CHAPTER 2

THEORY

Catalytic hydrodesulfurization of light petroleum oils is widely applied to pretreat charge for catalytic reforming and isomerization processes. It is generally accomplished by passing a feedstock concurrently with hydrogen, flowing downward through solid catalyst particles in a fixed-bed reactor. A typical flow diagram of a hydrotreating unit is shown in Fig 2.1.

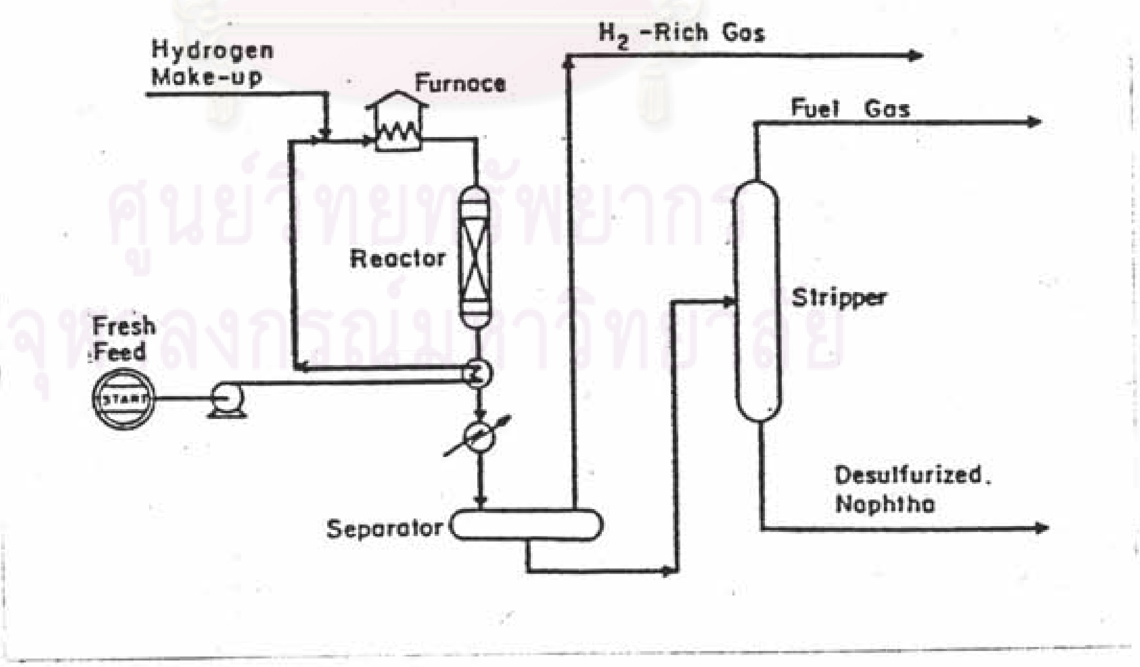

Figure 2.1 Typical naphtha hydrotreater

A hydrogen-rich gas (usually above 70% H_2) joins the feed. This mixture is then heated and, in almost all cases , totally vaporized. The feed-hydrogen mixture then passes over a fixed catalyst bed at conditions which depend on the feedstock properties and the desired product specifications. In the most common light hydrocarbon application of catalytic hydrotreating (naphtha pretreating), the reactor effluent is cooled and sent to a separator where most of the hydrogen, methane, ethane, and some of the hydrogen sulfide and ammonia are flashed off as gas. This gas can be scrubbed and either recycled or used for other purposes. The liquid phase from the separator is sent to a stripper (a pressurized distillation column) in order to remove any residual H_2S or ammonia that may be dissolved in the liquid. The stripper is also used to separate any C_3 and C_4 material from the pretreated naptha product. In the pretreatment of napthas for catalytic reforming (or other processes which employ noble metal catalysts), the stripper operation is important since residual dissolved H_2S in the naptha could easily cause sulfur tolerance limits to be exceeded.

Typical yields and product specifications are shown in Table 2.1 for the catalytic hydrotreatment of virgin naphtha for a catalytic reforming operation. Such data for the pretreatment of cracked napthas or gasolines would be similar with one exception. Hydrogen consumption for cracked stocks would be much higher and would depend heavily on the olefin content of the charge.

Table 2.1 Typical yields and product specifications for naphtha hydrotreating

Feed: Typical virgin naphtha (sulfur content 100–700 ppm
nitrogen content ~ 0.3–2 ppm)

Product stream to be used for catalytic reforming

Operating condition: 7–15 LHSV ; 200–400 lb/in^2 gauge total pressure
400 SCF/bbl gas rate (85% H_2 purity)
450–600 ^{o}F average catalyst bed temperature

Yield:	
H_2S, wt%	0.01–0.07
C_1–C_2, wt%	0.2
C_3–C_4, wt%	0.1–0.3
C_5+, vol%	99.5–100.0
Hydrogen consumption, SCF/bbl	10–20
Product inspections:	
Sulfur, ppm	<1
Nitrogen, ppm	<0.5
Olefin, vol%	<0.5
Oxygen, ppm	<5
API	Same as feed
Distillation	Same as feed
Hydrocarbon analysis	Essentially same as feed

2.1 REACTION

A summary of the most important classes of reactions occurring in the hydrodesulfurization process is given here, to be followed in another section by an account of the hydrodesulfurization reactions themselves. The desired reactions, hydrogenolysis, result in cleavage of the C-S bond ; eg.,

$$R\text{-}SH + H_2 \longrightarrow RH + H_2S$$

Under industrial reaction condition, hydrogenolysis reactions resulting in breakage of C-C bonds also occur, eg., the hydrocracking reaction

$$RCH_2CH_2R' + H_2 \longrightarrow RCH_3 + R'CH_3$$

Another kind of hydrogenolysis reaction is hydrodenitrogenation, hydroxygenation and olefin saturation ,eg.,

$$RNH_2 + H_2 \longrightarrow RH + NH_3$$

$$ROH + H_2 \longrightarrow RH + H_2O$$

$$R\text{-}CH{=}CH\text{-}R' + H_2 \longrightarrow R\text{-}CH_2\text{-}CH_2\text{-}R'$$

These C-N and C-O bond cleavages are much more difficult to acheive than the C-S bond cleavage. Consequently, denitrogenation and deoxygenation occur to a much lesser extent than does desulfurization.

Fortunately, nitrogen and oxygen usually are not significant problems in virgin napthas, although in cracked stocks or in synthetic napthas (such as those from coal or shale) concentrations of nitrogen and oxygen can be quite high (see **Table 2-2**). In such cases, very severe hydrotreating conditions are required to reduce the concentrations to a level acceptable for reforming or isomerization(<1 ppm).

Finally, olefin saturation is effected simply by the addition of hydrogen to an unsaturated hydrocarbon molecule (a molecule with one or more carbon-carbon double bonds)to produce a saturated product. For example, $R-CH=CH-R$ is saturated to form $R-CH_2-CH_2-R$. The olefin saturation reaction is very exothermic and proceeds relatively easily. Straight-chain monoolefins are easy to hydrogenate while branched and cyclic diolefins are somewhat more difficult. Aromatic rings are not hydrogenated except under the most severe hydrotreating conditions. As with nitrogen and oxygen compounds, olefins are not found to any great extent in virgin naphthas, but concentrations can get as high as 40 or 50 vol% in cracked or synthetic stocks.

Table 2.2 Ranges of conditions used for various types of light oil hydrotreating

Case	I	II	III
General feedstock type	Virgin	Cracked or blends of virgin and cracked	Synthetic or blends of virgin and synthetic
Severity	Mild	Intermediate	Severe
Feedstock Sulfur, ppm	100–700	100–3000	500–8000
Feedstock Nitrogen, ppm	<2	2–30	500–6000
Feedstock Oxygen, ppm	<10	10–100	100–5000
Feedstock Olefin, vol%	<1.0	5–40	<1[b]–45[c]
Operating conditions :			
Space velocity,LHSV	7.0–15.0	3.0–6.0	8–20
Total pressure,lb/in^2 gauge	200–400	400–700	800–1500
H_2 partial pressure, lb/in^2 gauge	60–150	150–400	500–1000
Hydrogen purity in reactor gas, mol%	70–90	70–90	70–90
Gas rate, SCF/bbl	200–400	400–1000	1000–6000
Average temperature, ^{o}F	450–600	550–680	650–730
Cycle life,months	6–24	6–18	3–12

[a] For example :Naphthas from coal or shale oil

[b] For naphtha from coal. [c] For naphtha from shale oil

2.2 CATALYSTS

The catalysts applied in hydrodesulfurization have evolved from those developed in prewar Germany for hydrogenation of coal and coal-derived liquids. They are formed from alumina-supported oxides of Co and Mo, and the surfaces are usually sulfided in operation. Catalysts of this type are often referred to as cobalt molybdate, which is a jargon term. Industrial catalysts may contain as much as 10 to 20 percent of Co and Mo. A number of related compositions have been applied including, for example, Ni and W instead of Co and Mo. Cobalt- molybdenum (CoMo) catalysts are widely used throughout the industry for naphtha hydrotreating although nickel-molybdenum (NiMo) or nickel-cobalt-molybdenum (NiCoMo) catalysts are often chosen when better nitrogen removal activity is desired. In extreme cases where feedstock nitrogen levels are very high, nickel-tungsten (NiW) catalysts are sometimes considered. NiW catalysts have not, however, had wide application in naphtha hydrotreating because of their relatively high cost.

Hydrotreating catalysts are generally either in the form of sphere or cylindrical extrudate, though currently some catalyst manufacturers are reporting advantages for shaped extrudates. Some typical ranges of catalyst properties are shown in **Table 2.3**.

Table 2.3 Typical range of hydrotreating catalyst properties

Nominal catalyst diameter,in.	1/8 to 1/20
Average length for extrudates,in.	~ 1/4
Packed catalyst density, lb/ft^3	30 to 50
Surface area,m^2/g	200 to 300
Nickel content, wt%	0 to 6
Cobalt content, wt%	0 to 6
Molybdenum content, wt%	5 to 15

2.3 PROCESS CONSIDERATION

So far the two most important factors in determining the operating conditions needed for a given hydrotreater are the feedstock properties and the desired product properties. These two factors set the general severity that is required in the hydrotreating operation although other considerations (such as catalyst type, heater limitation, or the amount, pressure, and purity of the hydrogen available) will have a bearing on the actual conditions that are used. The major processing considerations are now discussed.

Feedstock Properties

As the concentrations of sulfur, nitrogen, oxygen, and / or olefins increase, more severe hydrotreating conditions will be needed to bring the concentrations down to a given level. The rate of hydrodesulfurization reactions of single sulfur compounds follows first-order kinetics; however, when present in combinations , the compounds taken as a group exhibit apparent reaction order of up to 1.6. There are three very broad categories of light hydrocarbon feedstocks that can be hydrotreated : (1) virgin, (2) cracked (e.g. coker naphtha), and (3)synthetic (e.g. coal or shale liquids). The conditions typically used to hydrotreat virgin stocks are mild, whereas treating cracked feed (or blends of cracked and virgin feeds) requires more severe conditions. Hydrotreating synthetic stocks represents the most severe type of operation. **Table 2.2** presents typical ranges of conditions for three hydrotreating cases. Case I is mild hydrotreating of a virgin naphtha, Case II represents relatively severe treating of blend of virgin naphthas , Case III is the severe pretreating of shale oil or coal naphtha or blend of these feeds with petroleum naphthas. In these cases it is assumed that the product is to be charged to a reformer. This means that the product sulfur and nitrogen levels must be reduced to below 1 and 0.5 ppm, respectively, and the olefin content must be less than 0.5 vol%.

Space Velocity

When holding all other conditions constant, increasing space velocity will cause product sulfur (and/or other contaminant concentrations) to increase. This effect can in some cases be offset by increasing either the reactor temperature and/or the hydrogen partial pressure. Table 2.2 shows typical space velocity ranges for the various types of hydrotreating. In mild operations, space velocities range from 7 to 10 or even as high as 15 hr^{-1}. In more severe operations, space velocities are usually between about 3 and 6 hr^{-1}, and in the most severe cases space velocities typically vary between 0.8 and 2 hr^{-1}.

Hydrogen Partial Pressure

Increasing hydrogen partial pressure increases the rate of desulfurization, denitrogenation, olefin saturation, and deoxygenation, if all other conditions are held constant. Studies have shown that desulfurization reactions are first-order in hydrogen partial pressure at least for pressures below 420 lb/in^2 gauge. It should be noted that hydrogen partial pressure can be altered by changing (1) total pressure, (2) gas circulation rate, or (3) the hydrogen purity of the circulating gas. Typical ranges of these variables are presented in Table 2.2.

Temperature

Higher temeratures increase the rates of desulfurization and other desired reactions which remove contaminants. In the design of hydrotreaters, the intial (start-of-cycle) temperature is set by design throughput, the operating pressure, and other economic factors. Enough temperature flexibility is built into the unit so that temperature may be increased throughout the cycle to offset the loss in catalyst activity that occurs as the catalyst ages. **Table 2-2** shows that hydrotreater temperatures are normally kept between 500 and 700 °F, with a maximum of about 800 °F. Above 800 °F, hydrocracking reactions and coke deposition become too prominent for economical operation.

Catalyst Aging and Hydrotreater Cycle Life

The major factor in determining naphtha hydrotreater cycle lives and catalyst aging rates is the feedstock character. If the charged stock is high in unstable olefins or organometallic compounds and other heavy contaminants which can deposit on the catalyst, then catalyst aging will be relatively fast and pressure drop problems could force an early unit shutdown. These contaminants are usually a problem only when treating synthetic feeds or high concentrations of cracked stocks.

In general, catalyst aging due to coke laydown increases with increasing temperature or with decreasing hydrogen partial pressure.

When hydrotreating a virgin naphtha, catalyst aging due to coke laydown generally occurs very slowly and, in fact, does not usually determine cycle life. Most commercial hydrotreaters that are in mild naphtha pretreating service are shut down when it is convenient and often for some purposes other than needed catalyst regeneration, such as general cleaning and maintainance or a refinery turnaround. Catalyst regenerations are done at such times as a matter of expedience. Typical cycle lives for the different types of light oil hydrotreating are present in **Table 2.2.**

2.4 LITERATURE SURVEY ABOUT HYDRODESULFURIZATION OF LIGHT OILS

Norman E. Perry (1960) studied about hydrodesulfurization of hydrocarbon oil by first suspending a finely ground metal which can react with H_2S in the oil to be desulfurized, adding H_2 and passing the mixture over a S-active hydrogenation catalyst. Thus, Luxmass($Fe(OH)_3$, 62 g/l)finely ground to 300-mesh, was mixed with oil (density = 0.901, 3.1 wt% S , acid value 3.2, diesel index 29 and boiling point > 248 ^{o}C). The suspension along with H_2 (49 ft^3 H_2 /ton of product) was heated and passed over a catalyst containing Co 0.8, Mo 6.5 and bauxite 92.7 % at the rate of 5.06 kg/l/hr, 375 ^{o}C and 50 atm. The product was S-free.

National Aluminate Corp. (1960) reported that a porous Al_2O_3 catalyst was prepared by spray-drying an aqueous Al hydrate to obtain microspherical particles, adding a catalytically active promoter, drying the impregnated catalyst with a hot gas and extruding it. Thus, 1500 lb. of the dried Al_2O_3 hydrate particles containing 10-15 % free H_2O prepared by atomizing the aqueous slurry containing 6% Al_2O_3 hydrate at 900-1000 lb./ sq. in. and 1000-1100 °F was added to 527 gal. of H_2O. The mixture was heated to 180 °F and agitated with 175 lb. of MoO_3 stirred in 15-20 gal. H_2O. Then 107 lb. $CoCO_3$ stirred with 15-20 gal.H_2O was added, and the mixture was agitated for 1 hour at 180 °F. After filtering quickly and drying at 200-250 °F , a product was obtained containing 25% total H_2O and 5-10% free H_2O for 10-20 minute at 60-80 °F. The moisture content was increased to about 33% by weight free H_2O. The impregnated Al_2O_3 was pelleted in an extrusion mill, predried at 250 °F, screened to remove fines, and calcined at 1050-1100 °F to give pellets. The latter had a bulk density of 47 lb./cu.ft., a hardness of 15 lb. crushing per 1/8 in. length and containing 11-12% CoO and MoO_3. When a fluid cycle oil of 25.9 API gravity containing 1.8% sulfur and 0.03% N, and having a bromine no. of 23.1 was brought into contact with the catalyst at 700 °F., 500 psig at a weight hourly space velocity of 2, a product having an API gravity of 29.2, 0.08% by weight S, 0.015% N, and a bromine no. of 8.1 was obtained.

Roy P. Northcott, and Ernest C. Housam (1960) reported that improved results in desulfurization by autorefining were obtained by incorporation of 2.5-3.0% fluorine in the Co-Mo catalyst and operation at 810 °F, using the equilibrium-pressure method. For example, Kuwait gas oil, boiling point 248-358 °F, sp.gr. 0.844 , containing 1.29 %sulfur was autorefined over a catalyst containing 17.6 % MoO_3, 2.7 % CoO , and 0.25 % fluorine, and supported on Al_2O_3. At 810 °F, an equilibrium pressure starting at 100 psig and space velocity of 4 vols./vol./hr., the organic S content of the product after various periods of operation was :10 hrs., 0.04%; 50 hrs., 0.09%; and 100 hrs., 0.23%. Under similar conditions, but with a temperature of 780 ^{o}F, the organic S content of the product was 0.17% after 5 hrs. and 0.27% after 25 hrs. The use of autorefining to desulfurize blends of straight-run and thermally cracked gas oils was described.

David K. Beavon (1961) studied about hydrodesulfurization of petroleum hydrocarbon by using an arsenic-containing catalyst. Hydrocarbon fractions, such as catalytically or thermally cracked naphtha, kerosine, gas oil or coal tar distillate are brought into contact at 500-800 ^{o}F and 50-800 psig in the presence of H_2 with Co-Mo-Al catalyst previously used for treatment of straight-run naphthas. The catalyst has a deposit containing at least 0.01% by wt As. Thus, a mixture of 63% by vol heavy, catalytically cracked gasoline and 37% heavy, thermally cracked gasoline was processed in one case over the used catalyst and in another case over the fresh catalyst at 555 ^{o}F,650 psig, space velocity (wt/hr/wt) 4.66, with a H_2 : hydrocarbon ratio of 0.8. The used catalyst contained Co 2.0, Mo 5.6 and As 0.037% by wt. The fresh catalyst contained Co 2.4, Mo 5.5% and no As. The run gave 100.85% by vol. recovery with the used catalyst and 100.43% with the fresh catalyst; Br.no. of the treated fluids are 35 and 43, S content 0.42 and 0.45% by wt. and basic N_2 213 and 233 ppm, respectively.

Jame E. McEvoy(1961) reported that a $CoO-MoO_3.Al_2O_3$ catalyst having a higher surface and lower bulk density was prepared by using a mixture of $\alpha-Al_2O_3.H_2O$ and $\beta-Al_2O_3.3H_2O$ as support material.

Thus, a catalyst comprising CoO 3%, MoO_3 15%, Al_2O_3 82% and Na_2O 0.02% and having a surface area of 308 in^2/g and a bulk density of 0.7, desulfurized and reduced the nitrogen content of a naphtha charge stock by hydrotreating for 300 hours at 750 °F and 555 psig, at a space rate 3 vols. liquid to 1 vol. catalyst per hour and H_2 : oil ratio of 3.

Lawrence B. Van Ingen (1962) reported that kerosine was stabilized and desulfurized by hydrotreating it in the presence of a CoO-MoO_3 catalyst. After deaeration kerosine, boiling point 320-460 °F, was hydrotreated at 675 °F, 420 psig, and a space velocity of 5 vols./vol./hr. in the presence of an alumina catalyst (I) containing 4% CoO and 10% by wt MoO_3; hydrogen from a subsequent hydrodesulfurization step was circulated at 320 standard cu.ft./bbl. of charge. After gas removal, the kerosine was steam stripped and washed succesively with an alkaline metal hydroxide and water. The treated kerosine contained 0.0001- 0.0003% mercaptan sulfur and 0.001-0.002% by weight total S, representing a removal of 99% and 98%, respectively. The naphtha from the stripper overhead was mixed with straight-run naphtha to form a feedstock (7-10 ppm.of nitrogen) which is hydrodecontaminated at 700 °F, 470 psig, and a space velocity of 5 vols./vol./hr. in the presence of a catalyst similar to I. Hydrogen from a subsequent reforming step was circulated at 200 standard cu.ft./bbl.of charge. The treated stock (S<20 and N<1 ppm.) was reformed at 930°F., 550 psig, and a space velocity of 2 vols./vol./hr. in the presence of a catalyst containing 0.35% Pt and 0.71% by wt. Cl. The hydrogen:naptha mole ratio was 6. Excess hydrogen-containing gas was delivered to the hydrodesulfurization step. The circulation of hydrogen in the kerosine stablization step was 25-40% of the amount usually used.

L.N. Osipov, E.S. Semenova and S.P.Rogov (1963) reported that the relative efficiencies of hydrofining catalysts were determined by comparing the activity of an unknown catalyst with that of a concentrated Al-Co-Mo catalyst containing 12.6% MoO_3 and 5.6% CoO with a surface area of 197 m^2/g and an average pore radius of 41 A. The feedstock used was a 200-350 ^{o}C fraction of 1.10% S straight-run Romanshkino crude. Runs were carried out in a laboratory hydrofining approximatety at 20 atm, 380 ^{o}C and a H_2 flow rate 500 l/l of feedstock and at feedstock rate of 2.0 ,4.0 and 6.0 vols./vol./hr. Runs were of 16-24 hours.

Robert F. Vance and John F. Strotman (1963) studied about the hydrodesulfurization catalyst and process. Catalyst extrusions were described, which were highly active in the hydrodesulfurization of petroleum, physically strong and capable of withstanding high-temp regeneration without deterioration. These extrusions were easier to make and had a lower density than catalyst tablets. Al_2O_3 hydrate and MoO_3 were mixed with an aqueous solution of a Co salt to form a damp, solid mixture. A strong acid, e.g. HNO_3, was added in a controlled amount to convert the solid into an extrudable paste. The amount of acid used should be 2.5-10% of total wt. of the final product. The extruded mixture was dried at 1000 ^{o}F to evaporate the moisture, decompose the Co and Mo salts, partially dehydrate the Al_2O_3, and convert the catalyst into hard pellets having great physical strength and capable of withstanding repeated regeneration. The acid could be added simultaneously with incorporation of the Co and Mo compound compounds and needed not be highly concentrated. These catalysts have an increased activity, especially in desulfurization. To prevent "deadburned" Al_2O_3, the calcination temperature should be 600-1000 ^oF. The color of the catalyst could be improved by adding a small amount of Al stearate of other fatty acid salt or other C-containing material. The amount of C-containing compounds in the catalyst could vary over a wide range, but it was desirable to have >= 1 atom C/mol of Co compound. The atom ratio of Co to Mo may vary from 1:5 to 1:1. The Co salt could be any H_2O-solution salt convertible to CoO upon calcination. The Co (as CoO) should form 1-5% and Mo (as MoO_3) 2-20% of the catalyst. Thus 100 lb. hydrated Al_2O_3 (27 % H_2O, equal proportions of α and β), 4 lb. corn starch, and 9 lb. MoO_3 were dry-mulled for approx. 20 min. Then 26.5 lb. of an aqueous solution of $Co(NO_3)_2$ (sp.gr. 1.196), containing 1.8 lb CoO, was added and the mixture wet-mulled for about 10 min. Next, 2.5 lb HNO_3 (63%) diluted with H_2O was added and wet mulling continued. Water (approx. 4.5 gal) was added to give an extrudable paste which was extruded through a 1/8 in. stainless steel die. The extrudates were calcined for 1 hr. at 400 ^oF., 1 hr. at 650 ^oF, and 6 hrs. at 950 ^oF. The catalyst was sulfided by heating at 700 ^oF for 2 hrs. in an atmosphere of H_2S. A No.2 diesel fuel containing 1400 ppm S was hydrodesulfurized over a bed of this catalyst at 700^oF in the presence of H_2 at a rate of 1500 ft^3/bbl., 300 psig, and a liquid hourly space velocity of 3. The catalyst reduced the S content of the oil to 150 ppm.

Shell International Research Maatschappij N.V.(1964) reported that hydrocarbon oils containing cyclic and(or) acyclic S compounds were treated with steam at 350-450 ^{o}C and above 15 atm. in the presence of a catalyst which contained a sulfide of a metal of Group VIA and FeS, NiS, or CoS and was supported by Al_2O_3. H_2 had to be absent. For example, 1 l C_6H_6 contaminated with 10% by wt thiophene and containing 4.5 % S was treated with 1 kg. H_2 at 20 atm and 400 ^{o}C in the presence of a catalyst obtained by sulfiding a mixture of CoO 3.8, MoO 9.9 , SiO_2 1.0 and Al_2O_3 85.3 % by wt; 90% of the S was removed. When the catalyst was not sulfided, only 3.5% of the S was removed under similar conditions.

Adams Clark E., Kimberlin Charles N.Jr.(1971) studied the 2-stage desulfurization-hydrodesulfurization of a hydrocarbon oil, boiling point above 200 ^{o}F. The rapidly deactivated, S-resistant 1st stage Co-Mo or Ni-W catalyst was regenerated by stripping with H_2 or a H_2-H_2S mixture. Thus, a gas oil containing 3.1 % S was desulfurized at 0.25 vol. feed/vol. catalyst/hr, 700 ^{o}F and 800 psig in the presence of a catalyst containing 3.5 wt% CoO and 12.5 wt% MoO_3 on an Al_2O_3 support containing 2.0 wt% SiO_2 and having a surface area of 266 m^2/g, a pore volume of 0.5 cm^3/g, and a surface area in 30-70 A pores of 174 g/m^2. The reactor was operated in alternate cycle of 6 hr running and 18 hr regeneration with a H_2 stream containing 10% H_2S. During 9 cycles of operation, S removal for each cycle was 64-75%. Similarly, WO_3-NiO catalyst was used.

Hatano Takanori, Okagami Akio, Matsuoka Seiichi(1974) reported that in hydrodesulfurization of petroleum hydrocarbons containing S compounds., the petroleum hydrocarbons and H_2 or a H_2-containing gas were passed simultaneously through a hydrodesulfurization zone packed with a solid hydrodesulfurization catalyst to convert the S compounds to H_2S in the presence of H_2,and with an adsorbent (different from the hydrodesulfurization catalyst) for adsorbing the S compounds and H_2S formed. Thus, spherical γ-Al_2O_3 (1.5-2.0 mm) were soaked in an aqueous solution containing $Co(NO_3)_2$ and $(NH_4)_6Mo_7O_{24}$, dried, calcined at 500 °C in air for 4 hr to yield a catalyst containing Co 1.61 wt% and Mo 3.64 wt%, then reduced with H_2 at 300 °C for 2 hr, sulfided with a kerosine containing 1 wt% CS_2, mixed with an adsorbent (containing ZnO and some graphite) in a 100:200 vol ratio, and packed in a fixed-bed reactor. A gas oil (boiling point 169-320 °C, density 0.8261, total S 1200 ppm) at 83 ml/hr was passed through the reactor (300 ml) at 400 °C, 50 kg/cm^2 gauge, and 360 $l.H_2/l.$ oil. The desulfurized gas oil contained 0.9 ppm S.

Simpson Howard D.(1978) reported that catalysts with increased activity in hydrodesulfurization of hydrocarbon oils, containing less than 30 % MoO_3, were prepared by mulling boehmite with aqueous ammonium molybdate, mulling the dried mixture with aqueous Co salt, and calcining at a temperature controlled to prevent the formation of large cobalt molybdate crystallites. Thus, 230 g boehmite (H_2O content 20-25%) was mulled 20 min with 230 ml solution of 83 g $(NH_4)_6Mo_7O_{24}$ in 1:1 H_2O-28% NH_3, dried at 180 °F, mulled with 230 ml aqueous solution of 97 g $Co(NO_3)_2 \cdot 6\,H_2O$, extruded, dried at 250 °F, and calcined 2 hr at 1200 °F to give a catalyst containing 26.2% MoO_3 and 8.8% CoO, surface area 198 m^2/g. In desulfurization of light diesel oil containing 0.65% S at 700 °F, 700 psig and liquid space velocity 5/hr, this catalyst had relative activity 139, compared with 100 for a catalyst containing 15.9% MoO_3 and 6.0 % CoO with surface area 313 m^2/g.

Yu Albert P., Myers Edward C. (1979) reported that cracked naptha was catalytically hydrodesulfurized, with minimum saturation of olefins. A catalyst containing 4 wt % CoO and 5 wt% MoO_3 on MgO support was presulfided and used to hydrodesulfurize cracked naphtha at 450-750 ^oF, 75-600 psig, H_2 to feedstock ratio 200-500 ft^3/bbl and liquid space velocity 0.5-15 hr^{-1}. The desulfurization level was 91.5 wt% after 408 hr, 93.9 wt% after 480 hr for high-metal catalyst, i.e., 3 wt% CoO and 16.6 wt% MoO_3.

2.5 CATALYTIC CHEMISTRY

As mentioned in the introduction, sulfur is present largely in the forms of thiols (mercaptans), sulfides, disulfides and various thiophenes. Mercaptans and sulfides react with H_2 to form hydrogen sulfide and hydrocarbons.

$$RSSR' + H_2 \longrightarrow RH + R'H + H_2S$$

$$RSH + H_2 \longrightarrow RH + H_2S$$

$$RSR' + H_2 \longrightarrow RH + R'H + H_2S$$

where R and R' are various hydrocarbon groups.

The order of reactivity is roughly RSH > RSSR' > RSR' > thiophenes. Reactivity decreases with increased molecular size and varies depending upon whether R is a aliphatic or aromatic group. Thiophenic compounds are the least reactive sulfur compounds in petroleum, and being the simplest and most easily obtained compound in this class, thiophene itself, has frequently been chosen for study, being regarded as a model reactant. Thiophene hydrodesulfurization was examined in a series of kinetic studies by Amberg and coworker. The catalysts were a commercial Co-Mo/Al_2O_3 (1.3 % Co and 6.1 % Mo), chromia, and several molybdenum disulfides. Kinetic data were obtained from a pulse microreactor and from a steady-state flow reactor operated at very low conversion (<0.5 %). Reaction products were included in the feeds to provide identification of reaction inhibitors and stable reaction intermediates. Some conversion and product-distribution data from the steady-state flow-reactor study are collected in **Tables 2.4** and 2.5.

Table 2.4 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_3 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 and 0.005. Tabulated values were average rates between these two conversions.

[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 3×10^{-7} m^3/s. The amount of catalyst was varied to give a surface area of 2 to 5 m^2 for each.

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Table 2.5 Product distribution in thiophene hydrodesulfurization

Products from a steady-state flow reactor at 0.5% conversion of thiophene.

Catalyst	Mol % in C_4 hydrocarbon product				
	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-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

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Owens and Amberg (1961) also used the microreactor containing chromia catalyst to determine the conversions of the individual compounds listed in Table 2-6. The data of Tables 2-5 and 2-6 lead to the reaction network suggested in **Fig.2-2** for thiophene hydrodesulfurization catalysts by chromia and by Co-Mo/Al_2O_3.

Table 2.6 Product distribution in reactions catalyzed by chromia Conversions in a pulse microreactor at 415 °C

	Mol % in C_4 hydrocarbon product				
Reactant	Iso-butane	n-Butane	1-Butene+ isobutene[a]	trans-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[c]	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	...	100.0	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.

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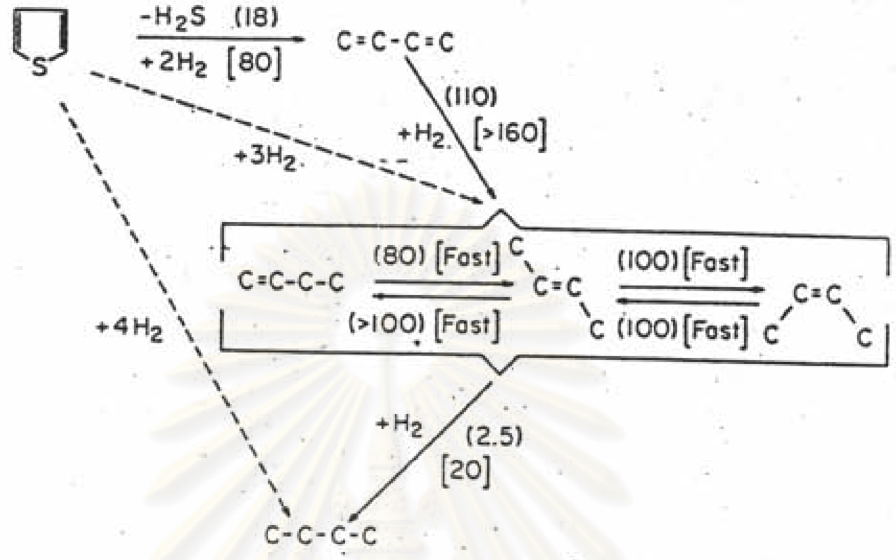

Figure 2.2 Thiophene hydrodesulfurization reaction network. Numbers in parentheses are approximate rates [(m mol)/g·s] with chromia catalyst at 415 °C; numbers in brackets are for Co-Mo/Al_2O_3 catalyst at 400 °C. (Reprinted with permission from Adcances in Chemistry Series. Copyright by the American Chemical Society.)

The suggestion that the first reaction of thiophene in the primary reaction path was the C-S bond cleavage to form 1,3-butadiene, rather than hydrogenation of the C=C bond, was supported by further data of Desikan and Amberg (1964). Their results showed that hydrogenating compounds with the C-S bonds intact(tetrahydrothiophene) gave products in hydrodesulfurization different from those observed for thiophene.

Amberg and coworkers also observed that H_2S inhibited hydrodesulfurization reaction of thiophene and hydrogenation of butene but had little effect on cis-trans isomerization, double-bond shift, or butadiene conversion to butenes. These result led them to suggest that more than one kind of sites were operative in hydrodesulfurization; we shall return to this point later.

Though quantitative studies of hydrodesulfurization kinetics, convering wide ranges of temperature and pressure and including effects of all reactants and products are still generally lacking, a partial determination of kinetics of thiophene hydrodesulfurization in the absence of mass-tranfer influence has been reported by Satterfield and Robert (1968), who used a $Co\text{-}Mo/Al_2O_3$ catalyst containing about 3% Co and 7% Mo. Reaction-rate data were determined at low conversions attained in a steady-state recirculation-flow reactor. Pressure was slightly above atmospheric, temperature was 235 to 265 ^{o}C, and feeds contained various concentrations of thiophene and H_2S; hydrogen partial pressure was varied only insignificantly. The products observed were consistent with Amberg's reaction network (Fig 2.2). The data for rates of thiophene disappearance (hydrogenolysis) and rates of butane formation (butene hydrogenation) were represented by Langmuir-Hinshelwood rate eqations as follows:

$$r_{HDS} = \frac{kP_TP_H}{(1+K_TP_T+K_{H_2S}P_{H_2S})^2} \qquad (1)$$

$$r_{hyd} = \frac{k'P_BP_H}{(1+K'_BP_B+K'_{H_2S}P_{H_2S})} \qquad (2)$$

Values of the rate equation parameters are summarized in **Table 2.7**.

Table 2.7 Rate equation parameters of thiophene hydrodesulfurization kinetics

Temp., ^oC	10^5 x k, mol/ $g.atm^2.s$	10^{-1} x K_T, atm^{-1}	10^{-1} x K_{H_2S}, atm^{-1}	10^8 x K', mol/ g.atm.s	10^{-2} x $K_{,3}$, atm^{-1}	10^{-1} x K'_{H_2S}, atm^{-1}
235	1.5	4.3	3.1	3.0	9.8	9.1
251	1.6	2.3	1.3	12.2	1.2	1.9
265	1.8	2.5	0.56	...	~0	1.3

Although the appropiateness of these equations is not firmly established by the data, several clearly important qualitative results have been confirmed by the literature as follows: (1) H_2S inhibits both the hydrogenolysis and hydrogenation reactions; (2) significant amount of reactant thiophene and butene are adsorbed on the catalyst surface in competition with H_2S; (3) less clear, but more important, is the conclusion that the hydrogenolysis and hydrogenation reactions proceed on separate catalytic sites, consistent with the results of Amberg mentioned previously.

Hydrodesulfurization catalysts with cobalt molybdates are commercially produced in their oxidic form. Structurally, the hydrodesulfurization catalyst may be defined as a porous γ-Al_2O_3 support which carries molybdenum oxide as a bound monolayer. Cobalt promoter ions are deposited onto the surface of the molybdenum alumina structure. The most active form of CoMo catalysts is with the metals in the sulfided form. During presulfiding competing reactions between reduction and sulfiding take place.

De Beer, et al. (1975), has proposed a model in which the monolayer oxide present in oxidic state breaks apart during sulfiding to form discrete MoS_2 crystals and probably Co_9S_8. Raman spectroscopy has been applied to investigate the sulfided catalyst by Brown(1977). Molecular MoS_2 structures were found after sulfiding with a mixture of H_2S/H_2 but no evidence of cobalt sulfides such as Co_9S_8 was obtained. From electron scanning results, Stevens and Edmonds (1979) have found indication that activated CoMo-Al catalysts contain the same sulfided state of Mo and Co as the separate components do, and that in particular a Mo state resembling Mo^{4+}-S in MoS_2 is common to sulfided catalysts. Massoth (1975) presents a sulfiding model for a Mo-Al catalyst in which the major reaction at moderate sulfiding temperature is replacement of oxygen by sulfide, with some loss of extra oxygen at higher temperatures. From careful measurement of surface area for both oxidic and sulfided catalysts, Massoth (1977) suggested that a monolayer of Mo on alumina remained after sulfiding.

In such ways the activated Mo-state varies between investigations. These disagreements may come from differences in catalysts or presulfiding techniques. However, generally the amount of sulfur required for activation of the HDS catalysts must be calculated from the following formulas: MoS_2 and Co_9S_8.

2.5.1 Sulfiding techniques

Undoubtedly it is accepted these days that presulfiding results in higher catalyst activity. Which method of presulfiding is the best in a specific case is less easy to say. In the presulfiding procedure we recognize the following main steps:

1. Catalyst drying
2. Catalyst soaking
3. Presulfiding itself

The following is a discussion of the parameters of the different steps.

Drying

The catalyst can take up water to 10 wt% (normally 1-3 wt%) because of the hygroscopic nature of the alumina carrier. When heating up in wet conditions in the presence of oil, the catalyst can mechanically be damaged, causing pressure drop problems in the unit. Proper drying is possible with any gas, normally available at a refinery (air/nitrogen/treat gas). However, the temperature should be watched carefully, especially when treat gas is used.

Experiments have shown for both NiMo and CoMo that under hydrogen catalyst activity is not affected when the temperature is kept below 200 °C. Pressure should be held at the atmospheric level during drying in order to release water at a low temperature. High catalyst bed inlet temperature might cause damage of the catalyst because of rapid evaporation and an exothermic reaction due to generation of adsorption heat when steam condenses in the lower (still cold) part of the catalyst bed. Therefore, when drying is started, temperature should be kept at 120 ^{o}C until water released in the separator levels off (0.1 wt%/hr). Finally the catalyst can be dried at 250 ^{o}C (200 ^{o}C in hydrogen atmosphere) until hardly any water is released (less than 0.01 wt%).

Soaking

Soaking of the catalyst is done to wet the catalyst particles properly. This will prevent the presence of dry areas in the catalyst bed. These dry areas lower the overall activity of the catalyst inventory.

Presulfiding techniques

There are three different routes in presulfiding:

1. Nonspiked feedstock

This method, in wet phase, is applied very often and is most popular in Japan. Sulfiding is done with the sulfur from the normal feedstock. To prevent reduction, the presulfiding can only be applied succesfully at low temperatures, which means this technique will take a long time before sulfiding has been completed.

2. H_2/H_2S

This presulfiding is carried out in gas phase. Conversion of the metal oxide into sulfides is done by H_2S from the treat-gas (3-10 vol% H_2S). In commercial practice this method is a common practice in laboratory experiments.

3. Spiked feedstock

This method, in wet process, is applied in Europe and increasingly in the U.S. Sulfiding is mainly done by the sulfur of the spiking agent(about 1 wt% S on feedstock). A spiking agent is chosen which decomposes at low temperatures.

The following are details of these techniques.

2.5.1.1 Presulfiding with nonspiked feedstock

Catalyst soaking

In the case of liquid-phase presulfiding a soaking step at 150 $^{\circ}$C is recommended. Soaking with the feedstock can result in substantial sulfur adsorption by the catalyst. Up to 50% of the stoichiometric amount of sulfur necessary for sulfiding of the metal oxides can be adsorbed during this step. This amount of adsorbed sulfur might play an important role as safeguard for the following step. Soaking is an important step also for good wetting of the catalyst.

Temperature/nonspiked feed

After soaking has been completed at 150°C, the temperature must be increased to decompose the sulfur compounds into H_2S. For a nonspiked feedstock, the temperature of presulfiding has been chosen to be 300 and 350 $^{\circ}$C. The constant rate of temperature increase may be from 12 to 25 $^{\circ}$C/hr until 300 $^{\circ}$C is reached. Thereafter, temperature increase was lowered to 7° to 12 $^{\circ}$C/hr until 350 $^{\circ}$C is reached.

2.5.1.2 Presulfiding with H_2/H_2S

The most widely used procedure involves contacting the catalyst with a gaseous mixture of hydrogen and H_2S at elevated temperatures. The presence of hydrogen appears to give a more active catalyst, apparently by maintaining the Group VIB metal sulfide component in an optimum valence state. However, the use of hydrogen in such a process presents certain problems. At elevated temperatures, above about 260 ^{o}C (which are normally required to complete the sulfiding) hydrogen in the absence of H_2S tends to reduce some of the active metal oxides to free metals, resulting in agglomeration, particularly with respect to molybdenum. When a mixed gas stream of H_2/H_2S is passed through a deep bed of catalyst, all of the H_2S is initially chemisorbed or combined with the upper layers of the catalyst bed, leaving the lower portion of the bed substantially free of H_2S. It is therefore necessary to first sulfide the entire bed of catalyst at a relatively low temperature, and then gradually raise the temperature to complete the sulfiding. Another difficulty with gas phase presulfiding is that the reaction is exothermic, and depending on the metal concentration, can generate very high instantaneous temperatures at the active sites, resulting in a lower activity.

2.5.1.3 Presulfiding with spiked feedstock

The process is the same as the presulfiding with nonspiked feedstock but spiking agents are added to the feedstock. Spiking agents are sulfur-containing organic compounds which release H_2S at a much lower temperature than the sulfur compounds present in normal feedstocks. The spiking agents can be ranked according to their temperature of decomposition and price per kilogram sulfur produced. All agents given in **Table 2.8** result in a catalyst with maximum performance.

Table 2.8 Spiking agents used in presulfiding

Compound	Temperature of decomposition, ^{o}C.	S, wt%	S/kgS
Carbon disulfide	175	84.2	0.52
Dimethyldisulfide	200	68.1	2.35
n-Butylmercaptan	225	34.7	5.18
Dimethylsulfide	250	51.1	2.94
TNPS	160	37.7	6.25

In the past, carbon disulfide (CS_2) has been applied as a spiking agent. However recently it is seldom used because of environmental restrictions. Mercaptans, such as butanethiol , are successful alternatives but their bad odor has prompted search for other alternatives.

Nowadays spiking agents such as dimethylsulfide (DMS) and dimethyldisulfide (DMDS) are applied successfully. They can be delivered in steel containers and road tankers.

The success of presulfiding depends on the decomposition temperature. The lower the decomposition temperature, the better. Commercial experiences show that in the use of DMDS, a presulfiding temperature of 250 °C is enough; for DMS about 275 °C is necessary before adequate reaction takes place. No noticeable activity difference, however, has been found in commercial operation between DMS and DMDS presulfiding. On the laboratory scale spiking with ditertiary nonyl polysulfide (TNPS) produces comparative activity with DMDS spiking.