heteroatoms was as follows: S>N>O.

The ratio of transition metal group VIB/group VIII is always considerably greater than 1 which was encouraged by the following researches. Lebedev, et al. [68] studied the effect of composition on activity of Co-Mo-Al catalysts in hydrogenolysis of thiophene. They suggested that hydrodesulfurization activity was achieved with 20.8-25.0% MoO_3 and 8.7% CoO catalysts. Activity of unsupported and alumina supported cobalt-molybdenum catalysts with various Co/(Co+Mo) ratios in thiophene hydrodesulfurization was studied by Koranyi, et al. [69]. They found that the Mo-rich catalyst, at r=0.38, showed a maximum curve in thiophene hydrodesulfurization activity. While the Co-rich catalysts, at r=0.50 and 0.75, showed a slowly decreasing curve for supported and a rapidly decreasing curve for unsupported catalysts in thiophene hydrodesulfurization activities. The hydrodesulfurization activity of the supported catalysts reached a relatively high constant level, but the unsupported catalysts were quickly deactivated.

Okamoto, et al. [70] used XPS to studied the surface characterization of supported Co-Mo catalysts. They suggested that the activity and selectivity of Co-Mo catalysts for hydrodesulfurization of thiophene were related to the sulfidation degree of Mo and the effective amount of Co_9S_8. While Maria, et al. [71] studied hydrogenolysis of thiophene and hydrogenation of cyclohexane. They found that the highest catalytic activity occurred with the MoS_2-$CoAl_2O_4$ catalyst.

Zrucevic and Youn [72] tested the catalytic activity of CoO-MoO_3-Al_2O_3 catalyst in thiophene hydrodesulfurization. They found that there were the Mo^{3+} and Mo^{4+} concentrations in these catalysts, the former being much more reactive but more easily deactivated than the latter. The stationary catalysts was characterized by Scheffer, et al. [73]. They found that sulfur species on Co/Al_2O_3 catalysts were hydrogenated at a higher temperature than that of corresponding species in Mo/Al_2O_3. Similar sulfur species on Co-Mo/Al_2O_3 were hydrogenated at a lower temperature than that found for either Co/Al_2O_3 or Mo/Al_2O_3. Hydrogenation of stoichiometric sulfur of bulk Co_9S_8 and MoS_2 occured at much higher temperatures than hydrodesulfurization operating temperatures. Hydrogenation of sulfur at a low temperature corresponded with a high hydrodesulfurization activity for Co-Mo/Al_2O_3 catalysts.

Pratt, et al. [74] used unsupported Ni-Mo sulfided catalysts for thiophene hydrodesulfurization. They suggested that the 55 atomic % Ni showed the highest specific activity for thiophene hydrodesulfurization. The hydrodesulfurization sites were coordinatively unsaturated Mo^{3+} cations while edge-intercalated nickel served as an olefin hydrogenation sites and in reducing Mo^{4+} to Mo^{3+}. Highly dispersed Ni_3S_2 is suggested to play a role in hydrogen activation, transfering protons and electrons to the MoS_2, and this may form the origin of the synergistic mechanism. Sulfided Ni-Mo/Al_2O_3 catalysts with constant, 7 and 16 wt% MoO_3 respectively, and variable Ni concentration in hydrodesulfurization of thiophene was characterized by Bachelier, et al. [75]. They suggested that the main enhancement of activity was in the ranges 0.2-0.6 of Ni/Mo ratio. The active structures of sulfidized aluminum-nickel-molybdenum catalysts for hydrogenation and hydrodesulfurization was studied by Agievskii, et al. [76]. They suggested that the active center of supported Al-Ni-Mo catalyst was MoS_2. The Mo:Ni ratio of the center can be taken to be 2. Consequently only one type of center existed on these catalysts for hydrogenation of aromatic hydrocarbons and for hydrodesulfurization of thiophene. They found that an increased in thermal treatment temperature in sulfur-containing media could increased the level of MoS_2 promotion.

Laine, et al. [77] found that the initial hydrode sulfurization activity behavior of supported nickel molybdate catalysts had been markedly influenced by the presence of nickel promoter. The nickel promoter diminished both the rate and the extent of deactivation of the fresh catalyst when exposed to a mixture of hydrogen and thiophene at atmospheric pressure. Presulfidation of the catalysts with pure H_2S did not affect the optimum nickel concentration but increase the optimum molybdenum concentration. They suggested that there was the positive influence of the promoter on the initial transformation of the catalyst to maintain the dispersion of molybdenum during the sulfidation of the catalyst and deminish carbon deposition.

Development of the activity for hydrodesulfurization catalysts was studied by Laine, et al. [78]. They prepared a series of trimetallic (NiCoMo) hydrodesulfurization supported catalysts by varying the ratio of promoters Ni/(Ni+Co) and maintaining the ratio (Ni+Co)/Mo constant. The Ni/(Ni+Co) ratios of 0.7 and 0.8 were appropriate for higher thiophene hydrodesulfurization activity. They suggested that presulfidation was found to increase the activity in NiMo more than in CoMo.

The effectiveness of sulfided nickel-molybdenum and nickel-tungsten on Al_2O_3 catalysts in hydrogenation of oxylene and the hydrodesulfurization of thiophene were compared by Landau, et al. [79]. They suggested that in the kinetic region, the Ni-W catalyst was more active in hydrogenation and the Ni-Mo catalyst was more active in hydrodesulfurization.

Lacrvix, et al. [80] investigated the behavior of a series of unsupported Ni-W sulfide catalysts in hydrodesulfurization of dibenzothiophene and hydrogenation of biphenyl under medium-high-pressure conditions (2.25 MPa). They suggested that the activity may be related to the presence of a mixed NiWS phase and the NiWS entity strongly promoted the hydrogenation function in contrast to the CoMoS species

Kondrat'ev, et al. [80] studied the effect of nickel on tungsten disulfide catalysts. They suggested that the promotion of WS_2 by Ni caused a decrease of the activation energy of hydrodesulfurization of thiophene. The mechanism of WS_2 promotion by Ni was analogous to that of MoS_2 promotion by Co. This conclusion agreed with the following research. Burmistrov, et al. [82] suggested that Ni/WS_2 catalysts were characterized by changes of the activation energies in thiophene hydrogenolysis.

Ermakav, et al. [83] studied highly dispersed sulfided $Ni\text{-}W/SiO_2$ and $Ni\text{-}Mo/SiO_2$ catalysts prepared from organometallic precursors, the structure of the active phase and active centers for C-S bond hydrogenolysis. They found that the active phase of hydrodesulfurization catalysts represented layered sulfide structure with the same M-S and M-M distances as in bulk disulfides where M was W or Mo. The active centers probably included Ni atoms, on which thiophene adsorption occured, and W (or Mo) atoms on the side planes of the MS_2 sheet. Sulfur atoms bond with Ni atom were involved in the catalytic cycle.

Garrean, et al. [84] studied structural, textural and catalytic properties of unsupported NiMo sulfide catalysts. They suggested that this MoS_2-like structure was supported on Ni_xS_y if Ni/(Ni+Mo) was more than 0.25, resulting an enhancement of catalytic activities on hydrogenolysis and hydrogenation.

Borodin and Lazutin [85] studied hydrogenolysis of thiophene on nickel-molybdenum catalysts. They suggested that the activity of these catalysts was the sum of the partial activities of the Ni and Mo phases, accounting for their surface area in binary systems. A recent research in the adsorption parameters and surface species of the nickel-molybdenum alumina catalysts was studied that by Rodriguez [86]. They found that the presence of Ni on the support did not affect the total number of sites occupied by Mo. However, when the Ni content on the solid was increased, the Mo species occupied a higher propertion of octahedral sites. They suggested that a higher Ni content possessed a better dispersion of Mo species and exhibited a higher intrinsic activity of thiophene hydrodesulfurization. Apart from the above researchs, Alias and Srinivason [87] studied the interaction of thiophene with Co and Ni-promoted MoO_3 and tungsta catalysts with the surface activity for hydrodesulfurization reaction. They found that MoO_3 catalysts had good thiophene adsorption properties as compared to tungsta catalysts. They suggested that the Ni-Mo system was the most suitable catalyst system for the hydrodesulfurization reaction.

The comparison of the activities of cobalt-molybdenum/gamma-aluminum oxide and nickle-molybdenum gamma-alminum oxide hydrodesulfurization catalysts was studied by Bouyssieres, et al. [88]. The catalysts were prepared by simultaneous impregnation and calcination at the temperature ranges from 400 to 700 °C. They found that Ni-Mo/γ-Al_2O_3 catalyst calcined at 470 °C was more cative in thiophene hydrodesulfurization than any Co-Mo/γ-Al_2O_3 catalysts. This conclusion was the same as the following research. Bouyssieres et al. [89] studied the relative catalytic activity of Co-Mo/γ-Al_2O_3 and Co-Mo/γ-Al_2O_3 catalysts for the hydrodesulfurization of thiophene at atmospheric pressure and at the temperature range from 226 to 326 °C. They found that the most active Ni-Mo/γ-Al_2O_3 catalyst was more active than the most active Co-Mo/γ-Al_2O_3 catalyst, although the last mentioned ones could become as active as Ni-Mo/γ-Al_2O_3 catalysts at higher reaction temperatures.

Brito, et al. [90] studied the coke deposition rates on Al_2O_3, Mo/Al_2O_3, Ni-Mo/Al_2O_3 or Co-Mo/Al_2O_3 hydrodesulfurization catalysts which decreased their activity in the hydrodesulfurization of thiophene. They suggested that presulfided Ni-Mo/Al_2O_3 in hydrogen atmosphere had the lowest coking and the best retention of catalytic activation.

2.4 Effect of Other Elements on Catalyst Activity [6, 17]

There were some investigation about the effect of various elements on hydrodesulfurization activity. Same elements could be promoted the hydrodesulfurization reaction and other elements could be decreased the hydrodesulfurization activity. The effect of phosphorus on the activity and selectivity on Ni-Mo/Al_2O_3 catalysts was studied by Fitz and Rose [91]. The catalysts contained varying amounts of Mo and P and had essentially a constant Ni/Mo ratio. Component feeds were used composed of cyclohexane and thiophene, with piperidine also present in some cases. For hydrodesulfurization service alone, the optinum catalyst recipe was a low-metals formation with a medium P content. For N-containing feed the high-metals/high-P catalyst gave the best performance and the lowest hydrogenation/dehydrogenation activity. P-containing catalysts were less susceptible to coke formation and produce a more H-rich coke and the added Phosphorus apparently reduced the activity of Al_2O_3 carrier. While Visser, et al. [92] investigated the promotion and poisoning of the hydrodesulfurization of thiophene by phosphate-containing Mo/C catalysts. They suggested that increasing the phosphate content from 0.03 wt% (7.93 wt% Mo) to 2.7 wt% (7.40 wt% Mo) decreased the hydrodesulfurization activity for thiophene from 2.7×10^{-3} m^3/kg-s to 0.3×10^{-3} m^3/kg-s but decreased the butane hydrogenation activity only from 8.0×10^{-3} m^3/kg-s to 5.2×10^{-3} m^3/kg-s. The low activity of phosphate-doped sulfided Mo/C required intrinate contact between the MoS_2 phase and the phosphate ions. Tischer, et al. [93] investigated the effect of phosphorus on the activity of Ni-Mo/Al_2O_3 in hydrotreating of coal-liquid residuum at the temperature of 390 °C and at the pressure of 2000 psig in a batch autoclave reactor. The initial addition of phosphorus pentoxide caused an increase in this conversion, while addition of amounts in excess of 8 wt% reversed the trend and caused the activity to decline to values less than the activity of the phosphorus-free catalyst. However, the phosphorus addition to the catalyst did not improve its hydrogenation activity and caused only a very slight improvement in the hydrodenitrogenation and hydrodesulfurization activities. They suggested that the addition of phosphorus did reduce the amount of carbon deposited on the catalyst during the batch test.

Later, Spozhakina, et al. [94] studied the influence of phosphorus over Al_2O_3-supported Ni-Mo catalysts on the surface properties and catalytic activity in thiophene hydrodesulfurization. They found that a strong interaction between phosphorus and support are formed Aluminium phosphates. The promoting effect of P decreased in coke formation. They suggested that 1 wt% P was the optimum composition of the polymolybdate surface structures and their homogeneous distribution.

Ohga, et al. [95] studied desulfurization with metallic sodium at the temperature of 200 °C. In hexane or xylene, diphenyl sulfide and benzothiophene were readily decomposed, while the decomposition rates of thiophene, dibenzothiophene and dibutyl sulfide were comparatively slow. They also found that the decomposition rate of thiophene was accelerated by the hydrogen donors solvent. Whereas the effects of Na-ions on the physiochem properties and catalytic activity of Co-Mo/γ-Al_2O_3 hydrodesulfurization catalysts for thiophene by Lycourghiotis and Vattis [96], they found that the Na doping tended to decrease in the catalytic activity.

The effect of group IA elements to promote the Ni/Al_2O_3 hydrodesulfurization catalysts of the temperature of 500 °C by Abdukadypov, et al. [97]. Liquid feed consisted of thiophene in cyclohexane. The thiophene conversion increased from 71.6 % to 81.1 % when the used group IA elements as the promoter and the cyclohexane dehydration conversion increased from 1.19 % to 2.64 %.

Guerrero-Ruz and Rodriguez-Ramos [98] added Fe on C-supported nobel metals (Ru, Rh and Pd) to study hydrodesulfurization and hydrogenation activity of carbon supported bimetallic. They found that adding Fe in such a manner that undesirable hydrogenation reaction were prevented without decrease of the catalytic activity of hydrodesulfurization.

The effect of treatment with triethylaluminum on the hydrogenation and hydrodesulfurization activity of molybdenum, cobalt and nickel sulfide catalysts was studied by Bhaduri and Mitchell [99]. This treatment increased the hydrogenation activity of the individual sulfides but decrease that of the sulfided Co-Mo/γ-Al_2O_3, and increased the hydrodesulfurization activity of sulfided Mo/γ-Al_2O_3 but decreased that of the other catalysts, and the loss of promoting effect of Co on sulfided Mo in the sulfided Co-Mo/γ-Al_2O_3 catalyst. The hydrogenation activities of the catalysts decreased after they used for hydrodesulfurization.

Lur'e, et al. [100] studied the activity of catalyst for hydrogenolysis of thiophene. They found that the catalytic activity was increased when added TiO, on Ni and Mo oxides over SiO_2 catalyst. This result was in goverment with that of Fu, et al. [101], who studied the surface characteristics of MoO_3-CoO-TiO_2/γ-Al_2O_3 hydrodesulfurization catalyst during sulfidation. They found that TiO_2 improved the dispersion of MoO_3 on the support, as well as acting as a promoter.

2.5 Deactivation of Catalysts [102-104]

Most catalysts used in heterogenous catalytic processes are subject to a decrease in the activity, Deactivation of catalysts, over a period of time. The time required for the activity of a catalyst to fall to an undesirable level varies with the severity of the process conditions and with the type of reaction being catalysted. Deactivation of catalysts effect to decrease continuously the reaction rate. Basically, ther kinds of deactivation may occur: (1) sintering or thermal deactivation of the catalyst; (2) fouling or coking; (3) poisoning. These may occur singly or in combination, but the overall result is to remove active site from the catalytic surface. From the three major categories of catalytic deactivation, which are primary cause in other mechanisms. These include pore blockage via coke or metal decomposition on the internal pore structure of a catalyst, volatilization of an active catalytic component, distruction of active surface via detachment from the support, and incorporation of the active component into the support structure in an active form.

2.5.1 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 occurs when the catalyst is operated above the normal range of temperature. Such temperature rises may occur thoughout 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 is the incorporation of the active metal into the support that the new form is innert for the reaction. Sintering can be avoided by working at the operating temperature that below than the normal range of temperature.

2.5.2 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 compound in the feed stream of petroleum fraction which is then termed impurity poisoning. Though this is the most 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 desided and undesired reaction which may be preferentially adsorbed on the active sites of the catalyst, thus retarding the adsorption of reactant. Another poisoning is deactivation by metals which are the impurities in the petroleum feed stock. Trace metal impurities can permanently deposition on the active sites of the catalyst surface and cause a loss of catalytic activity. The deposition of metal impurities is considered to have a long term deactivation effect.

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 the degree of reversibility of chemisorption on the surface, and inhibitors of reaction rate which are either reactant 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 the 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 amount of poison chemisorbed. In essence, every active site looks like every other active site 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, so the catalyst has to be discarded ultimately, but there is an important class of poisons that are reversible in action. Example include the poisoning of reforming catalysts by sulfur, the poisoning of cracking catalysts by nitrogen, and the poisoning of nickel hydrogenation catalysts by oxygen and by water vapour. Therefore it is always possible to remove impurity poisons from the feed stream before using in the process by hydrotreating reaction. Such that hydrodesulfurization is used for removing sulfur impurity, hydrodenitrogenation for removing nitrogen impurity and hydrodeoxygenation for removing oxygen impurity.

Aspects of catalyst poisoning in major petroleum refining process were reviewed by Sie [105]. Particular attention was given to the hydroprocessing of residual feed stocks, where catalyst deactivation by poisoning and pore plugging with petroleum feedstocks a wide spectrum of contaminants was usually present, rather than just a single species. It was quit common to refer to poisoning by sulfur, nitrogen or metals. Hydrotreating process was sufficiently serve to convert these compounds to a common single species such as H_2S, NH_3. The presence of metals (V, Ni, and Fe) in crude oil damaged the catalysts by contaminating on the catalyst surfaces. Skala, et al. [106] studied hydrotreating of used oil in a pilot trickle-bed reactor on a commercial Co-Mo/Al_2O_3 catalyst at the temperature ranges from 270 to 350 °C and at the pressure ranges from 5 to 7 MPa. They suggested that hydrodesulfurization reaction could be described by pseudo-first-order kinetic. The removal of metals was found to be primerily due to the physical process of deposition on the catalyst bed. They found that both coke and metals despositions were responsible for the catalyst deactivation. These deposition of trace amounts of metals were on the catalyst surface whereas the coke deposite was on the catalyst surface and in the catalyst bed. The coke was found to affect the catalyst bed porosity. An empirical relation between the change in the bed porosity and the decline in catalyst activity had been found.

It was found that many heavy metals, including mercury, lead, bismuth, tin, and cadmium, could reduce the activity of the catalyst. There are many researches with respect to the metal impurities in petroleum feed. The catalyst contamination in the process of coal extract hydrotreatment was studied by Surygala and Radomyski [107]. They suggested that the amount of coke on Ni-Mo/Al_2O_3 catalyst at the temperature of 708 K and at the pressure of 19 MPa was higher than on Ni-Co-Mo/Al_2O_3 but the latter had mineral contaminant such as Fe, Ti, Si, B, Ca, Zn, Mg, Na. Both catalysts has selective adsorption of Ti, Fe, and Zn onto the surface. The catalyst deactivation was due to the deposition of 22-29 % coke and 3.4-5.7 wt% minerals. Some metals penetrated deeply into the catalyst grains.

Mann, et al. [1] studied the hydrotreatment of heavy gas oil in a trickle bed reactor over Ni-Mo, Ni-W, and Co-W supported on alumina catalyst at 350 °C and 4.25-12.5 MPa. Asphaltene and resins present in the heavy oil were converted to oil through a series of successive reaction. They found that heavy oil and residua contained large amounts of asphaltenes, heteroatoms like sulfur, nitrogen, and oxygen, and metalic impurities like vanadium and nickel. These are usually thick viscous liquids. These characteristics of heavy fractions and residual oils posed major problem in further processing. They suggested that catalytic hydrotreatment was most widely used for upgrading the residual and heavy fractions. Larocca, et al. [2] also found that nickel and vanadium were present in crude oil in the form of porphyrin complexs. Metal porphyrins decomposed under cracking conditions, depositing the metals on the catalyst as vanadium tetraoxide, vanadium pentoxide, and nickel oxide. Nickel and vanadium contaminants accelerated the deactivation of catalyst.

Song, et al. [3] found the deposition of trace amounts of some Fe, Ca, and Ti on used Ni-Mo/Al_2O_3 catalysts after coal liquids hydroprocessing.

Silbernagel and Riley [4] studied the chemistry and impact of vanadium deposits which conducted to catalyst deactivation. In particular, the effect of organically complexed metals on catalytic process was of great significance since vanadium and nickel often occured in crude oil feed at approximate 700 ppm levels. Metal effects can be physical plugging catalyst pores, or chemical reacting with active sites or the support. They also found the vanadium in the deasphalted component occured almost exchusively as a vanadyl porphyrin. VO^{2+} and V_2S_3 forms were found on catalysts run on the whole crude feed. The relative vanadium and nickel profiles along the beds were shown maximum valves near the reactor inlet. The interior of the catalyst had not get become inaccessible because of plugging of the pore mouths by metal deposition.

Hydrodemetallation was the reaction which decreased the metal impurities in petroleum feedstocks. Marsen, et al. [108] studied hydrotreating of Boscan crude oil by using different active phase on a bimodal alumina carrier. They found that the hydrodemetallation was only slightly influenced by the activity in hydrogenation and by the acidity. The H/C ratio decreased faster with the less hydrogenation catalysts. The metals contented in asphaltene varied as function of the active phase showing that the asphaltenes conversion and the hydrodemetallation were partially independent. Chiang and Yu [109] investigated the optimal pore size of a slab catalyst in hydrodemetallation reaction. They suggested that optinum pore size was better determined from the total lifetime activity. The total lifetime activity was calculated by the summation of the catalyst activity from the beginning to age that yields the limiting activity.

New fuel oil Development Technology Research Associate [110] reported about catalysts for determination of oil-sand bitumen or the residues at the temperature ranges from 350 to 500 °C and 50-250 Kg/cm^2hr. These catalysts containing CoO or NiO and MoO_3 over γ-Al_2O_3 (average pore diameter 80-250 Å) had increased reactivity in cracking and desulfurization when they added 3-10 wt% SiO_2 or P_2O_5. Thus,a thermal cracked distillation residue (b.>24 °C) containing 145 ppm V, 43 ppm Ni, and 2.83 wt% S was demetalated at 410 °C and 150 kg/cm^2 over 4.9:16.2 (wt%) NiO-MoO_3/Al_2O_3 containing 4 wt% SiO_2 (average pore diameter 124 A°) to remove 70 % metals and 90 % S.

Nourbakhsh, et al. [111] studied metal deposition in porous anodic alumina films under hydrotreating conditions. They used nickel etio-porphyrin as a reagent in hydrodemetallation over anodic Al_2O_3 films with ideal porous structures. Ni was presented in the form of relatively large discrete crystallitis rather than as a uniform layer on the walls as well as many other structures. Chen and Masoth [112] using a sulfided Co-Mo/Al_2O_3 catalyst investigated hydrodemetallation of vanadium and nickel porphyrins in a batch stirred autoclave at several temperatures, H pressures, and initial porphyrin concentrations. They found that the reaction followed pseudo first order at the temperature more than 350 °C but followed lower order at lower temperature. The reaction was inhibited by adsorption of reactant and product at different initial concentrations. Hydrodemetallation ratio increased with temperature and H pressure and were very low without catalyst or H present. An apparent activation energy was 24 Kcal/mol for both reactants.

Loos, et al. [113] studied hydrodemetallization of vanadyl porphyrins on hydroprocessing catalysts. They found that vanadyl porphyrin adsorbed and accumulated on an industrial Ni-Mo/Al_2O_3. The interaction of vanadyl porphyrins with hydrodemetallization catalysts was likely to be more specific than with the bare support, with the porphyrin ring probably lying flat on the oxomolybdenum phase of the oxidic Ni-Mo/Al_2O_3 catalyst. Dejohghe, et al. [114] also studied catalytic hydrodemetallation of a model vanadyl phorphyrin over a Mo/Al_2O_3 or a Ni-Mo/Al_2O_3 to investigate the catalytic role of V deposited on these catalysts. They found that V was able to partially replace Ni in the NiMoS phase and interact with MoS_2 platelets to form a similar VMoS phase. Another part of V in the displaced Ni species formed bulk sulfides.

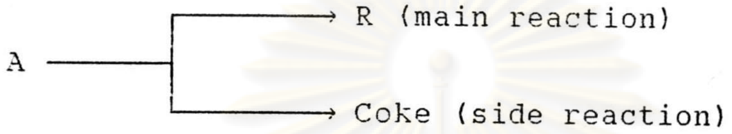
Takase, et al. [115] studied a method to regenerated spent catalysts for hydrotreating processes for heavy hydrocarbon oils when the catalytic activity was reduced as a result of accumulation of heavy metals such as V and Ni. The regeneration method was applied to the catalysts which were used in hydrodesulfurization, hydrodenitrogenation, hydrodemetallation, and hydrocracking by immersing the spent catalysts in iso-propyl alcohol at 90 °C for 20 hours, or ethylene glycol at 100 °C for 4 hours, to selectively extract V after removing coke accumulateed on them by combustion at

500 °C for 30 hours in air.

2.5.3 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 or "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 occurring and 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.

In general, coke can originate from the reactant or product by reactions (iv) or (v). Reaction (iv) is called parallel fouling, which (v) is called series fouling or consecutive fouling. Fouling may also occur by a combination of reactions (iv) and (v). The extent of coke formation will depend on the orders of reaction with respect to the formation of desired product R and the coke, and on the magnitudes of the temperature coefficients for each reaction. Coke deposition will be increased when the reaction rate is greatest.



(iv)

$$A \longrightarrow R \longrightarrow \text{Coke} \qquad (v)$$

Song, et al. [3] investigated the effect of pore structure of Ni-Mo/Al_2O_3 catalysts in hydrocracking of coal derived and oil sand derived asphaltenes. The experiments were conducted at a temperature of 425 °C and a hydrogen pressure of 4.9 MPa. They suggested that probably the catalyst pore size and pore volume reduction in the initial period were caused mainly by carbonaceous deposits, because their buildup was relatively rapid and the accumulation of contaminant metals was slower. Where about catalyst pore structure determined how easily the feed molecules could access the interior surface of the catalyst and the pore wall was not a continuous solid but had many intersections with other pores.

Tamm, et al. [116] studied the effect of feed metals on catalyst aging in hydroprocessing residuum. Petroleum residuum had a wide range in the amounts of organometallic impurities. Nickel, vanadium, and iron were most commonly in the highest concentrations and, therefor, of greatest importance. Of the three, vanadium is often the most abundant by far. Residuum hydrotreating was developed originally to produce low sulfur feed oil from high sulfur crudes. This hydrotreating process employed a porous solid catalyst which must be resistant to the soluble nickle, vanadium, and iron compounds present in most residual oils. Hydrodemetallation of these compounds leaved a deposit of mixed metal sulfides on and in the catalyst. The buildup of these metal deposits was irreversible and largely determines catalyst life. The demetalation reaction rate was limited by the rate of diffusion of the reactant through the liguid-filled catalyst pores. Both the distributions of the deposited metals and the effects of process and catalyst variables on those distribution indicated that the removal of nickel and vanadium is diffusion controlled and, usually of iron was reaction controlled. The metal sulfides concentration at the point of maximum deposit, catalyst near the reactor inlet, reached a limiting valve before the catalyst bed was fully deactivated. They found that metals were indeed removed from molecules of dismeter larger than the average catalyst pore diameter, although to a lesser extent than for smaller molecules. Iron was found primarily out side the catalyst particle as a thin scale. Both nickel and vanadium display a maximum concentration inside the edge of the particle. Nickel generally seemed to penetrate the catalyst to a greater extent than vanadium. These differences in depositional patterns were due to differences in the reactivities and diffusivities of the organometallic molecules. The deactivation of hydroprocessing catalyst by feed metal had been shown to proceed by two distinct mechanisms. These were poisoning of active catalyst surface and physical obstruction of the catalyst pore structure.

Yoshimura, et al. [117] studied the initial catalyst deactivation hydrotreatment of coal liquid over Ni-Mo and Co-Mo/γ-Al_2O_3 catalysts. They suggested that the initial catalyst deactivation was sinificant in the following order : hydrocracking > hydrodenitrogenation > hydrodesulfurization for each catalyst. Pore volumes and surface areas of the spent catalysts by the cabonaceous deposits and high amounts of N and O-accumulated. They found that the Ni-Mo catalyst had higher activity than the Co-Mo catalyst. The cabonaceous deposits and changes in chemical states of the supported metals were the main reasons for the initial catalyst deactivation.

Another class of fouling reactions is that of metal-sulfide deposition arising from the organometallic constituents of petroleum which react with sulfur-containing mole cules and deposit within the pores of the catalyst during hydrotreating operations. In this case, the metal site of the organometallic compounds will be adsorbed on the catalyst surface and the other site, organic site, will be polymerize. Then fouling will be occurred. Fouling is associated with relatively large amounts of deposit and, if it is excessive, in addition to covering the active sites of the catalyst it may affect the diffusional properties of the porous catalyst pellet. Pore blocking may occur for both coke and metal deposition, and if allowed to continue the deposits will block the void spaces between the catalyst pellets.

Surygala [118] studied the deactivation of Ni-Mo and Ni-Co-Mo catalyst in hydrogenation of coal extract in a flow reactor at the temperature of 408 K and at the pressure of 19 MPa. They were interested in amounts of coke and mineral deposit, specific surface area and porosity of the catalyst. They found that the deposit mainly contained Fe, Si and Ca, but also Ti, Zn, K, Na and Mg in minor amounts. The Fe and Ti penatrate into the catalyst grain core and irreversible changed the catalyst activity. Yoshimura, et al. [119] also studied hydrotreating of coal liquid drived on Co-Mo/γ-Al_2O_3 catalysts in a continuous stirred-tank reactor. They suggested that the deactivation of catalysts might be mainly the results of carbonaceous deposits and metal deposits on the catalyst surface were anather reason for catalyst deactivation. From these experiments, Fe was formed on the surface of spent catalysts.

The influence of asphaltene deposition on sulfides Co-Mo/Al_2O_3, Mo/Al_2O_3, Co/Al_2O_3 and Al_2O_3. They suggested that both pore blockage and surface poisoning, especially poisoning of acid centers caused the catalysts deactivation. There was a small hydrogenation activity of the products of asphaltene decomposition, presumably fouling by V and Ni sulfide. In the later, Shimada, et al. [120] studied the catalyst deactivation of Ni-Mo/Al_2O_3 during hydrotreating of coal-derived liquid for running the reaction more than 2000 hours. They found that the active sites for hydrocracking were poisoned more readily than hydrogenation. The amount of metallic foulants decreased with increasing distance from the reactor inlet to the outlet which caused the inlet catalyst deactivated more than outlet catalysts. A more serve pore plugging of the inlet catalyst than that of the outlet catalyst could be attributed to greater amounts of metallic foulants on the catalyst which caused more serious active-site poisoning and pore-mouth poisoning.

Reda [121] regenerated the spent hydroprocessing catalysts (contained residual oil, sulfur, carbon, vanadium, and nickel deposits) by leaching metal foulants from spent Ni-Mo/Al_2O_3 catalysts. Hydroprocessing catalysts used to upgrade heavy oils were found to deactivate as a result of deposition of coke and metals. Coke may be removed easily, but metal deactivated the catalyst irreversibly, so that replacement was required. Catalyst dumping was environmentally unacceptably due to the high concentrations of such heavy metal irons as vanadium, which was considered toxic. The metal contaminants in petroleum hydroprocessing were mainly nickel and vanadium salts, deposited on the catalyst. The most economic method of dealing with large amounts of spent catalysts would be regeneration. This experiment had shown that, when a redox couple, Fe(II)/Fe(III), was added to the solution used for leaching metal foulant from spent Ni-Mo/Al_2O_3 catalyst. The acids solutions were ranked for efficiency of vanadium removal, indicating that oxalic acid removed as much vanadium as molybdenum and that formic acid removed twice as mach vanadium as molybdenum. The addition of redox couple, such as Fe(II)/Fe(III), reduced the removal of catalytic metas during metal leaching and there were no major changes in the crystalline phases of the catalysts.

2.6 Deactivation of Hydrodesulfurization Catalysts [19, 103, 122]

Deactivation of the hydrodesulfurization catalyst was occurred due to fouling and impurity poisoning with various degrees of diffusional interaction. These characteristics are particularly pronounced when the feedstocks are heavy residuum stocks or coal-derived liquids. Such heavy feeds contain large trace concentrations of organometallic compounds that deposit on the catalyst under reaction conditions. The organometallic molecules are large and approach the same order of magnitude as the pore dimensions; as a consequence, they diffuse very slowly into the interior of the catalyst particles. The net result is that such compounds react close to the pore mouths of the catalyst and tend to restrict the passage of the sulfur-containing organic compounds into the interior. This can be viewed as a combination of pore mouth poisoning and pore mouth blockage, affecting both the activity and the transport properties of the catalyst. Coking occurs simultaneously with the demetallation process and contributes to aging; in most evaluation of hydrodesulfurization deactivation it appears that the coke deposition is not diffusion-limited, but this could be a subject of debate depending on specific catalysts and feedstocks. However, the coke can be removed by burning in oxygen, but the metals are not removed by such a procedure.

The hydrodesulfurization process presents an interesting and complex deactivation case in which the main reaction is moderately influenced by diffusion, coking occurs in paralled with the main reaction, and metal compounds plate out metal sulfides at the pore mouths and lead to pore plugging.

Newson [123] studied catalyst deactivation due to pore-plugging in hydrodesulfurization reaction. They found that the desired hydrodesulfurization reaction took place in parallel with undesired reactions such as demetallation and coking reactions. The pore plugging was due to deposition of metal sulfides and coke. Organometallic constituents of the oil, primarily vanadium, nickel, and iron compounds, reacted out of the oil and combined with hydrogen sulfide to produce solid deposites of metal sulfides. The deposition of these reaction products occurred both intra-particle deposits decreased the effective diffusivity of the catalyst particles for desulfurization, these causeing deactivation by a pore-plugging mechanism. There were the combination of coke deposition and metal sulfides plugging to decrease in pore radius which would be related to catalyst deactivation. They suggested that metal sulfides deposition was the greatest at the top of the catalyst bed, where strongly deactivated.

The correlation between hydrodevanadization of vanadylporphyrin and hydrodesulfurization of benzothiophene in the presence of tetralin as the hydrogen donor at 350 °C and 50 kgN/cm^2 was presented by Kameyama and Amano [124]. They found that the hydrodesulfurization was accelerated significantly and the removal of V from vanadyl tetraphenylporphyrin was promoted. In the early stages of the reaction, the sulfided V_2O_5 catalyst tended to increase in activity in a manner like that of an autocatalytic process, while the activity of $CoO-MoO_3/Al_2O_3$ leveled off. The desulfurization was accelerated by the concurrent removal of V. Mitchell and Scott [125] studied the binding of V and Ni porphyrins on hydrotreating catalysts in their oxide and sulfide forms. The subsequent decomposition reactions occurred when heated in N or exposed to hydrogen and thiophene in catalytic hydrodesulfurization. They suggested that the porphyrins were bond to the catalyst by a donor-acceptor interaction, the delocalized ¶-system of the porphyrin ring being the electron donor and the Bronsted and Lewis acid function of the catalyst being the acceptor.

Mohammed, et al. [126] investigated hydrodesulfurization of the residuum fraction of crude oil on a commercial $Ni-Mo/Al_2O_3$ catalyst in a trickle-bed reactor. This feedstock consisted of sulfur content 4.2 wt%, vanadium 114.5 ppm, nickel 27.1 ppm and iron 2.0 ppm. The reaction temperaature varied from 320 to 420 °C with the liquid hourly space velocity ranging from 0.37 to 2.6 h^{-1}. Hydrogen pressure was kept constant through out the experiments at

6.1 MPa. They found that nickel was more easily removed than vanadium in the low temperature region, with the reverse situation at high temperature. Babcock, et al. [127] studied thiophene hydrodesulfurization on commercial Co-Mo/Al_2O_3 fresh, spent, and treated sulfur catalysts. They found that the fresh and spent catalysts exhibited highest and lowest activites respectively. They improved the activity of spent catalysts by regeneration treatment to remove coke and contaminant metals. The adsorption parameter in the rate model was much higher for spent and treated catalysts than for fresh catalyst.

Ocampo, et al. [128] evaluated the deactivation of commercially available hydrodesulfurization catalysts due to cabonaceous diposites under coal liquefaction conditions. They found that loss of activity was generally attributed to the deposition within the catalyst's pores of carbonaceous materials formed from cracking the heavy aromatic and rejecting hydrogen the carbonaceous deposits had a high atomic carbon to hydrogen ratio of 48:1. While they rapidly reduced the activity of the catalysts. They might also act as adsorption carriers for the inorganic metallics that permanently poison the catalysts. Carbonaceous blockage at the pore mouths would drastically reduce intraparticle diffusion and hence reduce the rate of hydrodesulfurization. Thick deposits on the pore walls would cause a loss in the intrinsic activity. Thin deposits might be advantageous in that might screen our the large organometallic compounds that permanently poison catalysts. Permanent loss of activity resulted from residual deposition of metallic compounds emanating from the coal's mineral matter. During regeneration these were converted to oxides which were than permanently bound to the catalysts surface. Other permanent deactivation would occur when organometallic compounds, such as those of Ti and V, found in the coal's matrix reacted to form inorganics. These likewise became permanently bound to the surface sites. They concluded that the inference here was that the loss of catalyst activity in coal liquids which is a combination of two factors. First, it was the reversible deposition of heavy organics or coking that the early decline in activity caused by the deposition of carbonaceous materials in the pore structure of the catalyst. That could be fully regenerated after shot processing time to nearly their virgin active states. The other was the permanent poisoning due to the irreversible adsorption of inorganics. That slowly led to a permanent decline in activity.

Kovach, et al. [129] studied the deactivation of hydrodesulfurization catalysts due to adsorption of metallics by following the former reseach. This hydrodesulfurization condition was at the temperature of 630 K and at the pressure of 14 Mpa. The matals Na, K, Mg, Ca, P, Ti, Fe, and S were shown to permanently poison catalysts at different rates. Deposition of carbonaceous mineral within the catalyst pores suppressed the adsorption of cold-liquid insoluble constituents. However, organometallics, such as those of titanium, were soluble in coal liquids, gained access to the surfaces, and were adsorbed in high concentrations. The result from the impregnation of the metal salts on the catalyst showed that the alkali metals and Fe in their oxide forms produced the greatest degree of deactivation. While the salt forms of Ti, P and Si were easily adsorbed upon the catalyst, their oxides showed very little deactivation effect. They found that the amount of titanium deposited increased very slowly. Adsorbed inorganic forms of titanium had no poisoning effects on the catalysts, but that organometallic forms are easily adsorbed from even low concentration in coal liquids and lower the hydrogenation activity markedly. While iron was adsorbed quickly and had a high level of adsorption. They suggested that under liquefaction conditions iron sulfide might complex with certain types of aromatics and deposit as organometallics on the outer catalyst surfaces. For example, cyclopentadiene compounds were known to form complexes, i.e., ferrocenes.

Makovsky, et al. [130] found TiO_2 on and around a deactivated hydrodesulfurization catalyst. Deactivation of catalysts used in the liquefaction and desulfurization of cold was usually attributed to structure changes in the catalyst and buildups of carbonaceous materials, minerals, iron and titanium. Titanium was one of the major metals to deposit on and around catalysts. The titanium deposited around a used catalyst removed from a fixed-bed reactor was very similar to one of the Tio_2 polymorphs (anatase). This work showed that orgamically bound titanium would form anatase in liquefaction conditions. Two possible explanations for the origin of the anatase-like material were (1)

That the titanium was originally orgamically bound in the coal, but it become oxidized during coal liquefaction, or (2) That small crystallites of the oxide existed in the coal and were simply concerned on and around the catalyst during liquefation.

Treblow, et al. [131] also found anatase, as the titania polymorph, deposition on spent catalyst in a fixed-bed coal liquefaction. Anatase derived from organic titanium compounds accumulated on and around the catalyst pellets to an appreciable extent. They used Ti(IV) cresylate, Ti(IV) nonylate and O=Ti (tetraphynylporphyrin) as the model organically bound titanium compounds. They suggested that because of the irreversible nature of the metals deposition. Ti was necessary to determine their form in the coal. If the source could be located, it would lead to either the formulation of a better catalyst or a method of removing this material for a longer catalyst lifetime. Where as titanocene dichloride was used as a model organically titanium compound by Tscheikuna and Seapan [132]. They investigated the effects of titanocene dichloride on catalyst coking and hydrogenation activity. In this report, Tscheikuna and Seapan studied the effects of titanocene dichloride on catalyst coking and hydrogenation activity. In this report, tetralin and a mixture of 5 wt% phenanthrene in tetralin were doctored with 100 ppm of titanium as titanocene dichloride and hydrotreated in a trickle bed reactor over a commercial Ni-Mo/alumina catalyst. The experiments were conducted at a pressure of 10.4 MPa (1500 psig), a temperature of 350 °C (622 °F). They found that the addition of titanocene dichloride to tetralin increased both the catalyst coking and the hydrogenation rate. It indicated that titanocene dichloride had enhanced the hydrogenation of tetralin either by promoting the catalytic activity or by a homogeneous reaction in the liquid phase. The differences in the phenanthrene runs due to titanocene dichloride also confirmed that titanocene dichloride directly effected the hydrogenation.

Pereira [133] studied metal deposition in hydrotreating catalysts. Hydrotreating was used to upgrade the quality of petroleum feedstocks and to remove sulfur and metal contaminants from these feed (containing 0.5 wt% sulfur, V 151 wppm, Ni 71 wppm, Fe 5.0 wppm). Sulfur-containing molecules were hydrogenated, and the sulfur was removed as hydrogen sulfide. Metals in the feed deposit within the pores of the catalyst as metal sulfides. Demetallation kinetic was suggested in first-order. Galiasso, et al. [134] also investigated deactivation of hydrodemetallization catalyst in petroleum feedstock, containing 2.7 wt% S and 338 ppm of V, by pore plugging. This study dealt with the development of a simplified model to understand the general deactivation phenomena to improve metal storage capacity. During catalytic hydrodemetallization treatment of heavy material containing large amounts of large molecules such as asphaltenes, the catalyst typically showed three periods of deactivation and to compensate for this decline in activity the temperature had to be increased. The activity in the first period decreased because of deposition of coke in the micro and meso pores. Vanadium is deposited in accessible meso-macro pores. During the second period of deactivation, vanadium was deposited on the mouth of mesopores and in a meso-macro structure, which decreased diffusivity and reaction rates. During the last period of deactivation, vanadium and coke were accumulated in the external part of the meso-macro structure and in multilayers in the neck of narrow pore interconnecting the external and internal parts of the pallet. This impleded the penetration of large molecules to the internal part of the catalyst, and produced therefore a sharp decrease of the effectiveness factor of hydrodemetallation.

Nickel-molybdate and cobalt-molybdate catalysts were used for hydrotreating coal-derived oils and a petroleum vacuum gas oil. The metallic components deposited on the spent catalysts were characterized to reveal their inhibitory effects on hydrogenation and hydrocracking acti vities by Yoshimura, et al. [135]. Transition metals such as Ti and Fe, alkali metals such as Na and K, and alkaline earth metals such as Ca and Mg were the major components deposited on coal liquefaction catalysts. Some of these metals were also deposited on the catalysts in hydrotreating of coal-derived oils containing refractory fraction such as asphaltenes and preasphaltenes. On the contrary, Ni, V and Fe were the major deposits on the catalysts for hydrotreating petroleum feed stocks. Inhibition by typical metal components, such as Na, K, Mg, Ca, Fe, Ti, Ni and V, were also evaluated by doping such metals on the catalysts. They concluded that in hydrotreating of coal-derived oils, metal and carbonaceous materials deposit simultaneously from the start of the run; metals such as K, Na, Mg and Ti tend to deposit and accumulate selectively on the molybdate catalysts. Inhibitory effects of alkali and alkaline earth metals on hydrogenation and hydrocracking activities were significant in the order; K >Na > Ca> Mg. Alkali and alkaline earth metals not only segregate on the catalyst surface but also cause the lateral growth of MoS_2-like structures. In addition to covering the active sites (geometric effects), doped metals neutralize the acidity to decrease catalytic activities. On the other hand, V, Fe and Ti tend to disperse the MoS_2-like structures and to increase the catalyst acidity through the formation of acidic double oxides with molybdenum alumina support, increasing hydrocracking, but decreasing hydrogenation in the order; V>Fe>Ti.

Hung and Wei [136] removed V from vanadyl etioperphyrin in white oil solvent over CoO_3-MoO_3/Al_2O_3 as catalyst without presulfiding. In comparison to nickel removal, vanadium removal had a layer activation energy and a smaller hydrogen pressure dependence. Thus, vanadium adsorbed on the catalyst more strongly than nickel. The concentration decline in the transient period was layer for vanadium than for nickel. In mixed vanadium and nickel runs, the vanadium had to be removed first before nickel could be removed effectively. Later on, Chen and Massoth [137] used sulfided Co-Mo/Al_2O_3 catalyst in hydrodemetallation of vanadium and nickel porphyrins model compounds. Hydrodemetallation rate increased with temperature and hydrogen pressure but decreased with porphyrin concentration below 350 °C. An apparent activation energy of 24 kcal/mol for the overall disappearance was obtained for both reactants. Hydrodemetallation kinetics followed pseudo-first order above 350 °C and lower order temperatures. They found that hydrodemetallation rates were dependent on the square of the hydrogen pressure, with moderate surface coverage of hydrogen. Vanadium porphyrin was more reactive than nickel porphyrin, which was ascribed to a higher intrinsic reactivity of vanadium porphyrin.

2.7 Hydrodesulfurization of Thiophene [6, 18, 122]

Hydrodesulfurization of sulfur-containing fraction had long been one of the major catalytic operations in the industry. One of its purposes was the removal of sulfur petroleum feedstocks. The most commonly organosulfur compounds was thiophene which was generally used as sulfur model compound to study hydrodesulfurization reaction.

Thiophene, C_4H_4S as a heterocyclic sulfur compound, was a volatile, colorless liquid with a slight aromatic odor resembling that of benzene. In catalytic hydrodesulfurization of thiophene, the major product is mixed isomers of butene which was continuously hydrogenated to butane in excess hydrogen system. That will be describe in the reaction network section.

2.7.1 Thermodynamics of hydrodesulfurization.

Detailed thermodynamic data of desulfurization reactions have wildely reported in several papers [7, 17, 138]

For the reactions of hydrogen with thiols, sulfides, disulfides and thiophene to produce saturated hydrocarbons and hydrogen sulfide, if hydrogen was present in the stoichiometric quantity, there was no thermodynamic limitation in the temperature range most often used in technical processes (573-773 K). These data indicated that hydrodesulfurization reaction to produce butadiene and H_2S was also thermodynamically favoured in the temperature range of industrial practice. Hydrodesulfurization and accompanying hydrogenation reactions which occur during the process were highly exothermic [23, 24] and Table 2.2.

However, if the hydrogenolysis reaction resulting in C-S bond scission was not limited thermodynamically, hydrogenation was favoured only at low temperatures and at high pressures. An example was reported in Figure 2.1 in which the temperature dependence of the equilibrium constants for the various reactions involvded in thiophene desulfurization was shown. It could be seen that the formation of tetrahydrothiophene (reaction 2) is only favoured for temperature below 623 K. This fact must be kept in mind in the interpretation of likely reaction pathways and could explain the controvesy about the possibility of the formation of tetrahydrothiophene as an intermediate in thiophene hydrodesulfurization. This has been discussed by Devanneaux and Muarin [139] for thiophene and benzothiophene hydrodesulfurization

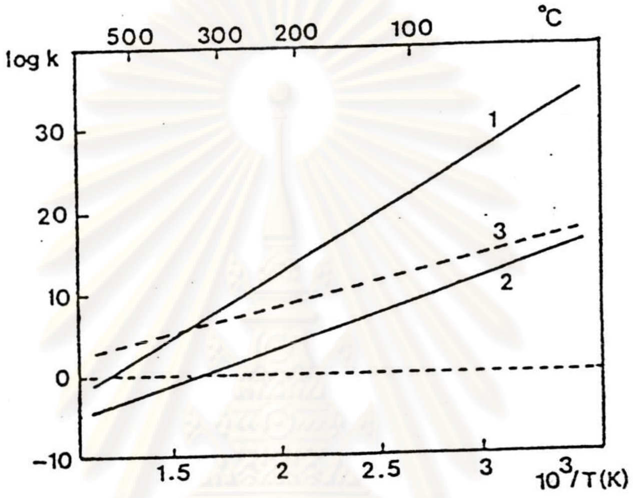


Figure 2.1 Equilibrium constants (k) of reactions involved during thiophene hydrodesulfurization

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

under low temperature and high pressure conditions.

Thus, it appears that new catalysts more active at low temperatures must be developed when extensive hydrogenation was also desired during the hydroprocessing.

The hydrodesulfurization of thiophene was exothermic and essentially irreversible under the reaction conditions employed industrially at the temperature ranges from 340 to 425°C and the pressure ranges from 55 to 170 atm [6, 10, 140]. Representative valves of the gas-phase-hydrodesulfurization equilibrium constants of several organosulfur compounds, including a mercaptan, a sulfide, and a heterocyclic compound, were listed by Speight, J.G. [10] in Table 2.3 with the corresponding standard enthalpies of reaction. The equilibrium constants all decreased with increasing temperature, consistent with the exothermicity of hydrodesulfurization, and approch valves much less than 1 only at the temperatures considerably higher than required in practice. In ICI research [18], it reported that the exothermic reaction of thiophene hydrodesulfurization had the heat of reaction of-66.98 kcal/mol at 700 K. The equilibrium constants for the hydrogenolysis of organic sulfur compounds were large and positive even at temperatures as great as 500 $^{\circ}$C (see Figure.2.2)

Sulfur removal occurred either with or without hydrogenation of the heterocyclic ring. The pathways involving prior hydrogenation of the ring could be affected by thermodynamics because hydrogenation of the sulfur-containing rings of organosulfur compound was equilibrium-limited at

TABLE 2.2 Thermodynamics of Reactions Involved during Hydrodesulfurization (Calculated from McKinly [128] and Vrinat [129]

Compounds	Reaction	ΔH_{300K}(kcal mol^{-1})
Methane thiol	CH_3-SH+$H_2 \longrightarrow CH_4$+H_2	-19
Dimethyl sulfide	CH_3-S-CH_3+2$CH_2 \longrightarrow$ 2CH_4+H_2S	-32
Thiophene	C_4H_8S+2$H_2 \longrightarrow C_4H_{10}$+$H_2S$	-27
Thiophene	C_4H_4S+4$H_2 \longrightarrow C_4H_{10}$+$H_2S$	-62
Dibenzothiophene	$C_{12}H_8S$+2$H_2 \longrightarrow C_{12}H_{10}$+$H_2S$	-11

TABLE 2.3 Equilibrium Constants for the Hydrodesulfurization of Selected Organosulfur Compounds (Speight, 1981).

	log K at		ΔH°_{rxd} [a] kcal/mol Organosulfur Reactant
	227°C	427°C	
2-Propanethiol + H_2 $\longrightarrow$ propane + H_2S	6.05	4.45	-13
thiacyclohexane + 2H_2 $\longrightarrow$ *n*-pentane + H_2S	9.22	5.92	-27
thiophene + 4H_2 $\longrightarrow$ *n*-butane + H_2S	12.07	3.85	-68

[a] The enthalpies are assumed to be standard enthalpies of reaction, although they are not listed as such by the author.

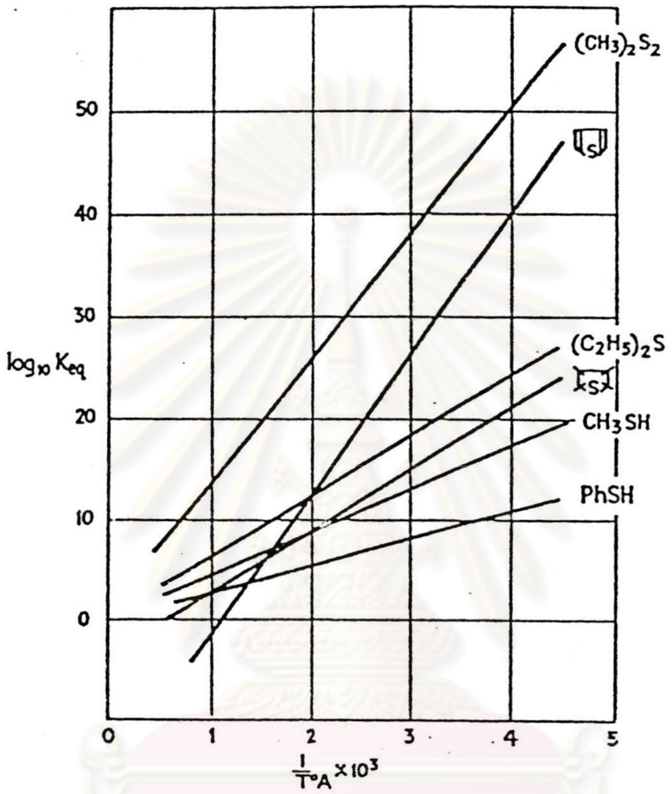


Figure 2.2 Variation of equilibrium constants for the hydrogenolysis of some organic sulfur compounds, with temperature.

practical hydrodesulfurization temperature. For example, the equilibrium constant for hydrogenation of thiophene to give tetrahydrothiophene was has than unity at temperature above 350 °C [140]. Thus, sulfur-removal pathways via hydrogenated organosulfur intermediates might be inhibited at low pressures and high temperatures because of the low equilibrium concentrations of the later species. Lee and Butt [142] found that more strongly adsorbed hydrogen increased with increasing temperature because of endothermic chemisorption of hydrogen.

2.7.2 Reaction conditions and processes.

The great variety of materials treated in hydrodesulfurization processees led to the development of a number of technological procedures which had been emply described [7, 17, 138, 143, 144]. The experimental conditions depended upon the boling range and character of the feedstock, The degree of desulfurization required and the catalyst employed : industrial hydrodesulfurization was generally carried out between 573 and 698 K and pressure from 10 to 200 atmospheres.

Nevertheless, although industrial hydrodesulfurization was a middle or high pressure, 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. Gradientless reactors for vapor phase or multiphase systems have been reported by Mahony, et al. [145] and new laboratory high pressure flow microreactors have been described by Eliezer, et al. [146] and by Vrinat and De Mourgues [147].

2.7.3 Kinetic and Mechanism of Hydrodesulfurization

Kinetic equations

Thiophene. The hydrodesulfurization 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 catalystically desulfurized. However, in spite of the large amount of research in the hydrodesulfurization of this compound, the reaction mechanism and kinetics are not completely understood and the results from different laboratories are not always in agreement.

The relative lack of reactivity of thiophenes compared with mercaptans, sulfides and desulfides has been widely demonstrated in the past by Obolentsev and Mashkina [148]. Perchenko and Sergienko [11] and more recently by Philippson [149].

The effect of substituents on the rate of hydrodesulfurization of thiophene was studied by Zdrazil [150] by competitive reactions of alkylthiophenes (573-723 K, 1 atm, Co-Mo/Al_2O_3) the reactivity increased with increasing molecular weight but the stearic effects of substituents in positions 2 and 3 were similar.

On the contrary, Deslkan and Amberg [151] reported that 3-methylthiophene is consistently more reactive than the 2-isomer and thiophene (443 K, 1 atm, Co-Mo/Al_2O_3). However, the order of reactivity of the reactants in competitive experiment does not generally agree with the results from isolated experiments. Different trends in adsorption and rate constants may lead to quite the opposite orders.

Product distribution and reaction intermediates during thiophene hydrodesulfurization have been thoroughly reviewed in recent papers [7, 144, 152-154] and a general reaction network is given in Figure 2.3. It showed that hydrodesulfurization of thiophene may proceed by two independent routes: (1) adsorption of thiophene through sulfur followed by loss of sulfur or (2) adsorption of thiophene parallel to the catalyst surface followed by hydrogenation and further C-S bond rupture.

Satterfield and Roberts [155] reported the first extensive determination of the kinetics of thiophene hydrodesulfurization, in a steady state recirculation flow reactor. The thiophene disappearance (508-538 K, 1 atm, Co-Mo/Al_2O_3) was represented by the following Langmuir-Hinshelwood rate equation :

$$r_{HDS} = k\frac{K_T P_T \; K_H P_H}{(1 + K_T P_T + K_S P_S)} \qquad .....(2.1)$$

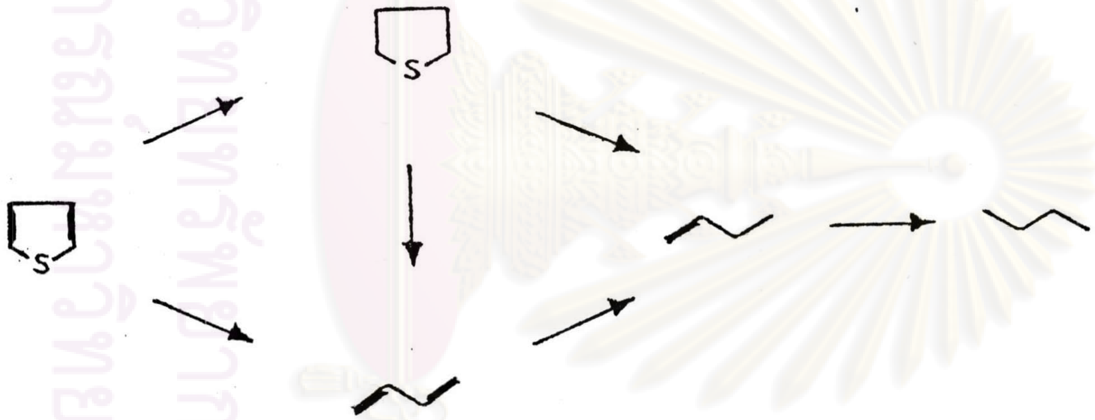


Figure 2.3 Thiophene reaction pathways suggested by early low-pressure

k - rate constant : K - equilibrium : P - partial pressure :
T - thiophene : H - hydrogen : S - hydrogen sulfide.

The form of the kinetic expression implies a two point thiophene adsorption in competition with H_2S on one type of site and hydrogen adsorption on another site. Unfortunately the variation in partial pressure of hydrogen was too small to determine with confidence the best mathematical from of P_{H_2} in the rate expression. This work is reported to have been performed in the absence of mass transfer influence, however the calculated activation energy of 3.7 kcal mol^{-1} would seem to indicate the contrary.

Rate equations similar to the above have been applied in order kinetic studies of thiophene hydrodesulfurization on Co-Mo/Al_2O_3 catalysts [38-40] and on Ni-Mo/Al_2O_3 catalysts [41, 42]: they are summerized in Table 2.4.

However, the rate equation could not be always unequivacally established, as proved by Massoth [156] for thiophene hydrogenolysis (673 K, 1 atm, Mo/Al_2O_3). In this study, the reaction is also assumed to involve a dual site mechanism in which hydrogen is adsorbed on one type of site and sulfur compounds are adsorbed on second.

A new important fact was to prove that a hydrogen partial pressure term was needed in the denominator of the rate expression in order to obtain this term from a kinetic analysis.

This observation can be illustrated by the results of Lee and Butt [157] obtained for thiophene hydrogenolysis on a Co-Mo/Al_2O_3 catalyst (523-586 K, 1 atm). In this

TABLE 2.4 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	$Co-Mo/Al_2O_3$	3.7	$r=k\frac{K_TP_T}{(1+K_TP_T+K_SP_S)^2}P_H$
Ozimek	1975	- 580-673 1	$Co-Mo/Al_2O_3$	21.6	$r=k\frac{K_TP_T^{\circ}}{(1+K_TP_T^{\circ})^2}P_H^{\circ}$
Massoth	1977	- 673 1	Mo/Al_2O_3	-	$r=k\frac{K_TP_T}{(1+K_TP_T+K_SP_S)^n}P_H^m$
Morooka	1977	benzene 523-623 1	$Co-Mo/Al_2O_3$	20	$r=k\frac{K_TP_T}{(1+K_TP_T+K_SP_S)^2}P_H$
Chakraborty	1978	naphtha 510-563 1	$Ni-Mo/Al_2O_3$	3	$r=k\frac{K_TP_T}{(1+K_SP_S)^2}P_H$
Kawaguchi	1978	n-hexane 543-623 1	$Ni-Mo/Al_2O_3$	16	$r=k\frac{K_TP_T}{(1+K_TP_T+K_SP_S)}\cdot\frac{K_HP_H}{(1+\sqrt{K_HP_H})^2}$
Vyskocil	1979	- 623 1	$Co-Mo/Al_2O_3$	-	$r=k\frac{K_TP_T}{(1+K_TP_T^{\circ})^2}P_H^{\circ}$
Lee	1977	- 523-586 1	$Co-Mo/Al_2O_3$	-	$r=k\frac{K_TP_T\ K_HP_H}{(1+K_TP_T+K_HP_H)}\left\{\frac{1}{1+K_HP_H}+k''\right\}$

work discrimination between various rate equation was also found difficult, but the rate appeared consistent with the following Langmuir-Hinshelwood modified rate equation:

$$r_{HDS} = k\frac{K_T P_T K_H P_H}{(1+K_T P_T+K_S P_S)} \times \left\{ \frac{1}{1+K_H P_H} + k'' \right\} \quad ......(2.2)$$

(with symbols as in Equation 1, and k" as a temperature dependent constant). This combined model implied a one point thiophene adsorption and a noncompetitive adsorption of hydrogen and sulfur compound : the constant k" - the contribution of adsorbed hydrogen at low temperature and the increasing contribution of more strongly adsorbed hydrogen with increasing temperature.

Previous investigators [158-163] working at a total pressure of about 1 atm. and in the temperature range from 200 to 500 °C , had determined the main products of the reaction, and had speculated about the reaction mechanism. There was general that the reaction proceeded on a number of catalysts as shown below.

$$C_4H_4S + 3H_2 \longrightarrow C_4H_8 + H_2S \quad \text{(vi)}$$

$$C_4H_8 + H_2 \longrightarrow C_4H_{10} \quad \text{(vii)}$$

The concensus was that the first step of the overall reaction, Reaction (vi) as hydrogenolysis of thiophene proceeded through a butadieine intermediate; butadieine had actually been isolated in small quantities in several studied [159-161, 164]. The second step of the overall reaction, Reaction (vii) as hydrogenation of butene, was not rapid compared with the first step, so that the C_4 product obtained consisted butane and a mixture of the n-butene isomers. A thermodynamic analysis encouraged that reverse reaction should be negligible for both thiophene disappearance and butane formation. The intrinsic kinetics of the hydrogenolysis of thiophene on a cobalt molybdate catalyst were studied in a differential reactor with recirculation, at a total pressure of about 1 atm. and temperatures of 235 to 265 °C by Satterfield and Roberts [155]. Their feed consisted of 2 % thiophene in hydrogen. The conversions varied from about 3.5 % at 210 °C to about 50 % at 280 °C. Retardation of the reaction by some products, both thiophene and hydrogen sulfide, was significant and the rate of thiophene disappearance was correlated by a Langmuir-Hinshelwood type of kinetic equation. Hydrogenation of the butene inter mediate was inhibited by both butene and hydrogen sulfide and the rate of this reaction was also described with a Langmuir-Hinshelwood rate equation. The forms of the kinetic expressions obtained implied that the butene was not hydrogenated at the original desulfurization site. They suggested that the catalyst surface had two types of sites. Thiophene and hydrogen sulfide competed with each other for one type, but only hydrogen adsorbed on the second type. Thiophene underwent a two-point adsorption; hydrogen sulfide adsorbed on a single site. The surface coverage of hydrogen was relatively low, and the rate limiting step was the combination of adsorbed thiophene with adsorbed hydrogen. Their results should that rate of thiophene disappearance was 19.2×10^{6} moles/min. whereas butane formation rate was 10.3×10^{6} moles/min.

Lee and Butt [142] investigated the desulfurization of thiophene on a representative $CoO\text{-}MoO_3/Al_2O_3$ in the temperature ranges from 250 to 313 °C for partial pressure of thiophene from 20 to 160 torr and for partial pressures of hydrogen from 550 to 750 torr. Rates of butane hydrogenation were determined in the same experiments for butene partial pressures from 3 to 31 torr. Primary products from thiophene were 1-butene, cis- and trans-2-butene, and hydrogen sulfide where isomerization occured simultaneously with the desulfurization. Tetrahydrothiophene was detected in small amounts in all experiments and no butadiene was found under any condition. They suggested that the primary step was the hydrogenolysis of thiophene and then the hydrogenation of butene occurred on different sites. There were two type of thiophene chemisorption. One occured via the heteroatom, called one point adsorption. The other occured across the ring double bond, the C-S bond, which was called two-point adsorption. In these experiments, single-site adsorption of thiophene was preferable via the heteroatom on the metal site.

Pease and Keighton [163] found that thiophene desulfurization was near zero order in hydrogen and less than first order in thiophene, while Owens and Amberg [161] reported an activation energy of 25 kcal/mol at the temperature ranges from 270 to 400 °C, base on an assumption of zero order in thiophene. Whereas Sharma, et al. [165, 166] studied the hydrogenolysis of thiophene in naphtha over a series of unsupported and Al_2O_3-supported Co-Mo catalysts at atmospheric pressure in a fixed-bed microreactor. The hydrogenolysis was 0.8th-order with respect to thiophene and first order with respect to hydrogen. On unsupported and Al_2O_3 supported Ni-Mo catalysts, the hydrogenolysis of thiophene was 0.8th order with respect to thiophene and 0.85th order with respect to hydrogen. The activation energy of the reaction was 19.23 kJ/mol at the temperature ranges from 250 to 350 °C. Nag, et al [167] reported that the pseudo-first order rate constant for the disappearance of thiophene at the temperature of 300 °C and the pressure of 71 atm was 1.38×10^{-3} L/g of Co-Mo/Al_2O_3 catalyst.

Devanneaux and Maurin [168] studied kinetics analy sis of thiophene hydrogenolysis on Co-Mo catalysts. Two reaction occured on the two different catalytic sites, one for thiophene ring hydrogenation, and the other for C-S bond scission. Fotl and Schneider [169] found butane in small amount in the reaction products of thiophene hydrogenolysis at low conversion. The operating condition were at 360 °C and atmospheric pressure. The hydrogenation activities of sulfides MoO_3/Al_2O_3 catalysts for butenes produced in the hydrodesulfurization of thiophene at the temperature of 400 °C and atmospheric pressure was investigated by Okamoto, et al. [170]. The relative activity for the hydrogenation to the hydrodesulfurization was constant in the low-S-content catalysts (S/Mo<1). Blake, et al. [171] studied thiophene hydrodesulfurization and butadiene hydrogenation on MoS_2 and

$H_{0.06}MoS_2$ powdered catalysts. The presence of hydrogen in MoS_2 did not effect in thiophene hydrodesulfurization. The mechanism was reported as: (i) a major fraction of adsorbed thiophene underwent isotope exchange but was desorbed without chemical change; (ii) a smaller fraction of adsorbed thiophene proceeded desulfurization before hydrogenation of the hydrocarbon moiety to butadiene and butene; and (iii) a minority of adsorbed thiohene proceeded a degree of hydrogenation before desulfurization and this route was the source of butane.

Debrovolazky, et al. [172] studied hydrodesulfurization of thiophene over Co-Mo/Al_2O_3 catalysts. they found that the selectivity to C_4 hydrocarbons was 80-96 % at the Guass-constant activity level and the hydrodesulfurization activity was roughly proportional to the C_4H_{10} yields. Whereas the predominance of cis-2-butenes was suggested a mechanism for thiophene hydrodesulfurization. Kasanos, et al. [173] suggested that the rate-determining step at temperatures below 500 K was the chemical reaction on the catalyst surface. Above 500 K, the rate was diffusion-or-absorption-limited.

The reaction net work shown in Figure 2.4 was presented by Owens and Ambery [164]. The first reaction of thiophene in the primary reaction path way suggested to be the C-S bond cleavage to form 1,3-butadiene, rather than hydrogenation of the C=C bond. The figures in parentheses showed estimates of the rate of the various reaction steps in micromoles converted per gram of catalyst per second at

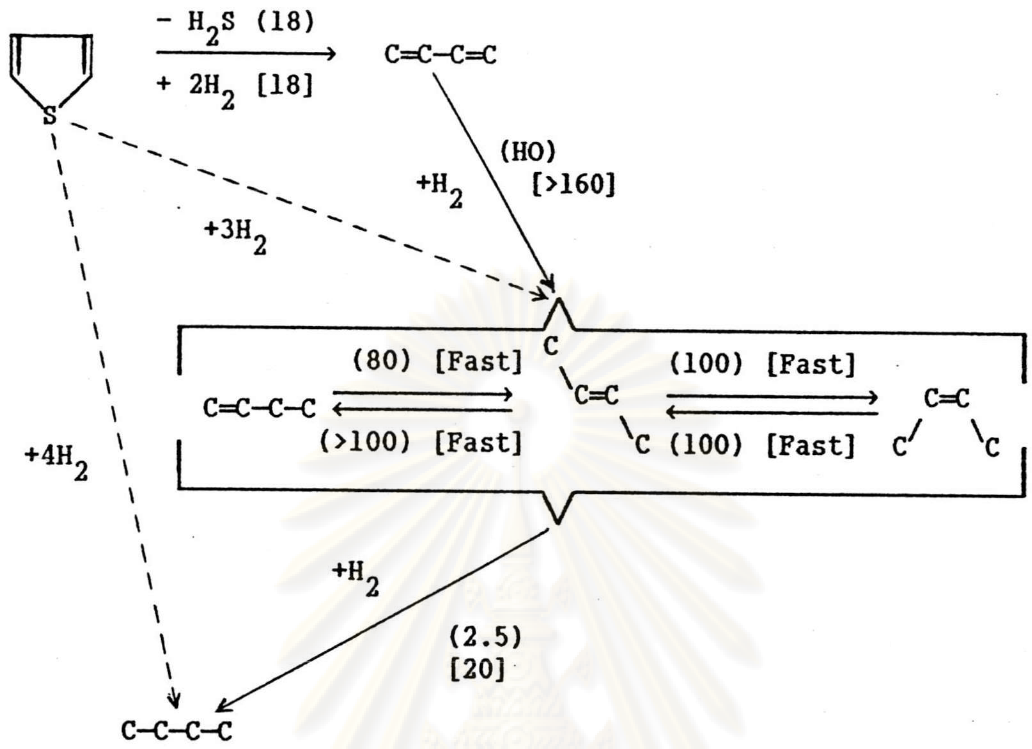


Figure 2.4 Thiophene Hydrodesulfurization Reaction Network (1). Numbers in parentheses are approximate rates $\left[(\mathrm{mmol})/\mathrm{g.s}\right]$ with chromia catalyst at 415°C; numbers in brackets are for Co-Mo/Al_2O_3 catalyst at 400°C. (Reprinted with premission from *Advances in Chemistry Series*. Copyright by the American Chemical Society.)

673 K. As 1,3-butadiene could not be detected in product gases, the hydrogenation rate was thought to be fairly fast. Reaction products were included in feeds to provide indentification of reaction inhibitors and stable reaction intermediates. Some conversion and product-distribution data from a steady-state flow-reactor study were collected in Tables 2.5, 2.6 and 2.7. They also observed that H_2 inhibited reaction of thiophene and hydrogenation of butene but had only little effect on cis-trans isomerization, double-bond shifts, or butadiene conversion to butenes. These results led them to suggest that more than one kind of site was operative in hydrodesulfurization [6].

The hydrogenolysis in the gas phase condition over a commercial hydrodesulfurization Co-Mo/Al_2O_3 catalyst was investigated in a bench-scale tubular reactor by Van Parijs and Froment [174]. The experiment conditions were at the temperature ranges from 533 to 623 K and total pressure from 2 to 30 bar. The experimental rate data were described by a set of Hougen-Watson rate equations for both the hydrogenolysis of thiophene into butene and the hydrogenation of butene into butane. The surface reactions between thiophene or butane and competitively adsorbed hydrogen were found to be the rate-determining step. The reactions products of hydrogenolysis of thiophene detected in measurable quantities were H_2S, n-butane, 1-butene, cis-2-butene, and trans-2-butene. Since tetrahydrothiophene and 1,3-butadiene were not detected in the present work, the following consecutive reaction scheme was adopted for the hydrogenolysis of thio-

TABLE 2.5 Catalyst Activities in Thiophene Hydrodesulfurization

Catalyst	BET area. m^2/g	Apparent reaction rate,^{a,b} $mol/m^2.s$
MoS_2	3.3	0.9
MoS_2 + 1% Co	3.3	0.5
MoS_2 from MoS_2, heated to		
400°C	154	11.0
700°C	67	1.6
800°C	12	1.5
$Co\text{-}Mo/Al_2O_3$	241	1.6
Cr_2O_3	150	2.0

[a] Rate of reaction varied significantly between fractional conversions of 0.005. Tabluated values are average rates between these two conversion.

[b] Data were obtained with a steady-state flow reactor at 288°C. Partial pressures of hydrogen and thiophene were 1.00 and 0.03 atm, respectively. Flow rate of hydrogen was maintained at about $3 \times 10^{-7} m^3/s$. Amounts of catalyst were varied to give a surface area of 2 to 5 m^2 for each.

Source: Reproduced with permission from *Canadian Journal of Chemistry*. Copyright by the National Research Council of Canada.

TABLE 2.6 Product Distribution in Thiophene Hydrosulfurization

Products from a steady-state flow reactor at 0.5% conversion of thiophene; other condition specified in TABLE 2.5

	Mol% in C_4 Hydrocarbon Product				
Catalyst	Butadiene	1-butene	*cis*-2-Butene	*trans*-2-Butene	Butane
MoS_2	6.9	42.5	22.3	19.2	8.8
MoS_2 + 1% Co	8.4	55.6	14.0	17.4	4.7
MoS_2 from MoS_3,					
heated to: 400°C	7.2	39.9	16.7	23.5	12.7
700°C	4.0	28.5	22.0	36.5	9.5
$Co\text{-}Mo/Al_2O_3$	2.2	47.5	19.8	24.3	6.2
Cr_2O_3	7.7	31.3	11.8	11.8	37.4

Source: Reproduced with permission from *Canadian Journal of Chemistry.* Copyright by the National Research Council of Canada.

TABLE 2.7 Product Distribution in Reactions Catalyzed by Chromia Conversions in a pulse microreactor at 415°C

	Mol% in C_4 Hydrocarbon Product				
Reactant	Isobutane	*n*-Butane	1-Butene + isobutene[a]	*tran*-2-butene	*cis*-2-Butene + butadiene
Thiophene	0.0	8.6	30.1	27.4	33.9[b]
1,3-Butadiene	0.0	2.0	23.1	36.7	38.2[b]
1-Butene	0.0	8.9	42.1	26.6	22.4
trans-2-Butene	0.0	1.9	22.3	52.4	23.5
cis-2-Butene	0.0	2.0	21.2	37.6	39.2
Isobutene	2.0	0.0	98.0	0.0	0.0
n-Butane	...	100.00	0.0	0.0	0.0
n-Butenes[d]	...		20	48	32

[a] Assumed to be absent when isobutane was absent.

[b] Butadiene present.

[c] Value possibly high.

[d] Gas-phase equilibrium attained.

Source : Reproduced with permission from *Advances in Chemistry Series*. Copyright by the American Chemical Society.

phene (T) into hydrogen sulfide, butene (B), and butane (A).

$$T \xrightarrow{r_{T,\sigma}} B \xrightarrow{r_{A,\tau}} A + H_2S \qquad \text{(viii)}$$

The hydrogenolysis of thiophene into butene and hydrogenation of butene into butane were considered to take place on different kinds of active sites, σ and τ. Since it was not detect in the effluent, 1,3-butadiene must be a highly reactive intermediate. Therefore, it was assimilated to butene. For the kinetic analysis, thiophene and n-butane were chosen as the independent reaction components. In the construction of plausible Hougen-Watson reaction mechanisms, a distinction was made between the active sites for hydrogenolysis of thiophene into 1,3-butadiene on the σ-sites, and those for hydrogenation on the τ-sites. Either the adsorption of the reactant (thiophene) or the surface reaction between the adsorbed species or the desorption of the reaction products could be rate-determining. For the hydrogenation of butene into butane on the τ-sites, the models with a competitive adsorption of hydrogen and for which the surface reaction was the rate-determining step were superior. Consequently, The rate-determining steps on the σ sites and the τ sites were independently chosen from one another. As an illustration, the reaction mechanism of the best kinetic model that hydrogen was adsorbed in molecular form was given below.

a.1 For the hydrogenolysis of thiophene on the σ-sites.

$$H_2 + \sigma \rightleftharpoons H_2.\sigma$$

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

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

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

b.1 For the formation of butane through hydrogenation of butene on τ sites

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

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

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

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

These first models were derived from a Hougen-Watson mechanism in which the surface reaction between the reactants and competitively adsorbed molecular hydrogen was the rate-determining step for both the hydrogenolysis and the hydrogenation.

The second model differed from the first model in that hydrogen was atomically adsorbed. The corresponding reaction mechanism was given below.

a.2 For the hydrogenolysis of thiophene on the σ-sites

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

$$T + \sigma \rightleftarrows T.\sigma$$

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

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

b.2 For the formation of butane through hydrogenation of butene on the τ-sites

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

$$B + \tau \rightleftarrows B.\tau$$

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

$$A.\tau \rightleftarrows A + \tau$$

It was concluded that the rigorous kinetic studied of the hydrodesulfurization of thiophene into butene the subsequent hydrogenation of butene into butane confirmed the existence of two types of active sites, one for hydrogenolysis and one for hydrogenation. On both types of active sites the surface reactions between the reactants and competitively adsorbed hydrogen were rate-determining. Within the experimental region used in this investigation, and in spite of the vast amount of data, it was impossible to discriminate between the kinetic models for which hydrogen adsorbed in molecular or atomic form.

Isagulyants, et al. [175, 176] studied the mechanism of hydrogenolysis of thiophene on Co-Mo/Al_2O_3 by using tritium. They suggested that hydrogen was irreversibly adsorbed on the sulfided catalyst and participated, along with catalyst sulfur, in the formation of H_2S. However, the irreversibly adsorbed hydrogen did not participate in isotope change or in hydrogenation of the double bonds in thiophene. The next research was reported that surface sulfur of the catalyst participated in formation of H_2S and sulfur of the catalyst was replaced by thiophene in the course of the hydrodesulfurization reaction. The activity of the catalyst depended on the amount of exchangeable sulfur. Introducing Co in to the Mo/alumina catalyst increased both the mobility of surface sulfur and its capacity for exchange. It found that the irreversible adsorbed hydrogen took part in H_2S formation but did not paticipate in hydrogenation reaction. H_2S was formed from SH-groups located on the catalyst surface under the reaction conditions. Hydrogen atoms of thiophene did not directly participate in production of H_2S, whereas hydrogenation occured with participation of either reversibly adsorbed hydrogen or gas-phase hydrogen. It was conclude that butadine was not an intermediate of thiophene hydrodesulfurization.

Araya, et al. [177] used commercial Al_2O_3-supported Co-Mo, Ni-Mo, and Ni-W catalysts to test hydrogenation, hydrodenitrogenation and hydrodesulfurization activity of cyclohexene, n-BuNH 2 and thiophene at the temperature of 623 K and atmospheric pressure in a plug-flow integral microreaction. They suggested that hydrogenation and hydrodesulfurization reactions occured on different sites of Co-Mo catalysts but there was a competition between hydrogenation and hydrodenitrogenation for the same active sites. On the Ni-Mo catalysts, hydrodesulfurization, hydrodenitrogenation and hydrogenation occured on different types of active sites, whereas on the Ni-W catalysts, there was a competition for the same sites only between hydrodesulfurization and hydrodenitrogenation reaction. Kuo and Tatarchuk [53] studied thiophene hydrodesulfurization, 1-hexene hydrogenation, and 1-hexane isomerization over sulfide Ru/Al_2O_3 catalysts and Co-Mo/Al_2O_3 catalyst at the temperature ranges from 548 to 623 K and at the pressure of 102 kPa. They found that thiophene hydrodesulfurization over sulfide ruthenium catalysts produced direct hydrogenolysis in the absence of tetrahydrothiophene formation. Sulfided Ru/Al_2O_3 catalysts provided a 2-fold higher thiophene hydrodesulfurization rate than Co-Mo/Al_2O_3 catalysts.

Irandoust and Gahne [178] investigated the competitive liquid-phase hydrodesulfurization of thiophene and hydrogenation of cyclohexane on a monolithic Co-Mo/Al_2O_3 catalyst at the temperature ranges from 509 to 523 K. They found that the reactions proceeded on 2 different type of active sites. The kinetic model was based on hydrogenation of thiophene ring period to S elimination. While thiophene hydrogenolysis over bimetallic sulfide catalyst was studied by Startsev [179]. A mechanism for thiophene hydrodesulfurization using Ni(or Co)-Mo(or W) catalyst was proposed which differed from previously described mechanisms in that (a) the reaction proceeded in the coordinate sphere of the bimetallic complex without participatation of the sulfur atoms. And (b) adsorption and activation of thiophene occured on coordinatively unsaturated Ni or Co while activation of hydrogen occurred on Mo or W.

Kinetic and adsorption of hydrodesulfurization of thiophene over Co-Mo, Ni-Mo and Ni-W/Al_2O_3 catalysts was investigated by Ihm, et al. [180]. The reaction condition was at the temperature ranges from 275 to 325 °C and atomspheric pressure. The major products from the thiophene hydrodesulfurization reaction were 1-butene, cis-2-butene, trans-2-butene, and a rather small portion of n-butane. Tetrahydrothiophene was detected in trace amounts under some reaction condition (below 1% of the products). Generally it was found that the relative portion of the hydrogenated compounds such as n-butane and tetrahydrothiophene increased in the order Co-Mo<Ni-Mo<Ni-W and that H_2S added in the feed retarded the rate, whereas C_4 compounds had little effect on the rate. They suggested Co-Mo and Ni-Mo/Al_2O_3 were superior for model 7 whereas Ni-W/Al_2O_3 was superior for both model 7 and 8. Model 7 implied a sigle type of adsorption site with one-point adsorption of thiophene and relatively weak adsorption of hydrogen, or a Rideal mechanism of hydrogen with two-point adsorption of thiophene. On the other hand, model 8 indicated a noncompetitive adsorption of thiophene and hydrogen with one-point adsorption of thiophene on one-site and the molecular adsorption of hydrogen on the other

sites. Accordingly, it was presumed that the Ni-W system had a relatively higher hydrogen adsorption capability than the Co-Mo or Ni-Mo system possibly due to the relatively weak adsorption of thiophene and hydrogen sulfide. Hydrogen sulfide acted as a poison and showed a slightly stronger adsorption than did thiophene in all systems. It was also found that hydrogen adsorption was very weak compared to other reactants and was not a dissociative type under the present reaction conditions. The apparent activation energy of the Co-Mo system was about 10 kcal/mol. The Ni-W system showed a higher temperature dependence with a larger value, about 14 kcal/mol. Although the Ni-Mo system followed a similar trend to the Co-Mo system in many aspects, it showed higher rate constants together with lower activation energies.

Vrinat [140] reported that thiophene hydrodesulfurization evidently proceeded by two parellel pathways (Figure 2.3), although the reaction network was not completely understood, with results of different investigators being in less than full agreement. Rate equations from the low-pressure experiments indicated that thiophene inhibited its own hydrodesulfurization; in some investigations, hydrogen sulfide had been found to inhibit hydrodesulfurization. The possibility of inhibition by hydrogen was difficult to assess because only small ranges of hydrogen partial pressure had been used. Hydrogenation and hydrogenolysis were inferred to occur on two different kinds of sites since hydrogen sulfide affects rates of thiophene hydrogenolysis and olefin hydrogenation differently [6].

In a thorough set of experiments characterizing hydrodesulfurization of thiophene in the vapor phase [174], conditions were varied over a wide range (Table 2.8). A reaction network was proposed in which thiophene was hydrodesulfurized to give 1-butene and cis-and trans-2-butene, followed by hydrogenation of the butenes. Neither tetrahydrothiophene nor butadiene (which was proposed to be hydrogenated rapidly to give the three butenes) was detected. Two different kinds of catalytic sites were assumed, one for thiophene hydrogenolysis and one for butene hydrogenation, in accordance with results of low-pressure experiments [140]. The data were correlated best by either of two sites of Langmuir-Hinshelwood rate equations, one based on a rate-determining surface reaction between adsorbed thiophene and molecularly adsorbed hydrogen and the other differing only in that hydrogen was assumed to be dissociatively adsorbed, which was a more realistic postulate. In each case, it was assumed that hydrogen sulfide was formed by reaction of gas-phase hydrogen with adsorbed sulfur by an Eley-Rideal mechanism. The rate equations base on the assumption of dissociatively adsorbed hydrogen were given in Table 2.9 with the parameter values for reaction at 260 °C by Van Parijs and Froment [174]. The existence of two different kinds of sites was justified a posterior by the large difference between adsorption equilibrium constants for hydrogen on the two sides. The adsorption parameters of the organic compounds exceeded those for hydrogen by 1-2 orders of magnitude.

TABLE 2.8 Reaction Condition for Hydrodesulfurization of Thiophene*

Reactor Type	: Vapor-Phase Flow Reactor
Reactor Temperature	: 260-350°C
Pressure	: 2-30 atm
Molar H_2/Thiophene Ratio	: 4-9
Catalyst	: $Co\text{-}Mo/Al_2O_3$

*Reference from Van Parijs and Froment, 1986.

TABLE 2.9 Rate Equations for Thiophene Hydrogenolysis and Butene Hydrogenation Assuming Dissociatively Adsorbed Hydrogen (Van Parijs and Froment, 1986)

---

1. Thiophene hydrogenolysis on σ sites:

$$r_{T,\sigma} = \frac{k_{T,\sigma}\ K_{T,\sigma}\ K_{H_2,\sigma}\ P_T P_{H_2}}{\left[1 + (K_{H_2,\sigma}\ P_{H_2})^{1/2} + K_{T,\sigma}P_T + K_{H_2S,\sigma}P_{H_2S,\sigma}/P_{H_2}\right]^3}$$

2. Butene hydrogenation on τ sites:

$$r_{A,\tau} = \frac{k_{B,\tau}\ K_{\beta,\tau}\ K_{H_2,\tau}\ P_B P_{H_2}}{\left[1 + (K_{H_2,\tau}P_{H_2})^{1/2} + K_{A,\tau}P_A + K_{B,\tau}P_B\right]^2}$$

---

where the subscripts T,A, and B denote thiophene, butane, and butene, respectively.

Parameter values at 260°C are as follows:

$k_{T,\sigma} = 5.22 \times 10^{7} \exp(-29.9/RT) = 2.82 \times 10^{-5}$

$K_{T,\sigma} = 5.60 \times 10^{-4} \exp(10.7/RT) = 13.7$

$K_{H_2,\sigma} = 0.536$

$K_{H_2S} = 91.2$

$k_{B,\tau} = 2.21 \times 10^{11} \exp(-38.1/RT) = 5.16 \times 10^{-5}$

$K_{A,\tau} = K_{B,\tau} = 4.07 \times 10^{-4} \exp(10.6/RT) = 8.87$

$K_{H_2,\tau} = 8.88 \times 10^{-13} \exp(-26.4/RT) = 6.02 \times 10^{-2}$

where the rate parameters k and adsorption parameters K have units of mol/(g of catalyst.s) and atm^{-1}, respectively. The adsorption parameter for hydrogen sulfide is dimensionless. These results pertain to the temperature range 260-350°C.

hydrogen sulfide was a strong inhibitor of hydrogenolysis but did not inhibit hydrogenation. The data were also fitted to a model in which the two kinds of sites were interconverted at a rate depending on the hydrogen sulfide partial pressure, but the fit was not substantially better with this more complicated modle [181].

Comments on the influence of H_2 partial pressure.

Although hydrogen is involved in all the reactions which take place during hydrorefining processes, there is a lack of information on the role of this reactant. From the point of view of mechanistic and kinetic correlations, interest so concerned with the following fundamental questions:

(1) Dose hydrogen adsorption take place on the same kind of catalytic sites as those required to adsorb sulfur compounds?

(2) Is the adsorbed hydrogen involved in the sulfur compound hydrogenolysis a molecular or an atomic species?

Although the assumption that adsorbed thiophene reacting with gas phase hydrogen has been reported by Ozimek and Redomyski [182]. The current literature concerning the kinetics of hydrogenolysis of thiophenic compounds is generally consistent with a dual site mechanism: hydrogen is adsorbed on type of the second question is, on the contrary, still much debated. For thiophene hydrodesulfurization , the dependence of rate on the H_2 partial pressure has typically been represented as first order at low partial pressures [155-157, 182, 183], which confirms that hydrogen adsorption is not sufficiently important to affect the Langmuir-Hinshewood adsorption term. Moreover, most of these studies have been done in too narrow a range of H_2 pressure and, in such cases discussion of a molecularly or atomically adsorbed hydrogen is kinetically meaningless.

The only kinetic analysis of thiophene hydrodesulfurization with an apparent kinetic order of 0.5 in hydrogen partial pressure of hydrogen was reported by Devanneaux and Muarin [139]. In this work the pressure of hydrogen was varied from 2.2-17.5 atm and a Langmuir-Hinshellwood kinetic analysis applied to hydrogen influence is represented by the following rate equation:

$$r_{HDS}=k\ f(P_T)\frac{K_H P_H}{1+(K_H P_H)^{0.5}} \qquad .....(2.3)$$

Although a knowledge of the way in which hydrogen interacts with the sulfided catalyst is essential to an understanding of the working of the catalyst, at the present time there is a lack of results on this subject. There is some evidence from inelastic neutron scattering and neutron diffraction experiments on MoS_2 [184, 185] that adsorption of hydrogen is dissociative and that dissociatively chemisorbed hydrogen is bound to sulfur rather than to molybdenum, but these studies do not prove that these species are involved in the hydrodesulfurization reaction.

Comments on the influence of the partial pressure of the products

Turning now to the dependence of hydrodesulfurization rate on product concentration, we shall discuss separately the influence of hydrogen sulfide and hydrocarbons.

By preadsorbing H_2S on a "cobalt molybdate" catalyst. Owens and Amberg [164] were the first to report that this product has a strong retarding effect on thiophene conversion. This observation was later confirmed by several investigators [155, 156, 183, 185-189] during hydrogenolysis of various thiophenic compounds.

In the most of the kinetic studies, this inhibition effect of H_2S is only retarded to a kinetic inhibition explained by adsorption on catalytic sites in competition with the sulfur compound: the adsorption parameter determined from kinetic analysis generally confirmed that the inhibiting influence of H_2S decreases with rising temperatures [155, 190-192].

In addition, Broderick, et al. [193] found that, during hydrodesulfurization of dibenzothiophene, H_2S added to the feed also induces a structural change of the catalyst when the $H_2S:H_2$ ratio is low, this fact was explained in terms of solid state reaction influencing the structure and activity of catalysts and could be related to the work of Gachet, et al. [194] who proved that on these catalysts about 20 wt% of the sulfur is liable. Furthermore, it is well known that a definite partial pressure of H_2S is required to maintain the activity of sulfur catalysts and experimental evidence of this behavior has been abundantly reported [195-197]. In view of these results, H_2S must be observed for kinetic interpretations on these catalysts.

Concerning the influence of the hydrocarbon products on the hydrogenolysis rate, differences exist between various results reported in the literature.

For thiophene hydrodesulfurization, Owens and Amberg [164] have shown that the butene hydrogenation and sulfur compound hydrodesulfurization might take place to some extent on different sites. Similarly, Satterfield and Roberts [155] reported that butene is quickly desorbed from its formation site and then subsequently adsorbed and hydrogenation on another site. These results are in agreement with experiments where excess 1-butene added to the same way, Lee and Butt [157] reported that incorporation of a competitive adsorption term for butene in the hydrodesulfurization rate equation was not necessary, which they take as evidence for a difference in hydrogenation and hydrogenolysis sites.

2.8 The effect of other compounds in hydrodesulfurization of thiophene

Matsumoto and Bondo [198] studied hydrodesulfurization of thiophene in benzene-toluene-xylene fraction. A catalyst consisted of 4.4% CoO and 21.0% MoO_3 on alumina. In this experiment catalysts promoted the hydrogenation of organic sulfur compounds but did not promote dearomatization. In product contained 0.08% less BTX than the feed and it lost more than 99.9% of its original sulfur content. Hydrogen transfer during hydrodesulfurization of thiophene over sulfided Mo/Al_2O_3 and Co-Mo/Al_2O_3 catalysts at the temperature ranges from 490 to 590 K and atmospheric pressure was investigated by Ramaswam, et al. [199]. Typical feeds containing thiophene (1 wt% sulfur) were prepared in different solvents such as benzene, cyclohexane and n-heptane. They suggested that the role of hydrogen transfer reactions occurred between these solvent molecules and thiophene adsorbed on the catalysts. H-rich molecules in the feed and H-rich supports facilitated the hydrodesulfurization of thiophene on Mo/Al_2O_3 samples. They also found that aromatic compounds could lead to poisoning of the active centers and to lower catalytic activity at temperature below 550 K.

Fujimoto, et al. [200] studied the liquid-phase hydrogenolysis of thiophene by added Decalin as hydrogen donor with active carbon-supported metal catalysts at the temperature ranges from 330 to 390 °C. Hydrogen atoms in Decalin were first transfered to the carbon surface and then to the metal sulfide surface to react with thiophene. Mo and Co on active carbon were the most active catalysts for thiophene hydrogenolysis and Decalin dehydrogenation.

Blekkan and Mitchell [201] investigated the interaction of organometalics with sulfide catalyst in hydrodesulfurization of thiophene. MoS_2 catalyst was doped with cobaltocene which was used in hydrodesulfurization of thiophene. The products of this experiment were the mixture of butane and butene. They suggested that the hydrodesulfurization activity rose when the cobaltocene decomposed because the released cobalt was incorporated as a promoter. At the same time, the hydrogenation activity decreased that related to the amount of butane in the product. The activation energy for the conversion of thiophene was the same for MoS_2 and the promoted catalyst.

Effect of metal-organic compounds on thiophene hydrodesulfurization over sulfided Co and Ni promoted Mo/Al_2O_3 catalysts was studied by Sarbak and Andersson [202]. The additions of vanadium and nickel naphthenate were used as metal-organic compounds in thiophene solution. The operating condition was at the temperature of 370 °C and atmospheric pressure. Deactivation by the addition of nickel or vanadium naphthenate in a low concentration worked similarly. At higher doses, vanadium naphthenate affected both catalysts more strongly than nickel naphthenate. They found that the metal compounds deposited to a higher extent at the catalyst particles' exterior than at interior surfaces at higher levels of additions. It should also be noted that the deactivation was much larger at higher temperature. The decomposition of organometallic compounds occured on the same sites as those active for hydrodesulfurization. The experiments showed that both Ni-Mo and $Co\text{-}Mo/Al_2O_3$ catalysts were strongly deactivated by the vanadium naphthenate, whereas nickel naphthenate mainly affected the $Ni\text{-}Mo/Al_2O_3$ catalyst. The decomposition of the naphthenate thus produced oxidic and sulfidic nickel species which indicated that poisoning might occur by physical blocking by nickel sulfide and changed in the carrier by the formation of nickel aluminate. The organic part of the naphthenate might additionally lead to deactivation by coke.

2.9 Hydrogenation of Toluene [6, 122, 203]

Hydrogenation is a reaction between unsaturated hydrocarbon compounds and hydrogen. The products of hydrogenation are saturated hydrocarbon compound. A great varity of hydrogenation reaction are carried out industrially. These range from large-scale, continuous catalytic operation in petroleum refineries, dealing with streams of couples composition, to small-scale batch operations in the pharmaceutical and fine chemical industry where a very precise hydrogenation step is often desire, starting with a relatively pure reactant.

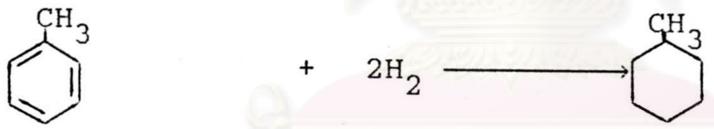
Hydrogenation is a catalytic and exothermic reaction. The most common catalyst so some form of nickel. Next is palladium, where its higher activity and/or selectivity more than compensates for its higher cost. Both of these metals readily adsorb. Other metals such as iron, copper and platinum are less adsorptive, which may account for the high catalytic activity of palladium and nickel.

Supported Ni-Mo or alumina is a widely used catalyst in petroleum hydroprocessing, and there are many established processes. Ni-Mo/Al_2O_3 catalyst can used in hydrogenation of unsaturated hydrocarbon compounds. Nagai [204] suggested that Ni-Mo/Al_2O_3 catalyst had two types of active sites. One was the desulfurization size and the other was the hydrogenation size.

Toluene, an aromatic compound as C_7H_8, is a good solvent which use in petroleum industry. It also uses as a solvent in coal liquid extraction [205]. This unsaturated hydrocarbon compound, toluene, can be hydrogenated over nickel catalysts [206] and hydrotreating catalysts such as Ni-Mo/Al_2O_3. Afonso, et al. [207] used sulfided Ni-Mo/Al_2O_3 in hydrotreatment of Irati shale oil, containing 0.87 % toluene content, to study behavior of the aromatic fraction under rather drastic hydrotreating condition (at 400 °C and 125 atm). They found that toluene was removed 30 % conversion.

Reaction

In hydrogenation, toluene react with hydrogen to produce methylcyclohexane over hydrogenation catalysts. The catalytic hydrogenation is showed in the following equation:


....(ix)

Pasynkiewiez and Jankowski [208] studied hydrogenation of toluene on Ziegler type catalyst at the temperature ranges from 130 to 230 °C and the pressure ranges from 6 to 10 MPa. They suggested that the bimetallic catalyst systems increased activity and the presences of water had a positive effect. Klvana, et al. [209] used a Ni/SiO_2 aerogel catalyst in hydrogenation of toluene to methylcyclohexane in a flow fixed bed reactor at the temperature ranges from 90 to 150 °C. Under integral conditions of conversion, the reaction mechanism obeyed the Langmuir-Hinshelwood model involving reactants both strongly adsorbed on specific sites and exhibiting a global reaction order of zero. The energy of activation was 47 KJ/mol. The catalytic activity was very stable with time on stream. Whereas Tran, et al. [210] investigated hydrogenation of toluene and benzene on group VIII metals. They found that both reactants were bonded to the metal surface via ¶ bonds involving an electron transfer from aromatic ring to unoccupied d-metal orbitals. Fujie, et al. [211] also used toluene and benzene as a hydrogenation reactant to study the catalytic activity of Ni/Al_2O_3 by added a small amount of BaO which resulted in higher activity of the catalyst. The highest avtivity was obtained with 1.5 wt% BaO. The hydrogenation activity was proportional of the amount of hydrogen chemisorbed on the catalyst, and introduction of BaO into Ni/Al_2O_3 increased the Ni-metal surface area. The adsorption of toluene and benzene in hydrogenation reaction was studied by Orozco and Webb [212]. They suggested that both reactants were dissociatively adsorbed on alumina- and silica-supported palladium and platinum catalyst. Toluene was more readily hydrogenated over both metals than benzene. The sites for the adsorption and hydrogenation of benzene were probably distinct from those involved in toluene adsorption and hydrogenation.

In hydrogenation of toluene, it may occur hydrodemethylation (hydrodealkylation) or hydrogenolysis reaction. Kham, et al. [213] investigated the activity of Zr-Co hydride on Co/ZrO_2 and Co/Al_2O_3 catalysts in the hydrogenation, hydrogenolysis, and hydrodemethylation of toluene.

The selectivity of the hydride catalysts for hydrodemethylation and complete degradation of toluene depended on the dispersion of Co and the hydrogen content. The characteristics of high temperature catalytic hydrogenolysis of toluene into benzene was studied by Isaev, et al. [214]. The hydrodemethylation of toluene to benzene was suggested to be a catalytic mechanism rather than a thermal mechanism even at a temperature as high as 600 °C and 20-50 atm.

Kozlov, et al. [215] used Ni-Mo/Al_2O_3 catalysts in hydrodealkylation of toluene for benzene production proceeded without transalkylation. The most active catalyst contained 4.0 % NiO and has 1:2 ratio of Ni-Mo. They suggested that there had to be an availability of surface paramagnetic Ni and there had to be a sufficiently high concentration of Mo^{5+} in the lattice of the reduce catalyst in order to obtain a highly active catalyst. Navalikhina, et al. [216] suggested that the content of heteropoly compound in Ni-W/Al_2O_3 catalyst determine their pore size distribution, activity in hydrogenaolysis reaction. It gave 93.4 % conversions of hydrodemethylation of toluene and 77.9 % conversions of the hydroliquefaction of coal at the temperature of 625 °C and at the pressure of 5 MPa when the catalyst contained 12 % heteropoly compounds.

Krichko, et al. [217] studied high-temperature hydrogenation of toluene in the BTX fraction on Cr_2O_3-Al_2O_3 catalyst at temperature ranges from 600 to 625 °C and a pressure of 4.9 MPa. Their results showed that there was a hydrodemethylation of toluene, 65.9-86.1 % conversion, on those catalysts which resulted in high concentration of C_2H_6 in BTX fraction, Boitiawx [218] used Ir/Al_2O_3 catalyst to study selectivity of toluene hydrodealkylation under super atmospheric pressure. They found that there was a strong sensitivity for ring hydrogenolysis and not insensitive for hydrodealkylation to benzene which resulted in higher concentration of methylcyclohexane, from hydrogenation of toluene, in the product than benzene. The selectivity to benzene was increased when crystallite size increased.

2.10 Organometallic Compounds [10, 102, 203]

Metal impurities in petroleum feedstocks are organometallic compounds, metal salts, and metal elements. The organometallic compounds are the major form of the metal impurities which are dissolved very well in petroleum, as organic solvents. Organometallics are compounds which contain carbon-metal bonds between organic and metal groups. Organometallic compounds, contaminants from feeds, deposite within the pores of the catalyst over time that causes irreversible catalyst deactivation.

Yoshimura, et al. [135] found the metal compounds (such as Na, K, Mg, Ca, Fe, Ti, Ni, and V) coal-derived oils and petroleim vacuum gas oil. Most of metal impurities in petroleum feedstocks were V>Ni>Fe>Ti, respectively [137, 152, 219]. Metal in crude oils are either in the form of salts dissolved in water suspended in the oil or in the form of organometallic compounds and metallic soaps. Metallic soaps of calcium and magnesium are surface active and act as emulsion stabilizers [203]. The metal impurities in different source of crude oil was showed in Table 2.10

Hydrotreatment must be use in these crude oil for impurities removment, metal and sulfur removement. In hydrotreatment, hydrodesulfurization and hydrodemetallization occur simultaneously on the catalyst surface to remove sulfur and metal components from feed. The metals are deposited on the catalyst in the form of metal sulfides. Generally, it is easier to crack a bond between carbon and a heavy metal than a carbon sulfur bond. Consequently, the rate of metals conversion from organometallic compounds to metal sulfides is faster than the rate of organosulfur conversion to hydrogen sulfide. The free metals or metal sulfides are solid and deposit on the catalyst surface.

Kovach et al. [220] studied the deposition patterns of inorganic metal salts and organometallics and found that after carboneceous deposition reached its maximum, the deposition of oil-insoluble inorganic metal salts would be hindered by carboneceous deposition. On the other hand, organometallics can still penetrate through the carboneceous deposition and into the pores of the catalyst and be deposited there. Chiou and Olson [221] analyzed the aged catalyst obtained from the H-coal process by scanning electron microscopy and electron microprobe. They showed that most inorganic metals deposit on the outer surface of the catalyst, whereas organometallics can penetrate into the catalyst pores and have the same distribution pattern as those of organo-vanadium and organo-nickel in petroleum hydrotreatment. DeRosset [222] also analyzed the aged catalysts

TABLE 2.10 Trace elements present in crude oils

Source	Elements Present
Canada	Fe, Al, Ca, Mg
Ohio	Fe, Al, Ca, Mg
California	Fe, Ni, V
Egypt	Fe, Ca, Ni, V
Irag	Fe, Ni, V
Venezuela	Fe, Ni, N

and found that higher percentages of organometallics were deposited on the catalyst than inorganic metal salts.

Some observation have suggested that the metal deposition can accelerate the coke formation. Habib et al. [223] observed a large increase in coke content due to catalyst metals poisoning in a cracking process. Tamm et al. [116] argued that instead of coke which was commonly blamed for the initial rapid catalyst deactivation, the organometallics are the primary deactivation agents. They found that the initial deactivation period was directly related to the concentration of organometallics in the feed but not to the coke precursers as measured by Conradson carbon content.

2.11 Literature Summary

1. The loss of catalyst activity in hydrodesulfurization reaction was a combination of two factor. First, it was the reversible deposition of heavy organics or coking. The other was the permanent poisoning due to the permanent adsorption of organometallics.

2. Metals in the feed deposited within the pores of the catalyst as mixed metal sulfides. Demetallation kinetic was suggested in first-order.

3. There was three periods of deactivation. The activity in the first period decreased because of deposition of coke in the mixed the micro and meso pores. Vanadium was deposited in accessible meso-macro pores. During the second period on deactivation, vanadium was deposited on the mouth of mesopores and in a meso-macro structure, which decreased diffusivity

and reaction rate. The last period of deactivation from coke and vanadium were accumulated in the external part of the meso-macro structure and in multilayers in the neck of narrow-pore interconnecting the external and internal parts of the pellet.

4. The desulfurization was accelerated by the concurrent removal of vanadium. It might be the effect of a donor-acceptor interaction between vanadium compounds and catalyst surface.

5. Decompositon of organometallic compounds occurred on the same sites as those active for hydrodesulfurization. Both Ni-Mo and Co-Mo/Al_2O_3 catalysts were strongly deactivation by vanadium whereas organo-nickel compounds mainly affected only Ni-Mo/Al_2O_3 catalyst.

6. Vanadium adsorbed on the catalyst more strongly than nickel. Nickel was more easily removed than vanadium in the low temperature region, with the reverse situation at high temperature. So the vanadium had to be removed before nickel could be removed.

7. Absorbed inorganic forms of titanium had no poisoning effects on the catalysts, but that organometallic forms were easily absorbed from even low concentration. The amount of titanium deposition increased very slowly.

8. Titanium and iron penetrate into the catalyst grain core and irreversible changed the catalyst activity.

9. Iron was adsorbed quickly and had high level of adsorption on catalyst surface. Iron sulfide might complex with certain types of aromatics and deposit as organometallics on

the catalyst surface. For example, cyclopentadiene compounds were known to form complex, i.e. ferrocenes.

10. Adding iron in such a manner that undesirable hydrogenation reaction were prevented without decrease of the catalytic activity of hydrodesulfurization.

11. Hydrodesulfurization activity rose when the cobaltocene decomposed because the released cobalt was incorporated as a promoter. Whereas the hydrodesulfurization activity decreased that related to the amount of butane in the product.

12. The operating condition of hydrodesulfurization was at the temperature ranges from 300 to 500 °C and at the pressure ranges from 1.01 to 20.27 MPa with the liquid hourly space velocity ranging from 0.37 to 2.6 h^{-1}.

13. The products of thiophene hydrodesulfurization were hydrogen sulfide, 1-butane, *cis-* and *trans*-2-butene, tetrahydrothiophene, 1,3-butadiene and a rather small portion of *n*-butane. Small amounts of butadiene was an intermediate, but this is rapidly hydrogenated to a butene. The butenes in turn were more slowly hydrogenated to butane.

14. Hydrogenation and hydrodesulfurization was occurred on different types of active sites of Ni-Mo/Al_2O_3 catalyst.

15. Aromatic compounds could lead to poison of active centers and to lower catalytic activity at temperature below 550 K.