Chapter 9

CURRENT PROGRESS IN CATALYSTS AND CATALYSIS FOR HYDROTREATING

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1. INTRODUCTION

There are a number of processes used in petroleum refining as shown in Fig. 1. These include thermal, catalytic and hydroprocessing upgrading processes. The hydroprocessing processes include three major classes, namely, hydrotreating, hydrocracking, and hydrofinishing. Hydrotreating includes hydrogenative heteroatom removal and hydrogenation. Hydrocracking performs hydrogenation and cracking successively and simultaneously. There are differences between combined hydrotreating/catalytic cracking and hydrotreating/hydrocracking in terms of conditions and reactions interactions, with associated advantages and disadvantages being included in these processes. Hydrofinishing is really another form of hydrotreating that is used to achieve the final specifications of fuels. Each process is individually optimized according to the boiling range and molecular composition of the specific petroleum fraction being treated.[1] Hence, it is very important to understand correctly the process objectives, conditions and configurations, the chemistry of fuels and products, catalytic materials and their functions and working mechanisms for all of the important hydroprocesses currently operated.[2]

The products in the refining processes are also hydrotreated, and are basically classified according to their boiling ranges. This overview describes the detailed chemistry of feeds, products, and their conversion mechanisms on the catalysts in hydrotreating on a molecular level, including the detailed structures of the reactants, their chemical and physical properties and the mechanisms of their conversion. The influences of the detailed molecular interactions on reactivity and inhibition are also reviewed. The preparation, activation, composition and structure of the catalysts in each process are discussed along with the associated causes of catalyst deactivation and ultimate catalyst lifetime for each process. Approaches to new and improved catalytic processes and more active catalysts are also discussed, even if the structure of the catalyst is still not fully described on atomic levels.

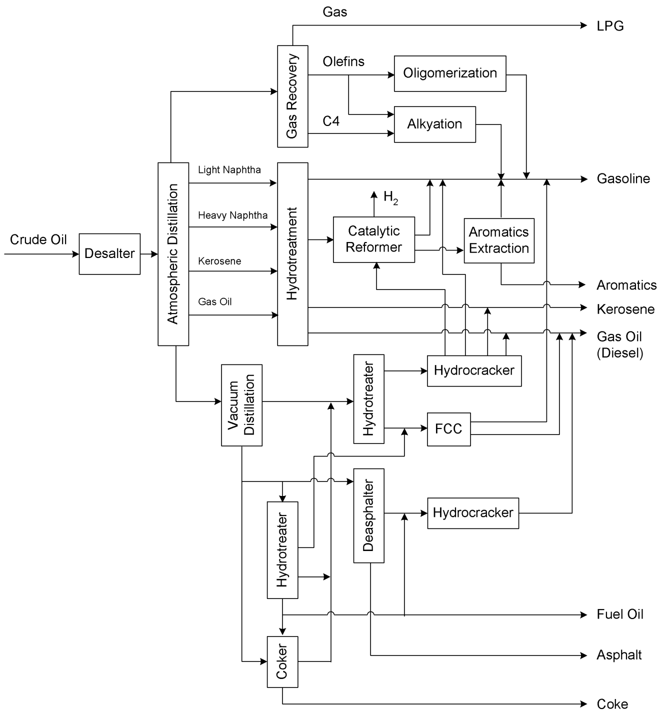


Figure 1. Stream of Petroleum Processes

Recently, some reviews on the hydrodesulfurization of middle distillates have been published. Song summarized the new aspects of deep HDS of diesel and gasoline fractions including a brief review of some commercial processes.[3] Moulijn also reported the recent advances in deep HDS.[4] His review described the conventional and non-conventional technology including adsorption and oxidation. In contrast, French groups summarized the chemical nature of HDS systems, including new acid catalysts and adsorption technology.[5]

Fig. 2 illustrates the diversity of composition by showing the elemental distribution of some typical petroleum fractions, such as LCO (light cycle oil), MCO (medium cycle oil), SRGO (straight run gas oil), H-SRGO (hydrotreated straight run gas oil), and gasoline, as determined by GC-AED

(Gas Chromatography with Atomic Emission Detection).[6,7] GC-AED chromatograms of hexane soluble fraction of VGO were also included. Also shown in this figure are the distributions of specific molecular species that must be converted into hydrocarbons by hydrotreating in the presence of partner species.

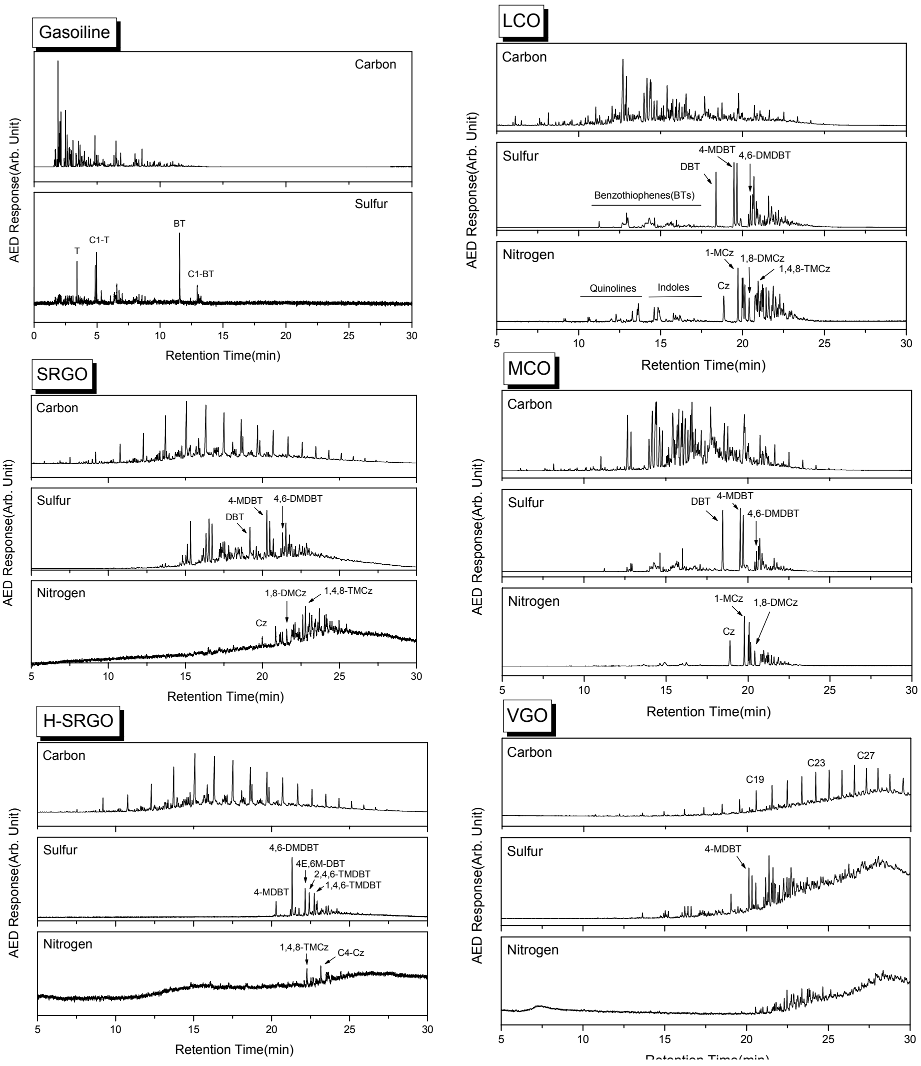


Figure 2. AED Chromatograms of Various Fuel Oils. LCO: light cycle oil, MCO: medium cycle oil, VGO(hexane soluble fraction):Vacuum Gas Oil, SRGO: straight run gas oil, H-SRGO: hydrotreated straight run gas oil. (Cn: Paraffin with n carbons, T: Thiophene, BT: Benzothiophenes, DBT:Dibenzothiophene, Cz: Carbazole, DM: Dimethyl, EM: Ethylmethyl, TM: Trimethyl.)

The molecular composition of heavier fractions such as atmospheric and vacuum residues are not fully solved at present, although high pressure liquid chromatography (HPLC), time-of-flight mass spectroscopy (TOF-MS) and their combinations have provided some clues to their molecular composition.[8,9] These heavier fractions are believed to be polymeric substances of aromatic unit structures that are basically similar to those found in the lighter fractions. It has been postulated that strong molecular associations of polymeric chains are present in the residual fractions.[10,11] Such intermolecular association is schematically illustrated in Fig. 3.[10] Thus, the major target of residue hydrotreating is to convert asphaltenes by liberating molecular association first and then breaking down to lower molecular weight molecular species. This kind of hydroprocess is very important and becomes even more important in the near future. However, the present review excludes this topic.

Light and medium cycle oils (MCO) in FCC products of the gas oil range are further hydroprocessed to yield high quality fuels. The problems originating from aromatic components in LCO and MCO have been clearly indicated in their deep HDS. Thermally cracked product can be characterized to have olefinic composition.

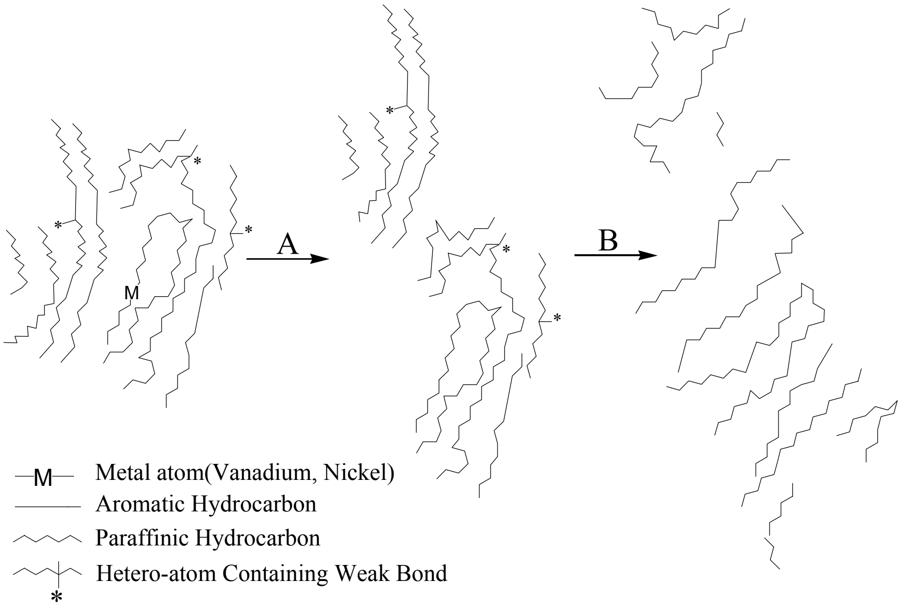


Figure 3. Model of Hydrocracking of Asphaltene. A: De-agglomeration of Asphaltene due to demetallation, B: Depolymerization due to desulfurization. * means heteroatom [10]

2. HYDROTREATING PROCESS

The primary objectives of hydrotreating are (a) to remove impurities, such as heteroatom and metal-containing compounds, from a feedstock, (b) to increase the hydrogen content of the feedstock, and (c) to lower molecular weight without a substantial loss in liquid product yield. The impurities of concern depend on the molecular weight of the feedstock being processed. Lower molecular weight feedstocks such as naphtha, gasoline, intermediate distillates (atmospheric and light vacuum), diesel fuels and home heating oils (kerosene etc.) have undesired impurities such as sulfur-containing compounds (S-compounds), nitrogen-containing compounds (N-compounds), oxygen-containing compounds (O-compounds), and polynuclear aromatic (PNA) compounds. Higher molecular weight feedstocks, such as high vacuum distillates, atmospheric and vacuum residues, have the same impurities as the above and in addition have significant concentrations of metal-containing compounds (M-compounds). V and Ni are the major metals in petroleum which are present in the form of porphyrin complexes of V^{4+}=O and Ni^{2+}.[10] The crude oils often contain NaCl, $MgCl_2$, $CaCl_2$, $CaSO_4$ and naphthenates of some metals such as Ca, Mg and Fe. The former metal compounds can be removed rather easily by washing before the distillation. However, small amounts of remaining metal compounds, particularly Fe or its derived FeS, often result in operational problems. Naphthenates may dissolve iron from valves or the reactor and transfer lines, which can be included in the feeds to downstream processes as described below.[12] In general, the concentration of these impurities increases with increasing boiling point. Thus, the hydrotreating process of choice depends primarily on the boiling range of the feedstock of concern. The boiling range is dictated by the molecular weight distribution of the feedstock. The next most important consideration in choosing a hydrotreating process is the product quality specification, which is predominantly related to the total hydrogen content of the product, which in turn is related to the content of PNA compounds.

O-compounds are generally not considered as major environmental hazards in petroleum products. Nevertheless, some O-impurity compounds such as phenols and naphthenic acids lead to corrosion problems in the reactors and storage vessels.[13] Some crudes which contain a large amount of naphthenic acids are classified as naphthenic crudes. Such naphthenic acids are extracted to be sold as lubricants. Iron dissolved by naphthenic acid in crude causes plugging by forming FeS in the catalyst bed or on the filter. Finely dispersed FeS may enhance coking reactions.[10] The O-compounds in the petroleum are much more reactive than other impurities and generally, hydrotreating is not developed specifically to remove O-compounds in the usual crudes. However, less reactive O-compounds such as phenols and benzofurans are found in significant amounts in coal derived oils. Hence their removal is one of the major concerns in the hydrotreating of coal derived oils.[15]

S-compounds, N-compounds and M (Metal) compounds have different reactivities and chemistry depending on the boiling ranges of fractions in which they are found. Thus, specific processes have been developed for the removal of each of these impurities. These are classified as hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrodemetallation (HDM) processes, respectively. These are in turn subdivided into processes, which are optimized for the boiling range of the particular feedstock being treated.

In general, the sulfur impurity is the major concern because S-compounds are often serious poisons and inhibitors for other secondary upgrading process catalysts. Their combustion products create serious environmental hazards such as acid rain. Thus, the main processes that have been developed for distillable feedstocks are HDS processes. N-compound impurities are also removed during HDS processes. When the successive acid-catalysis is important in conversion mechanisms, extensive N-removal is required since the basic N-compounds are both serious poisons and coke precursors on acid catalysts.[16] Lowering aromatic content through hydrotreating is classified as hydrodearomatization (HDA). HDA reactions occur during HDS and HDN processes, but product quality requirements often demand that an HDA process is conducted subsequent to an initial HDS and/or HDN process. Future environmental regulations may emphasize HDA further.[17]

M-compound impurities are found particularly in high boiling feedstocks, such as atmospheric and vacuum residues. Thus, HDM processes are tailored for high boiling and very viscous feedstocks.[18] Nevertheless, trace amounts of M compounds in the gas oil must not be overlooked since they cause the catalyst deactivation in long run.

3. BASES FOR HYDROTREATING

3.1 Hydrotreating Catalysts

Currently, catalysts for hydrotreating are alumina supported Mo and W based sulfides with promoters of Ni or Co sulfides. Alumina is believed to be the best and most balanced support in terms of surface area (200 - 300 m^2/g), pore size control, affinity to sulfide for high dispersion, mechanical strength and cost. Molybdenum precursor (15 - 20wt%) is first impregnated to be highly dispersed onto alumina and then the Co or Ni precursor (1 - 5wt%) is impregnated hopefully onto the Mo phase. The impregnated catalyst is carefully calcined and sulfided in the commercial application for the stable catalytic activity. The active species is believed to be the Co(Ni) MoS phase. Commercial catalysts also contain isolated Co(Ni)$_9$S$_8$, and Co(Ni)/Al$_2$O$_3$ which are not active. The Co(Ni)MoS phase consists of small layered crystals of S and Co/Mo as illustrated in Fig. 4.[19] The bottom of the CoMo layers, which contact the Al$_2$O$_3$ surface, is believed difficult to sulfide into the active form,[2] hence multi-layered stacks of these are believed to be more active on alumina supports. In order to disperse Mo and Co(Ni) to form more active crystallites, impregnation procedures have been developed which use P$_2$O$_5$ and chelating agents in commercial catalyst preparation as described below. The sulfiding medium and conditions have been extensively studied in order to achieve higher activity. The edge and rim of the Co(Ni)MoS phases are believed particularly active for hydrotreating reactions. However, active sites for hydrogenation and C-X fission are not fully solved.

Microscopic analyses have been used to understand the morphology of Co(Ni)MoS phase crystals on alumina. TEM and STM have shown that the crystal size of this phase in commercial catalysts is very small.[20]

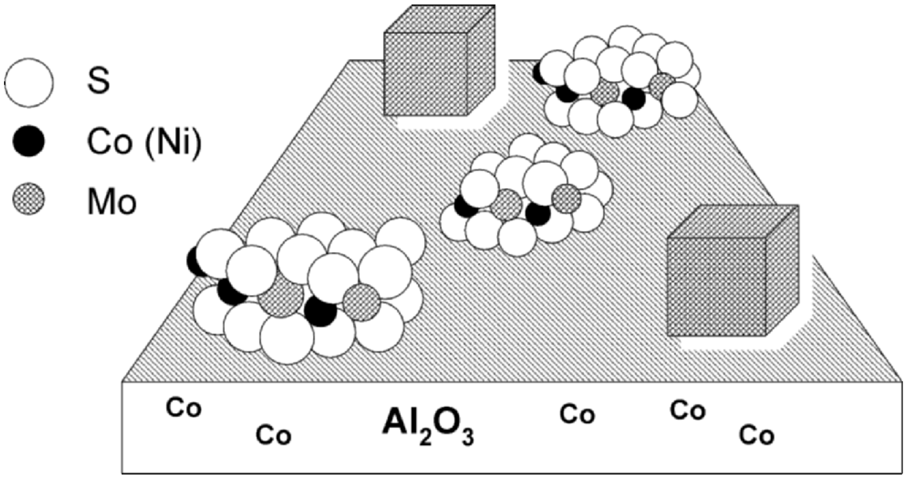


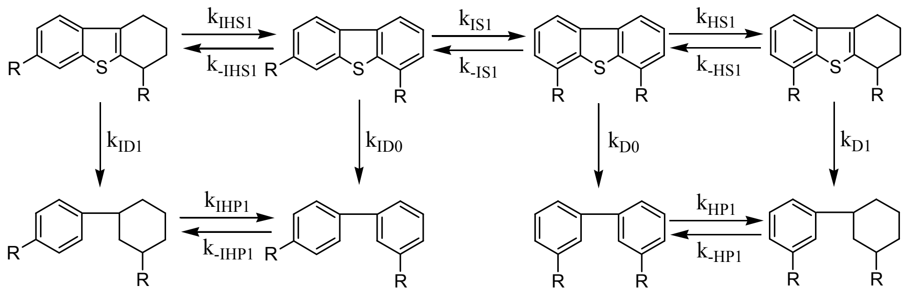
Figure 4. The Structure of CoMo Catalyst [2]

3.2 Chemistry of Hydrodesulfurization

The ease of removal of sulfur from a petroleum stream depends greatly on the structure of the sulfur compound being treated. The rates of sulfur removal can vary by several orders of magnitude. Generally, acyclic sulfur compounds such as thiols and disulfides are highly reactive and can be removed under very mild conditions. Saturated cyclic sulfur compounds and aromatic systems in which sulfur is present in six-membered rings are also highly reactive. However, compounds in which the sulfur atom is incorporated into a five-membered aromatic ring structure (such as thiophene), are much less reactive and the reactivity decreases as the ring structure becomes increasingly condensed (e.g. one ring > two rings > three rings).[2] For highly condensed ring structures (four or more rings), the reactivity trend reverses and reactivity tends to increase as the ring structure increases in size.[2] The reason for such behavior is that there are several different chemical pathways through which sulfur can be removed from a molecule and the preferred pathway changes for different sulfur compound structures.

An illustration of the various pathways is shown in Fig. 5 for dibenzothiophenes. In this scheme, there are two major pathways to desulfurized products. The first is called direct hydrodesulfurization, in which the sulfur atom is removed from the structure and replaced by hydrogen, without hydrogenation of any of the other carbon-carbon double bonds. The rate constant associated with this direct route is shown as k_{D0} in Fig. 5. The second route is called the hydrogenative route and assumes that at least one aromatic ring adjacent to the sulfur containing ring is hydrogenated before the sulfur atom is removed and replaced by hydrogen. The associated rate constants for hydrogenation and hydrodesulfurization routes are shown as k_{HS1} and k_{D1} in Fig. 5. In addition to hydrogenation of an aromatic ring before sulfur is removed, an aromatic ring may be hydrogenated after sulfur removal, and the associated rate constant for this reaction is shown as k_{HP1} in Fig. 5. This often leads to confusion in interpreting the results of experimental data as both routes can produce the cyclohexylbenzene final product.

It should also be noted that the hydrogenation pathways are subject to thermodynamic equilibrium constraints. Thus, the partially hydrogenated intermediates (such as tetrahydrodibenzothiophenes) have lower equilibrium concentrations at higher temperatures. This results in a maximum in the observed rates of HDS via the hydrogenative route, as a function of temperature. Thus, hydrodesulfurization via the hydrogenative route becomes limited at low pressures and high temperatures. Another route includes the isomerization and transmethylation of methyl groups at 4- or 6-position, which reduces the steric hindrance as in Fig. 5. The direct pathway is believed to involve the insertion of a metal atom on the surface of the catalyst into a sulfur-carbon bond in the sulfur-containing compound as shown in Fig. 6.[2] This insertion can occur even for fully aromatic sulfur compounds, such as thiophene, benzothiophene and dibenzothiophene. Such a pathway is possible because the resultant metal-sulfur bond is energetically favorable. After the insertion, several other steps occur in which the sulfur is expelled as hydrogen sulfide and the catalyst is restored to its original state.



Where R=H, CH_3 or Other

Figure 5. Reaction Pathways for Desulfurization of Dibenzothiophenes.

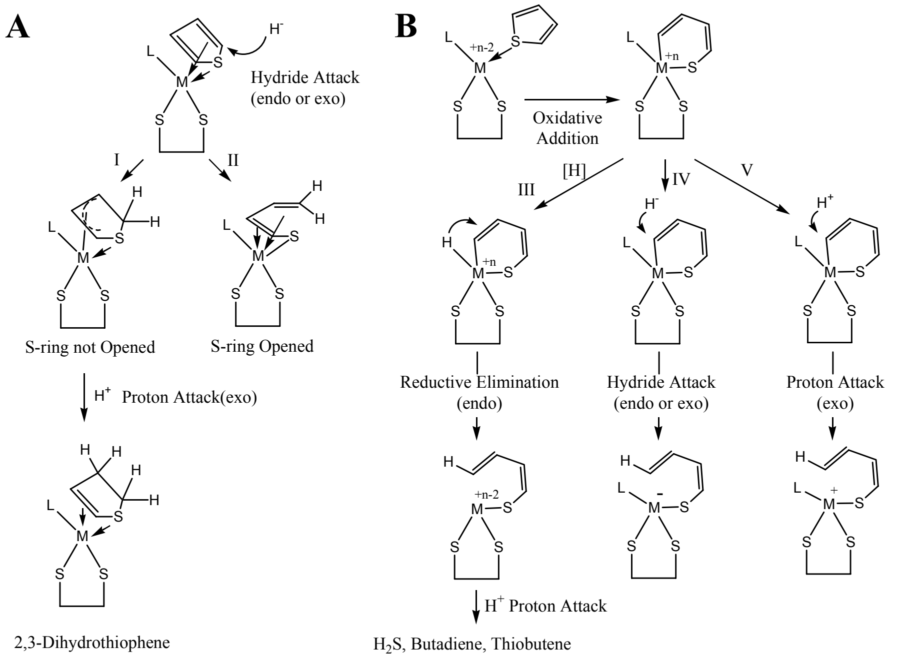


Figure 6. Possible Routes to Hydrogenation and Ring-opening Reactions [2]

The hydrogenative pathway involves the initial hydrogenation of one or more of the carbon-carbon double bonds adjacent to the sulfur atom in the aromatic system. Hydrogenation destabilizes the aromatic ring system, weakens the sulfur-carbon bond and provides a less sterically hindered environment for the sulfur atom. Metal insertion is thus more facile.

There are two active sites (functions) postulated on HDS catalysts based on the above discussion, S-extrusion and hydrogenation. Fig. 7 illustrates the schemes of both reactions including details of the active sites. The active center is a coordinatively unsaturated metal site where the S ligand is facile. Sulfur in aromatic rings can coordinate to the active center of both functions. It is believed that the initial adsorption of the S-compound is through σ-bonding, in the case of direct S-extrusion. However, in the hydrogenative function, S-compound coordination is through π-bonding. Neighboring S-H groups are believed to be involved in hydrogen transfer for both S extraction and hydrogenation. Differences in the active sites for S extraction and ring hydrogenation are not yet clear although they appear to be interconvertible. H_2S, NH_3 and nitrogen containing compounds can also coordinate to the active center, inhibiting the S-extraction and hydrogenation as discussed later.

The direct pathway becomes more difficult as the ring structure becomes larger because the aromatic structures become increasingly more stable and because the insertion becomes more hindered for the more condensed rings. To illustrate these factors, Fig. 8 provides examples of hydrodesulfurization reactivities of sulfur compounds having different ring structures.[21,22] For ease of discussion, all of the rate constants in this and following illustrations have been normalized relative to dibenzothiophene having a value of 100.

In Fig. 8 it can be seen that the overall hydrodesulfurization reactivity of the sulfur compounds decreases with increasing ring condensation from one ring to two rings to three rings, but then reverses for the four ring system. This is due to a switch in the preferred pathway from the direct route to the hydrogenative route. As mentioned above, increasing ring condensation is detrimental to the insertion step in the direct route, while with increasing ring condensation, hydrogenation becomes more facile.

Another complicating factor in reactivity is the proximity of alkyl groups to the sulfur atom in aromatic ring structures. Generally, as the sulfur atom becomes more crowded by adjacent alkyl groups the reactivity decreases. This has been attributed to steric crowding of the sulfur during adsorption on the catalyst surface or during some transition state. This steric crowding affects the direct hydrodesulfurization route most severely. Fig. 9 illustrates this factor for several alkyl-substituted benzothiophenes and dibenzothiophenes. In Fig. 9 it can be seen that the reactivity for hydrodesulfurization decreases as the number of substituents around the sulfur atom increases.[23] Alkyl groups that are not close to the sulfur atom have little effect. Recently, migration of alkyl groups before the hydrodesulfurization was proved to enhance the direct hydrodesulfurization on the catalyst of strong acidity as illustrated in Fig. 5.

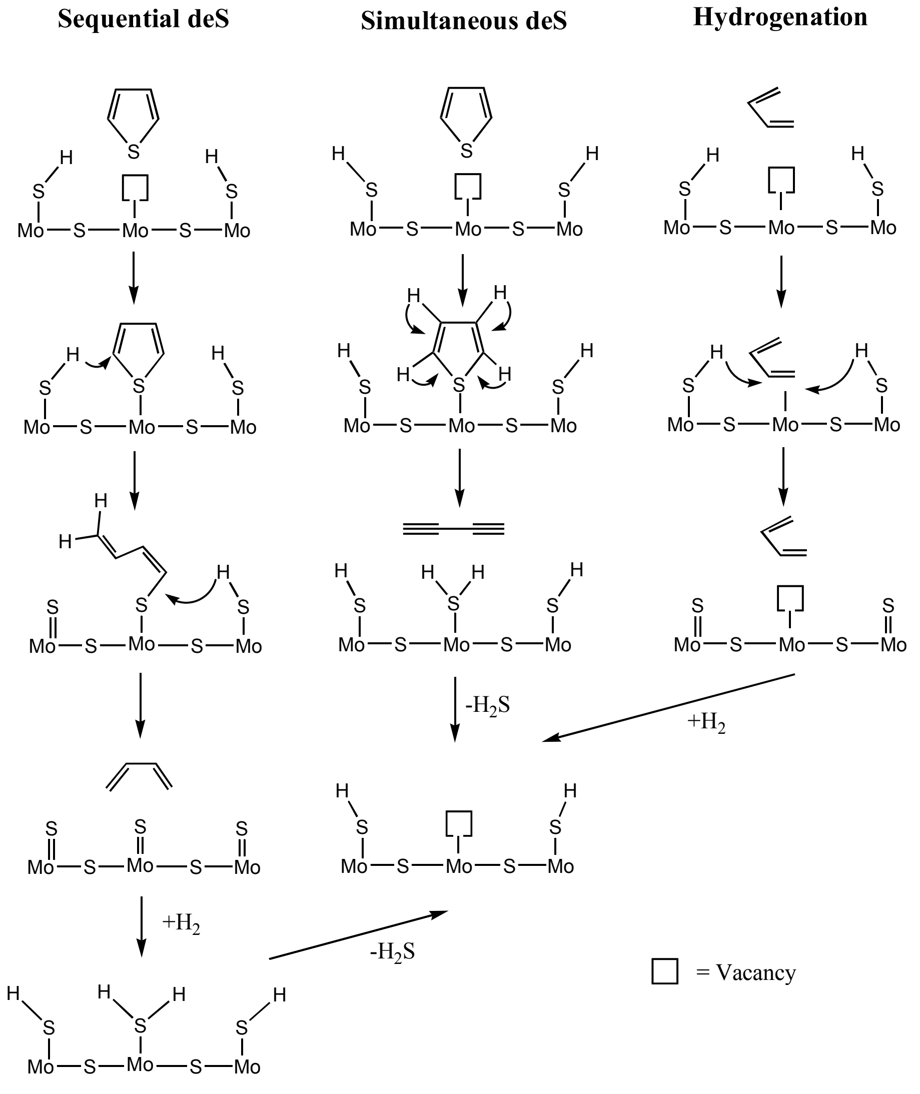


Figure 7. Vacancy Model of the HDS Mechanism [2]

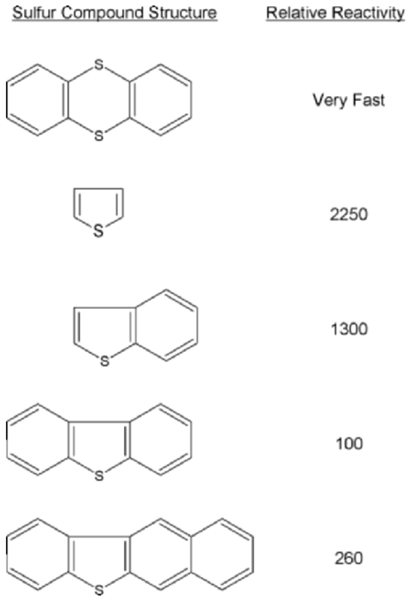


Figure 8. Desulfurization Reactivities of Compounds Having Different Ring Structures [21,22]

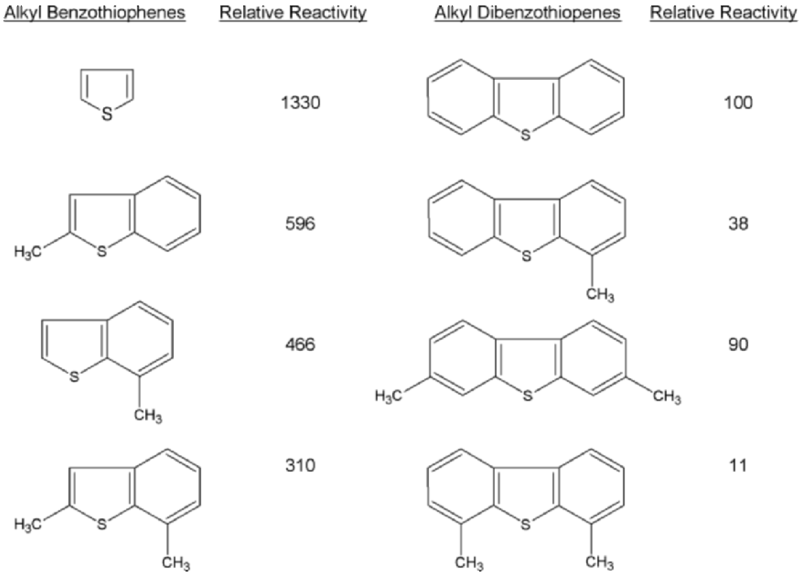


Figure 9. Desulfurization Reactivities of Alkyl-substituted Aromatic Sulfur Compounds [23]

It has been shown that the hydrogenative routes are not significantly affected by alkyl-substitution on the aromatic rings, while the direct route becomes lower when alkyl groups are adjacent to the sulfur atom. Thus, the relative rate changes shown in Fig. 9 are primarily due to loss in the ability for hydrodesulfurization to proceed via the direct route. For this reason, the catalyst, which is preferred for hydrodesulfurization, is often different for light and heavy feedstocks, as the numbers of alkyl groups and of condensed aromatic rings in the sulfur containing compounds increases with their boiling points.

4. DEEP HYDRODESULFURIZATION OF GASOLINE

Current regulations on the accepted sulfur levels in gasoline and diesel are becoming increasingly stringent in order to protect the environment from the exhaust gases of motor vehicles. Several different streams are blended to produce commercial gasoline in a refinery.[24] These include straight run gasoline, reformate, alkylate, crude FCC gasoline, RFCC gasoline, gasoline from HDS and hydrocracking of vacuum gas oil and residue. Reformate and alkylate are sulfur free. However, the other streams contain various amounts of S-compounds. Currently sulfur levels of such gasolines are separately controlled before blending.

Recent regulation forces deeper hydrodesulfurization. While HDS of FCC gasoline is rather difficult without hydrogenation of olefin and aromatic components, which are major sources for high octane number, sulfur species in gasoline are reactive forms of thiols, thiophenes and benzothiophenes, which are readily desulfurized. Selective HDS without olefin hydrogenation is being extensively explored at present.[25]

Such a selective hydrodesulfurization must clarify the active sites of CoMo and NiMo sulfides supported on alumina for hydrodesulfurization and hydrogenation. CoMo is certainly more selective for hydrodesulfurization with limited hydrogenation activity than NiMo. Hence, cobalt is applied for the present purpose. Coordinatively unsaturated Co sulfide on MoS_2 is often postulated as the active site for both reactions (see Fig.7). The metal with unsaturated valence is proposed as the hydrogenative site in cooperation with a Mo-S-H group while the metal with the unsaturated valences must be the hydrodesulfurization site. H_2S concentration in HDS can be reduced to enhance the hydrodesulfurization selectivity.

Several patents are issued for selective HDS of FCC gasoline by poisoning the hydrogenation site more than the hydrodesulfurization one over CoMoS/alumina.[25] Amines, alkali metal ions, and carbon deposition have been proposed in the patents to increase the selectivity for hydrogenation, although the hydrodesulfurization itself is also poisoned by reacting with CoMoS. The mechanism for selective poisoning is not clarified, but alumina support appears to principally be poisoned. Acidic natures of the support may be responsible for the hydrogenation activity as described with hydrogenative HDS of refractory sulfur species in diesel fuel.[26] Separated HDS of fractions in FCC gasoline was also proposed to fractionate olefins and aromatic sulfur species in the respective fractions.[3] More kinds of catalyst supports are worthwhile for detail examination.

Although FCC feed can be extensively desulfurized to produce FCC gasoline with lower sulfur content, the deep desulfurization of FCC gasoline is required. Vacuum gas oil feeds provide gases, gasoline, light cycle oil (LCO), heavy cycle oil (HCO), decant oil, and coke on the catalyst.[27] RFCC (Resid FCC) gives the same products, except it yields cracked residue instead of decant oil. Sulfur is produced from paraffins and aromatics. Other types of compounds may not yield gasoline, but they still can produce hydrogen sulfide, which influences product sulfur content. The opening of aromatic rings hardly occurs in the FCC process even though hydrogen-transfer reactions take place.

The strong acidity of zeolites is sometimes postulated to desulfurize through hydrogen transfer, however, its contribution must not be exaggerated. Thus, sulfur balances in FCC process are being carefully described to discover the origins of S-compounds in FCC products.[28]

Recombination of H_2S with olefins can not be neglected, even at sulfur levels below 30 ppm in FCC process.[29] Thiols may cyclize and dehydrogenate into thiophenes, which are the major sulfur species in very low sulfur level gasolines. A substantial amount of sulfur ends up in coke on FCC catalysts. Such sulfur is combusted into SO_2 in the regeneration stage. RFCC catalysts have been sophisticatedly designed as shown in Fig. 10.[79] A special additive can be added to prevent the crystal structure of zeolite from being destroyed by impurity metals. In Fig. 10, CMT-40 functions as metal trap. The next generation FCC promises to be a very sophisticated composite catalyst that carries out specified functions particular locations in the catalyst particles. Increasing SO_2 at the stack can be handled by dry desulfurization over active carbon fibers.[30]

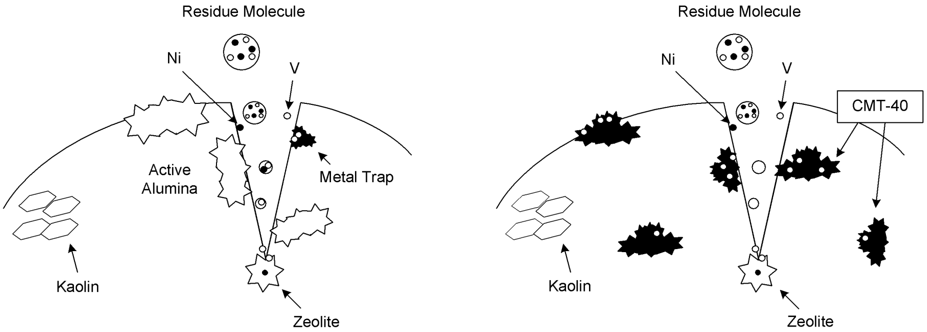


Figure 10. New Design Concept of RFCC Catalyst [79]

5. DEEP HYDRODESULFURIZATION OF DIESEL

Deep HDS of diesel fuel is currently a very important topic in refining. Basically, deep hydrodesulfurization of diesel involves the extensive elimination of refractory sulfur species such as 4-MDBT, 4,6-DMDBT, and 4,6,X-TMDBTs. Such deep hydrodesulfurization is difficult because of the lower reactivities of these compounds and strong inhibition by coexisting species such as H_2S, NH_3, nitrogen species and even aromatic species, especially when the sulfur level must be lowered to <300 ppm. H_2S and NH_3 are produced from the reactive sulfur and nitrogen species contained in the same feed.

There are four approaches for improving reactivity.

1. Introduction of more active sites by impregnating more active metals on the catalyst.
2. Removal or reduction of inhibitors in the process during or before HDS.
3. Novel catalyst designs to introduce new mechanistic pathways that are less subjective to inhibition.
4. A series of catalysts in two successive layers to remove reactive sulfur species and in the first layer, and to remove remaining refractory sulfur species to less than 10 ppm under the presence of H_2S, NH_3 and other remaining inhibitors, such as nitrogen species and aromatic compounds, in the other layer.

Currently the first method is the major commercial approach. The second approach has been proposed as a two-stage HDS process. Fig. 11 shows the efficiency of two-stage HDS, in which the produced H_2S and NH_3 in the first stage are eliminated before the second stage.[7]

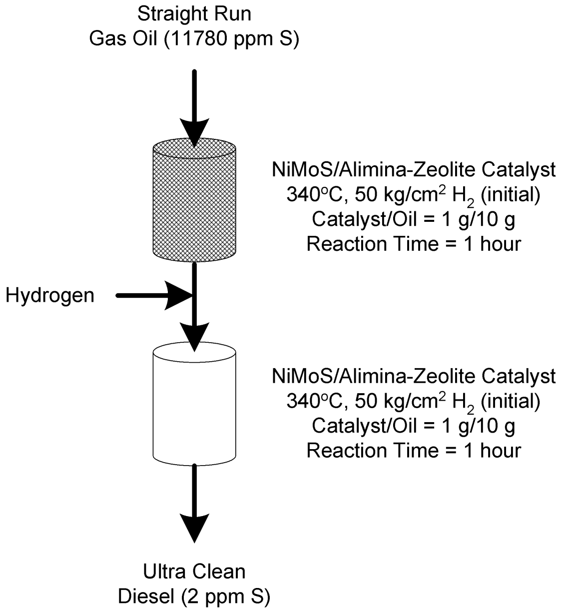


Figure 11. Schematic Diagram and Performance of Two-Stage Reaction Concept [7]

Another type of two stage HDS is to remove nitrogen species prior to HDS with silica-gel, silica-alumina or active carbon. The present authors suggest the high efficiency of active carbon for nitrogen species removal.[31] Some refractory sulfur species are also removed by the active carbon, which significantly helps deep hydrodesulfurization. Post removal of sulfur species after hydrodesulfurization can also be used to lower the total sulfur content below 10 ppm. However, the capacity for sulfur removal is rather limited, compared to the removal of nitrogen species. Hence the application of this approach is restricted to preparation of the ultra clean hydrodesulfurization for fuel cells.

The third approach has high potential and is being investigated extensively. The use of acidic supports appears to enhance catalyst activity by enhancing hydrogenation, methyl group migration, and by lowering H_2S inhibition. However, coking and NH_3 inhibition also must be overcome. TiO_2 and carbon are interesting supports for producing higher activity catalysts. High surface area TiO_2 is now available, due to a novel development. Deeper sulfiding is one of the proposed reasons for its higher activity. Strong interaction between active oxides and the support is designed for better dispersion of active species, but may hinder sulfiding. Reactive sulfide is recommended for sulfidation. Strong interaction between active sulfide and support must be explored. Carbon inclusion at the active species during the

the sulfiding stage is claimed to give higher HDS activity. Some metals are reported to give high HDS activity. Precise evaluation is still necessary by comparing the activity of catalysts currently lined up.

Highly aromatic feeds such as LCO and MCO appear now to require more severe conditions for their deep HDS because aromatic species exert strong inhibition on refractory sulfur species, especially at their very low concentrations. Catalytic species having higher affinity for sulfur than for olefins and aromatic hydrocarbons are currently targets of extensive research for achieving deep HDS of aromatic diesel. A sulfur atom can be an anchor to be ported to the soft acid site of the catalyst for the preferential hydrogenation of neighboring aromatic rings. Process design has been proved very effective for such feeds to separate the major aromatics from the refractory sulfur species fraction.

6. HDN, HDO AND HDM REACTIONS

Removal of nitrogen, oxygen and metal is also important to purify petroleum products. Such reactions progress concurrently together with HDS. Activated hydrogen can break C-X bonds over the same catalyst, although the affinity to the active site, the necessity of hydrogenation in the ring structure, and C-X bond reactivity are very different according to their own mechanisms.

HDM, HDS, HDN and HDO (hydrodeoxygenation) are generally recognized in the order of easiness, although the HDS and HDN of refractory sulfur and nitrogen species are comparable at deep levels of removal. HDN of the last non-basic carbazoles is completed before HDS reaches to the 10 ppm level. Basic nitrogen species occupy the active sites before sulfur compounds. HDN of aromatic nitrogen species is generally believed to proceed through the complete hydrogenation of aromatic rings because the aromatic C – N< bond is too strong to be fissioned by hydrogenolysis. In contrast, the aliphatic C – N< bond is easily broken. Thus, NiMoS and NiWS catalysts are often applied for HDN. Large hydrogen consumption is inevitable. An acidic support helps HDN on NiMoS by accelerating hydrogenation, although it also enhances the chance of deactivation due to coking. There is a competition between hydrogenation and acidic reactions on the same catalysts.

Recently, the C – N< bond was proposed to be associated with H_2S in the formation of C – SH and NH_3. The C – SH bond is easily eliminated under hydrotreating conditions. Prins et al.[32,33] reported that 2-methylcyclohexylamine (MCHA) is hydrodenitrogenated through three ways: (a) direct elimination of ammonia, (b) nucleophilic removal of the NH_2 group by H_2S followed by removal of the -SH group, and (c) direct hydrogenolysis of the C-N bond. They estimated the contribution of each pathway as shown in Fig. 12.[33] Such contribution of nucleophilic substitution was dependent on H_2S partial pressure. However, it is not clear that such a mechanism is relevant to the HDN of refractory nitrogen species, such as carbazole, because H_2S is a strong inhibitor for the HDN of such inert nitrogen species. The natures of the catalysts are also important since a variety of catalysts are now available.

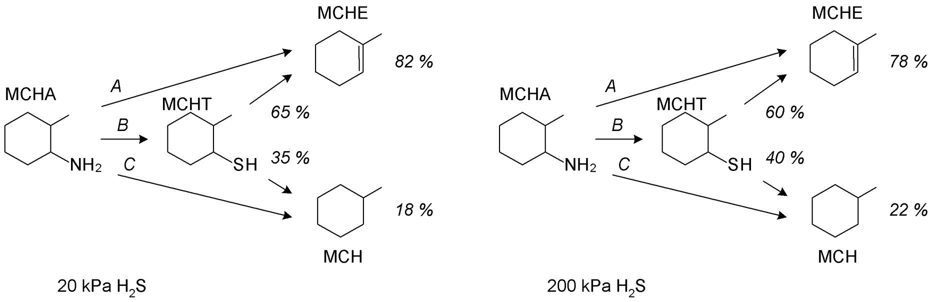


Figure 12. Selectivities for elimination (A), nucleophilic substitution (B), and hydrogenolysis (C) in the HDN of 2-methylcyclohexylamine (MCHA), and the observed selectivities of methylcyclohexene (MCHE) and methylcyclohexane (MCH) in the HDN of 2- ethylcyclohexylamine and in the HDS of 2-methylcyclohexanethiol (MCHT) in the presence of 20 kPa (left-hand side) and 200 kPa (righthand side) H_2S[33]

The involvement of aromatic C – N<, especially derivatives from carbazoles, is not definite yet. Such a mechanism would be desired to reduce hydrogen consumption. HDO is not an important reaction for petroleum products, but it is very important in stabilizing coal-derived liquids. HDO of dibenzofuran is very slow. An acidic support is helpful for the HDO of dibenzofuran species.

HDM is a key for the hydrotreatment of heavy oil because it removes asphaltenes and affects the capacity of downstream catalysts to hold eliminated metal sulfides.[18] Liberation of asphaltene aggregation as well as the pore-mouth size and pore volume are important criteria for the design of catalysts to enhance HDM of heavy feeds.

7. INHIBITION OF HDS

The active sites postulated for HDS catalysts promote sulfur extraction, hydrogenation and acid catalyzed reactions. Such active sites are all commonly or selectively subject to occupancy by the inhibitors. As mentioned above, several species in the feed and product are inhibitors for HDS. Reactive sulfur species appear to be less inhibited than the refractory species. This is because the S atom in the reactive species can easily undergo metal insertion to break the C-S bond via the direct HDS route. They are also the major S-compounds present and can compete effectively with inhibitors for the active sites on catalysts. By contrast, when proceeding by way of the direct HDS route, the sulfur atom in refractory sulfur species may be sterically hindered. Hence, their desulfurization must be performed after hydrogenation. Inhibition for their hydrogenation must be concerned. Also, their concentrations become very low while H_2S and NH_3 inhibitors increase their concentration during the initial stage of the HDS process. These inhibitors are in high concentration where the refractory species of very low content must be desulfurized. It must be recognized that the initial and last stages of the HDS of refractory species are very different in their rate. Some processes have been developed which remove H_2S and NH_3 between stages to minimize this problem as described above.

Other feed impurities, such as N-compounds, are severe inhibitors for the hydrogenative HDS route. They are strong π-bonding species and they hinder the interaction of the refractory S-compounds with the active hydrogenation site. The overall HDS process has been shown to be much more facile when the N-compound inhibitors are removed prior to hydrotreating. In addition, nitrogen species are removed during HDS, reducing their concentration through concurrent HDN.

Aromatic species are also inhibitors for HDS of refractory sulfur species as described above, because refractory sulfur species are desulfrized through the hydrogenation route. Aromatic species can be highly concentrated and can inhibit the last stages of HDS. Overcoming this difficulty is not easy.

8. DEACTIVATION AND REGENERATION OF HYDROTREATING CATALYSTS

Hydrotreating catalysts lose their activity in several ways:[34]

(1) Sintering of the active phase into large crystal units;
(2) Degradation of the active phase, including degradation of sulfided forms;
(3) Covering of the active sites by reactants and/or products including coke;

(4) Deposition of inactive metal sulfides (such as V and Ni sulfides);
(5) Deposition of other impurities such as salt and silica.

The deactivation usually occurs in three steps: initial rapid deactivation, intermediate slow but steady deactivation and rapid deactivation at the end of the cycle. Commercial processes are operated at constant conversion. This constant conversion is achieved by gradually heating the reactor to higher temperatures to compensate for the slow but steady catalyst deactivation.

The initial rapid deactivation phase is believed to be due to rapid coking on active sites having very high acidity.[34] Deposited carbon can be characterized by temperature programmed combustion and Raman spectroscopy.[35] The slow but steady deactivation is associated with metal deposition, sintering and/or coking during the course of the process cycle. Higher reaction temperatures utilized at the end of the process cycle may cause rapid deactivation at the final stage.

Currently, acidic supports are utilized to achieve high activity, hence coking deactivation appears important in current processes. Such deactivation schemes suggest that catalysts may be regenerable if suitable methods can be developed. Removal of strongly adsorbed heavier organic materials or coke precursor and coke could possibly be achieved by thermal extraction and/or combustion. However, during regeneration of the catalyst, the active sulfide form must be maintained or it must subsequently be regenerated.

More important to the design of the catalyst is to improve the hydrogenation activity in the vicinity of acidic sites. This could hydrogenate hydrogenate the coke precursors by cracking them or making them soluble in the matrix.

9. PROCESS FLOW OF HYDROTREATING

A typical hydrotreating flow diagram is shown in Fig. 13, where single stage hydrotreating is illustrated. The feed oil is pumped up to the required pressure and mixed with make-up and recycle hydrogen-rich gas. The temperature is initially raised by heat exchange with the reactor effluent then further increased by a furnace to achieve the required temperature. The feed oil is hydroprocessed over the catalyst in the reactor under a flow of pressurized hydrogen-rich gas. The figure shows one reactor, but the numbers of reactors may be increased even in single stage processes, depending upon the conditions or throughput rate.

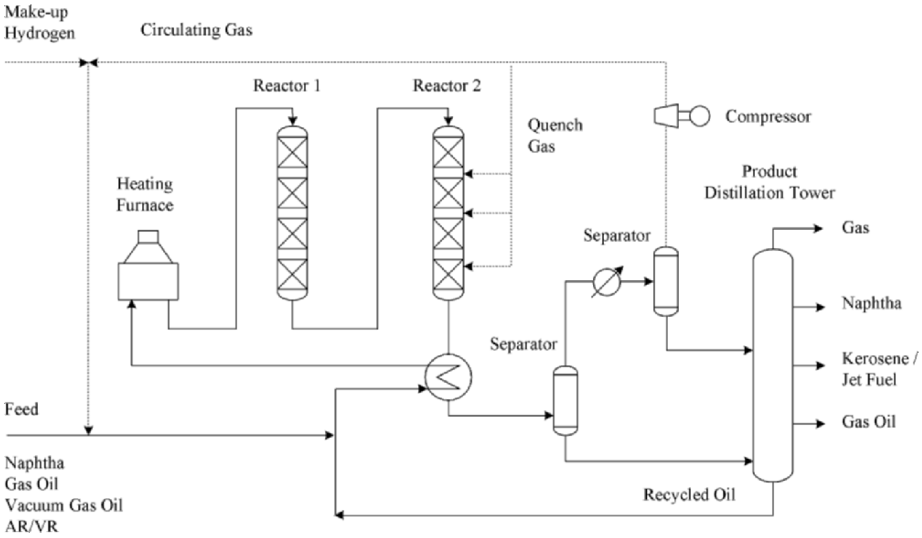


Figure 13. Singe-Stage Process Flow Diagram

In general, a fixed bed reactor is employed for hydrotreating process. However, a series of catalysts having different functions are generally packed sequentially in the reactor(s). Thus, optimum catalysts are packed in each bed according to the requirements of the bed. The feed oil and hydrogen rich gas are normally supplied from the top of the reactor. Quenching hydrogen gas is commonly injected at several points along the reactor to control the reaction temperature, because hydrotreating reactions are always exothermic. The reactor effluent is then cooled down by feed to the reactor in the heat exchanger. This recovers some of the exothermic heat of the reaction and improves the thermal efficiency of the overall process. Following heat exchange, the gas and liquid products are separated by a high temperature, high-pressure vessel followed by a low temperature, high-pressure vessel. Liquid products are further fractionated into the required products in the fractionating column according to their boiling points. The gaseous products from the high-pressure vessel are fed to an absorbing column to remove hydrogen sulfide, and the cleaned hydrogen-rich gas is recycled to the reactor after repressurizing with a recycle compressor.

There are two types of processes. One is called a single stage process, while another is termed a two or multiple stage process. The single stage process has the same process flow as mentioned above. The feed is hydroprocessed consecutively without obvious separation in between the reactors. However, a single stage process does not mean that only one reactor is employed, only that no separations are done until the final conversion is achieved.

In a two-stage process, the unwanted products of the first stage are separated and eliminated before the second stage. Thus, the unwanted secondary reactions of the product, poisons and inhibitors produced in the first stage are eliminated before beginning the second stage of the conversion.[7,36,37] This reduces the load on the second stage and enhances its reactivity. With staged processes, very high conversions, so called deep refining, are easily achieved.

The present authors proposed a new type of reactor as shown in Fig. 14, where fractions of a gas oil were reacted separately in upper and lower parts of the catalyst bed.[37] Hydrogen was charged from the bottom of the reactor. H_2S inhibition on the heavier fraction can be avoided. The optimum catalysts can be applied for the respective parts of the bed. Pressure drop is a possible worry at the lower part of the reactor, where the hydrogen is up flow while liquid feed is down flow. A honeycomb type catalyst bed is now available for this problem.

By lowering the end point of the starting diesel fuel, hydrotreating the lower end point diesel fuel feed to ultra low sulfur levels is much easier. For example, when the 90% distillation point (T90) of diesel fuel is lowered by 20 ^{o}C, the required reactor size is only about half that needed for the full range feed.[38] This diesel with lower T90 has another merit. It will produce less particulate matter in diesel exhaust gas. The downside of this approach would be the requirement for increasing the cracking capacity of the refinery to produce the required volume of diesel fuel with this T90. One solution is to revamp a VGO hydrotreater to mild hydrocracking service.

The color of finished diesel oil is a stringent requirement in some countries. Presently, hydrodesulfurization of faintly yellow diesel oil feedstocks produces colorless and transparent products at 500 ppm S. However, when severe conditions are used for deep HDS, the diesel oil becomes, a fluorescent yellowish green product. High hydrogen pressures suppress color formation, while a high reaction temperature conversely retards hydrogenation and enhances color formation.[39]

Finally, we must emphasize the advantage of fractionated HDS for LCO.[40] We may be able to avoid the real difficulty for HDS of refractory sulfur species in the presence of aromatic inhibitions.

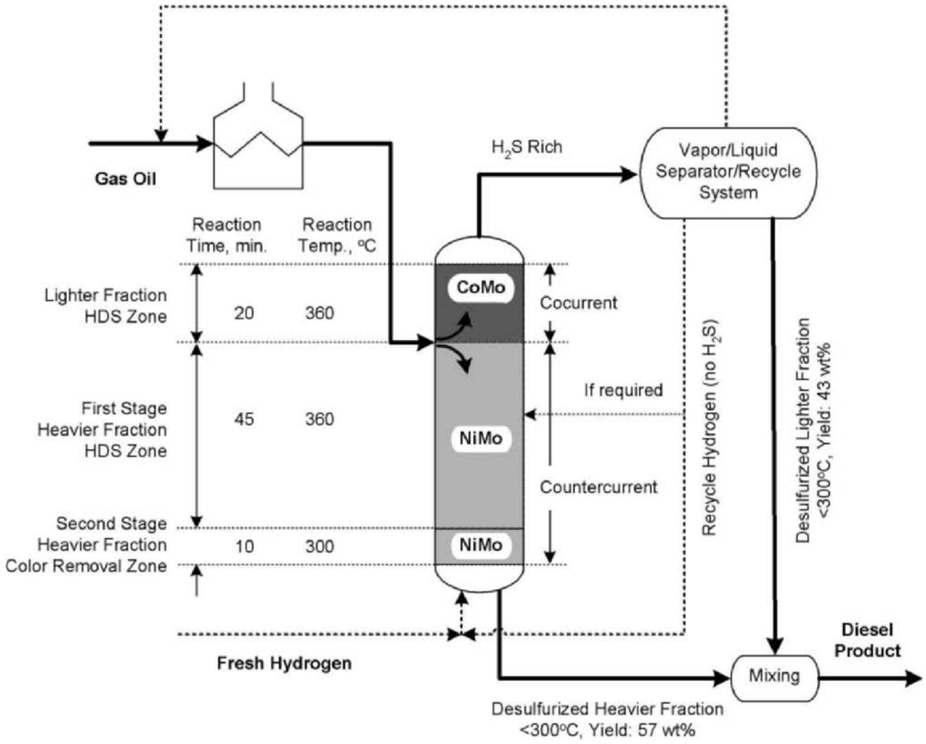


Figure 14. Reactor Design for Deep HDS [37]

10. TWO SUCCESSIVE LAYERS IN CATALYST BEDS[7]

Fig. 2 illustrates the sulfur distribution of a current 300 ppm diesel fuel (HSRGO). Comparison of its sulfur distribution to that of the straight run gas oil (SRGO) revealed that 100% of reactive sulfur species and 80% of refractory sulfur species are removed to obtain 300 ppm by current HDS units. The nitrogen species in the 300 ppm diesel are also illustrated in the same figure, showing carbazole of 50 ppm.

We can achieve sulfur levels less than 15 ppm when we can desulfurize remaining refractory sulfur species in the presence of inhibiting products such as H_2S and NH_3.[7] Table 1 summarizes the activity of some catalysts under such conditions. NiMo on acidic supports achieved a sulfur level less than 15 ppm. Acidic supports of proper strength overcome the inhibitions by H_2S and NH_3. The sulfur level of 300 ppm can be achieved with a space velocity larger than 3 over CoMo catalysts on acidic supports. Hence, in combination the two catalysts in the layers can achieve deep hydrodesulfurization with a overall space velocity larger than 1. It must be noted that the catalysts of the two layers are not always same. Optimum catalysts must be selected. The catalysts in the first layer and second layer are designed by selecting active species and supports. The activity of the catalyst for reactive and refractory sulfur species, and its resistance to inhibitors at the respective concentration levels of sulfur species must be taken into account. The activity for the reactive species reflects direct desulfurization access to rather small molecules. Larger surface area for a CoMoS catalyst, even if the pore size is rather small, is advised. Furthermore, denitrogenation in the first layer must be also considered since remaining nitrogen strongly influences the hydrodesulfurization of remaining refractory sulfur species. Examination of this reactor scheme is now under evaluation.

Table 1. Remaining Sulfur and Nitrogen Content (ppmS, ppmN) over Catalysts after 1 hour reaction at 340ºC. (Catalyst/Oil=1g/10g, H_2=50 kg/cm^2 (initial charging pressure), H_2S=1.66 vol% in H_2, NH_3=200 ppmN).

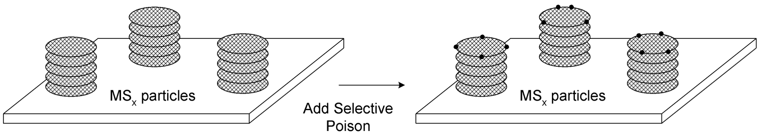
Name	SRGO (ppmS)	SRGO (ppmN)	HSRGO in the Absence of H_2S and NH_3 (ppmS)	HSRGO in the Presence of H_2S and NH_3 (ppmS)
CoMo-A	1,118	81.0	22.5	36.7
NiMo-A	2,229	12.2	2.1	5.9
CoMo-SA	576	41.6	7.1	36.4
NiMo-SA	477	19.6	4.4	32.7
CoMo-AZ	323	17.1	5.3	17.8
NiMo-AZ	242	5.4	3.6	15.5

* A:Alumina support, SA: silica-alumina support, AZ:alumina-zeolite support

11. PROCESS AND CATALYST DEVELOPMENT FOR DEEP AND SELECTIVE HDS OF FCC GASOLINE

As described above, catalytic deep hydrodesulfurization of FCC gasoline must make ultra low sulfur gasoline while maintaining octane number. Hence, novel catalytic and non-catalytic processes have been proposed and evaluated.

First of all, selective HDS of cracked gasoline by novel catalysts has been developed by ExxonMobil and IFP, named as SCANfining [41,42] and Prime G+[3], respectively. In the SCANfining process, RT-225 catalyst, jointly developed by Albemarle and ExxonMobil Research and Engineering Co., is used. The catalyst is known to be based on CoMo catalyst of low metals content and high dispersion to avoid hydrogenation of olefins while maintaining HDS activity. In order to block the hydrogenation active site, which is believed to lie on rim sites of sulfide crystals, a selective poison is added[41-43] as shown in Fig. 15. Over 20 refineries have selected SCANfining as their major clean gasoline production process.



$$\text{Olefin} + H_2 \xrightarrow{\text{Rim Sites}} \text{Alkane (lower octane)}$$

$$\text{R-S-R'} + H_2 \xrightarrow{\text{Rim and Edge Sites}} \text{RH} + H_2S$$

Figure 15. Schematic Diagram for Selective HDS catalyst for Gasoline [41]

Prime G+ process uses two reactors. In the first reactor, selective hydrogenation of diolefins and conversion of mercaptans occurs, as shown in Fig. 16.[44] FRCN means full range catalytic naphtha. The bottom stream from the splitter, which separates Light Catalytic Naphtha (LCN) and Heavy Catalytic Naphtha (HCN) after the first reactor, is desulfurized by a novel catalyst. The Prime G+ process is reported to be operating at more than 50 refineries. Fractionation is a practical approach to separate competing components to be treated separately over the best catalysts.

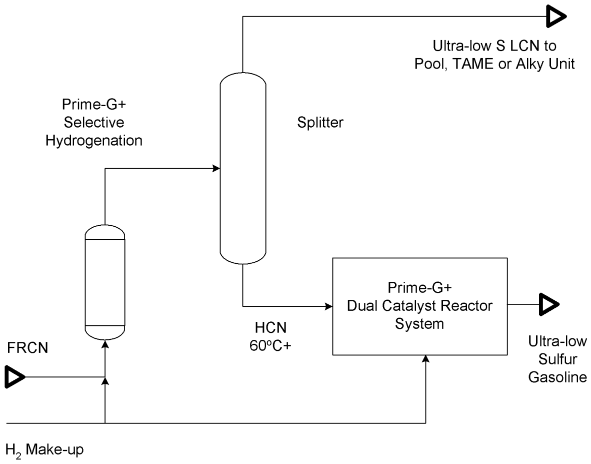


Figure 16. Process Diagram of Prime G+ [44]

Like the Prime G+ process concept, CDTech proposed the catalytic distillation process, in which olefin and sulfur-rich streams are separated. Those are called CDHydro and CDHDS. The C_5+ gasoline fraction from the FCC is fed into the CDHydro reactor, in which fractionation into light cut naphtha (LCN) and middle/heavy cut naphtha (MCN/HCN) occurs simultaneously with the combination reaction between mercaptans and diolefins. MCN/HCN from the bottom of CDHydro is fed into the CDHDS unit. The CDHDS unit is packed with two catalyst layers. The upper and lower catalyst layers desulfurize MCN and HCN, respectively. Because olefins are concentrated in the upper part of the CDHDS unit, selective HDS of rather heavy sulfur species can be performed in its lower part without saturation of olefins.

Table 2 shows the comparison of various technologies for low sulfur gasoline.[45]

Table 2. Comparison of FCC Gasoline Desulfurization Technology[44]

	OCTGain 125	OCTGain 220	SCAN Fining	Prime G+	CDTech	S Zorb
Processing capacity (BBL/day)	1500	31,000	25,000	24,000	30,000	25,000
Investment (million $)	14.9	23.8	16.8	21.7	18.5	13.8
Hydrogen consumption (M3/kL)	66	23	14	22	18	12
Power Consumption (KWH/kL)	12.6	9.4	3.8	8.2	2.8	4.4
Steam Use (kG/kL)	214	128	180	70	13	
Home-use Fuel (L/kL)	13.6	5.8	2.4	1.5	5.3	6.3
Catalyst Cost ($/BBL)	0.43	0.22	0.22	0.01	0.25	0.27
Cooling Water (Ton/kL)	6	5.4	3.2	3.1	1.3	3.1
Yield Loss (%)	5	0.7	0	0.8	0	0
Octane Loss	0	0.1	1	1.3	1	0.75

Zeolite-based adsorbents for gasoline desulfurization were proposed by R. T. Yang.[46] He used Cu or Ag-exchanged Y-type zeolite in purifying gasoline and diesel. The capacity of such an adsorbent was reported to be 14.7 cc/1g. Regeneration was not intensively discussed, although such π-complexation may require rather severe regeneration conditions.

There is still a sacrifice of octane number due to olefin saturation, which can be made-up by isomerization and alkylation of saturated olefins. The OCTGain process developed by ExxonMobil lies in this category. In such a process, olefins are saturated to a large extent, but octane number loss is compensated by subsequent isomerization and alkylation steps. A more selective catalyst is needed. Selective poisons are targeted. The alumina support is also neutralized by alkali hydroxide or carbon deposition.[47,48]

In spite of these efforts to produce ultra low sulfur gasoline, catalytic processes will require large investment and a meaningful increase of operating costs. Hence, non-catalytic processes with lower investment and operating cost have been proposed, especially by applying adsorption technology.

S-Zorb, developed by Phillips Petroleum, may be the first adsorption process to remove sulfur molecules contained in cracked gasoline. In the process, the adsorbent encounters sulfur molecules and selectively traps them on its surface. Sulfur-bearing adsorbent is regenerated by combusting sulfur in to SO_2. The S-Zorb Process looks very attractive to reduce the sulfur content of gasoline below a few ppm to a few tens of ppb. S Zorb consumes the least amount of hydrogen among the gasoline desulfurization technologies. Olefin loss is also very small, as low as 1 vol%.

Activated carbon materials have been proven to have enough sulfur retaining capacity in gas oil adsorption by the present authors.[31] However, its application to gasoline seems to have some problems due to strong adsorption of co-present olefins and aromatic compounds.

Besides the technologies on the way to commercialization, new catalysts have been proposed to achieve the effective desulfurization of gasoline without loss of octane number. Yin et al.[49] reported that FCC naphtha could be desulfurized over Ni/HZSM-5 catalyst without octane loss due to aromatization activity of the catalyst. In their concept, an olefin is aromatized before the hydrogenation. Excess cracking as well as rapid saturation are a concern. The present authors are examining CoMoS catalysts supported on carbon materials in HDS of cracked gasoline.

12. PROGRESS IN SUPPORT MATERIALS FOR MORE ACTIVE HDS CATALYSTS

There have been several significant advances in HDS catalysts. Although some suggest active species other than CoMo and NiMo, enhancement of catalytic activity has been intended particularly for the HDS of refractory sulfur species to find more active support materials. Some oxides and carbon materials have been evaluated to show their superiority to alumina in HDS reactions, although it could not be generalized due to the wide variation of reaction conditions and feed characteristics in HDS. Support influences the catalytic activity in HDS through two ways, modifying the active species on itself and participating in the HDS reaction as a co-catalyst.

Acidic supports, such as zeolites, have been tested by many researchers, and show superiority in the HDS reaction. Acidic zeolite was reported to facilitate isomerization and trans-alkylation of alkylated DBT, resulting in the enhanced HDS activity of such refractory sulfur species.[50]

Acidity has been recognized as important in deep HDS to improve resistivity against inhibition by H_2S. Strong acidity must be inhibited by basic polar nitrogen species, such as NH_3 and pyridines, and carbazoles. Nevertheless HDN is also accelerated due to reduced N inhibition. A series of CoMo and NiMo catalysts supported on alumina, silica-alumina, and alumina-zeolite were examined in the deep HDS of SRGO to evaluate enhanced activity by such supports in the presence of H_2S and NH_3, by the present authors.[7] Although H_2S and NH_3 inhibit the HDS of refractory sulfur species over all catalysts examined, a catalyst of high acidity achieved deep HDS even under such conditions. Adsorption of gas-phase inhibitors on the acidic sites and weakening of the metal-sulfur bond in the active sulfide caused by acidity of the support are believed to improve the resistivity against H_2S. Reduction of inhibition by NH_3 is moderate.

Functions of zeolite, as a representative acidic support, have been discussed just from the viewpoint of enhanced hydrogenation and isomerization. In addition, zeolite itself has been found to desulfurize some sulfur species, such as thiophene. Acidic C-S bond breakage and hydrogen transfer can be postulated over the acidic zeolite. More research is needed.

In spite of the above advantages in using zeolite as a support material, an inevitable problem is present in such an acidic catalyst system, that is fast coking. Strong acidic sites cause extensive coking, which shortens the lifetime of the catalyst, covering particularly the strong acid sites. Although such behavior can not be discussed in detail now due to the lack of information, a disadvantage such as fast coking may be moderated by blocking particular acidic sites by a third ingredient. We examined CoMoS and NiMoS catalysts supported on USY, modified by an alumina additive. Acidity, measured by NH_3 desorption, was lower on the modified USY. However, its activity toward refractory sulfur species contained in the conventionally hydrotreated gas oil was only slightly improved over that of the zeolite support. Furthermore, cracking occurring on acid site was much less over the alumina-coated zeolite catalyst. It is also important to locate the hydrogenation active site in the vicinity of the acidic site to hydrogenate strongly adsorbed species on the acidic site for desorption before coking.

Incorporation of MCM-41 into alumina provided higher activity for the CoMo catalyst in DBT HDS.[51] MCM-41 was reported to reduce the interaction of Co and Mo with the support. As a result, it enhances the formation of polymeric Mo octahedral species, which are regarded as an active form on alumina. Furthermore, it modifies the dispersion of Co to suppress the formation of an inactive $CoAl_2O_4$ phase. Such results indicate the importance of the acidic nature of the support in modifying active sites. Such a function can be ascribed to finer particles of alumina among the matrix with poor affinity for the active oxides, such as SiO_2, TiO_2, B_2O_3 and P_2O_5. It is intended to incorporate active species in the pore of zeolite. Difficulty for diffusion of large refractory species must be considered.

SiO_2-Al_2O_3 is also an acidic support like zeolites. HDS activity toward 4,6-DMDBT was reported to increase from the mixing of the conventional NiMo/Al_2O_3 catalyst with SiO_2-Al_2O_3.[52] Such observation is believed to be caused by enhanced hydrogenation and isomerization by the acidic component in the catalyst. However, there are many questions on the fundamental aspects of HDS catalysts supported on SiO_2-Al_2O_3. First of all, the difference in MoS_2 morphology on Al_2O_3 and SiO_2-Al_2O_3 must be clarified. It is generally accepted that SiO_2 can't disperse MoO_3 well in a monolayer due to very weak interaction with MoO_3.[53] However, Al_2O_3 incorporation alters the nature of surface to increase the monolayer capacity. Hence, the form of active species may be different from that observed on Al_2O_3 supports. Higher activity of SiO_2-Al_2O_3 supported catalysts may come from a more favorable form of active species in addition to the stronger acidity of the support, but definite evidence has not been found yet.

Addition of P_2O_5, ZrO_2, and B_2O_3 to Al_2O_3 were reported to increase the acidity of catalysts and as a result enhance the HDS of refractory sulfur species.[54] Phosphorus was also known to form NiP, which is active for hydrodesulfurization.[55] However, their effects on the morphology of active species are not confirmed yet. Roles of acidic supports in HDS by sulfide catalysts are summarized in Table 3.

Table 3. Role of Acidic Supports in HDS by Sulfide Catalyst.

1. Influences on the Active Species(Catalyst-Support Interaction)
    (1) Acidic modification on the natures of active sulfides
        - Long and short-range interaction
    (2) Restriction of the area(site) for dispersion of active oxide precursors
    (3) Reverse spillover of proton from support to active sulfides

2. Catalytic Functions of Support(Bifunctional Catalysts)
    (1) Acidic activation of substrate
        - Cracking, isomerization, trans-alkylation
    (2) Acidic adsorption of substrate in σ- and π-coordination
        - Spillover of coordinated substrate to active sulfide

3. Influence of Active Species on the Substrate Adsorbed on the Support)
    (1) Hydrogen spillover for sulfide to oxide support

TiO_2 was evaluated as an active support material for HDS. Its main drawback, low surface area, was reported to be overcome by a kind of sol-gel process, giving as high as 120 m /g.^{2}[56] It could carry a higher loading of Mo as (19 wt% as MoO_3) than conventional TiO_2 supports, allowing well dispersed Mo species. This catalyst showed higher HDS activity for 4,6-DMDBT than the alumina supported one. An Al_2O_3-TiO_2 composite support was also tested to provide higher surface area. It showed higher activity than Al_2O_3 and TiO_2 alone in HDS of 4,6-DMDBT while its activity for the HDS of DBT was inferior to the alumina support.[57,58,59] Such binary oxides carry more Brønsted acidic sites and as a result have rather high activity in hydrogenation. This gives an increase in the activity for 4,6-DMDBT HDS. It should be also noted that TiO_2 is believed to have much less interaction with active species than Al_2O_3, inducing a more easily reducible oxide phase of Mo and Co(Ni) due to the partial sulfidation of TiO_2.[60]

Carbon has been regarded as a promising catalyst support due to its very high surface area, peculiar pore structure, and surface-functional groups.[24] HDS catalysts supported on carbon can provide higher activity than alumina supported ones.[36,61,62] Presumably, weak interaction of carbon with sulfide precursors provides the more sulfidable species on carbon than on alumina, resulting in the more active sites for HDS. The very large surface area of carbon supports must be also helpful although the acidic contribution is not expected.

Life of catalysts due to the sintering of active species must be carefully tested since such supports interact weakly with active species.

13. RECOGNITION AND CONTROL OF THE SHAPE AND SIZE OF ACTIVE SITES ON HDS CATALYSTS

There have been several proposals to describe the active sites for HDS, such as intercalation, surface complex, and rim-edge models of cobalt and nickel in their location.[63] Such models include the stacked layer structure of MoS_2, which is believed to constitute the major part of the active sites. Daage and Chianelli suggested that there are two types of active sites on a MoS_2 slab, rim and edge.[63] Rim sites are assumed to be responsible for the hydrogenation while edge sites are for both hydrogenation and direct hydrodesulfurization, respectively. Such images have provided design concepts of active sites for higher activity toward HDS by larger numbers of slabs or stacking providing higher activity.[64] Furthermore, Mo species directly contacting the support surface could not easily be sulfided, showing lower activity. Such concepts distinguish Type I and Type II phases. The former is a highly dispersed monolayer of MoS_2 and latter has lower dispersion and a higher extent of stacking.[65,66]

Although extensive examination to clarify the morphology of active species has been conducted by several research groups, it is not definitely concluded whether MoS_2 slabs sit with perpendicular or parallel orientation on supports.[67] Two types of MoS_2 slabs are depicted in Fig. 17.

Hence, methods to make the MoS_2 phase taller have been attempted. Among several types of anchoring sites on γ-Al_2O_3, an OH group bound to a tetrahedrally coordinated aluminum cation has been proposed to give strong interaction with Mo, resulting in less sulfidable Mo species.[68] In order to suppress the anchoring of Mo precursor on such inactive sites, Ti could be deposited on alumina prior to the impregnation of Mo.[68] This observation may be related to the dependence of the morphology of MoS_2 on the support type and preparation conditions. Additive agents are used to improve the dispersion of active species. There are two approaches. One is to disperse MoO_2 on the support to be highly stacked. The additive on the support restricts the site, leading to MoO_2 accumulation to make tall crystals. B_2O_3 and P_2O_5 can be such additives. Their acidic natures must not be excluded by mixing B_2O_3, P_2O_5 and TiO_2 with alumina.

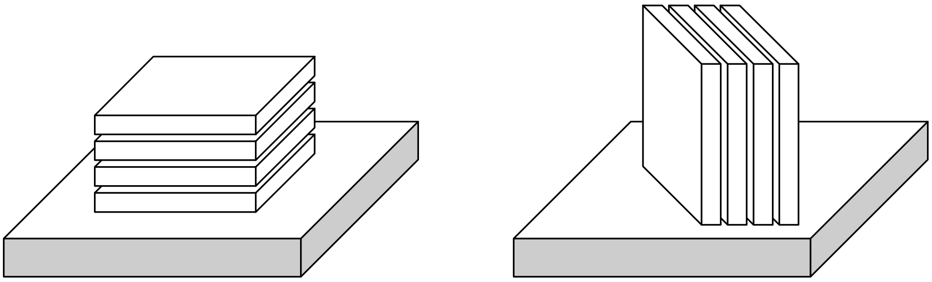


Figure 17. Schematic models for MoS_2 slabs sitting on support with parallel (left) and perpendicular (right) orientation

The second approach is to disperse Co and Ni on the particular sites of MoO_2. In practical catalysts, EDTA (ethylenediaminetetraacetic acid), NTA (nitriloacetic acid) complexing agents can be applied to prevent interaction of Co(Ni) ions with the Al_2O_3 surface.[64,68,69,70]

A more sophisticated approach is to make microcrystal shapes of nano size by micelle technology, which is a common methodology in nanotechnology. Atomic scale observation of HDS catalyst could provide deep insight for morphological understanding. Examination of model Mo-S structures on well defined substrates by scanning tunneling microscopy (STM) revealed that Co changes the morphology of MoS_2 from triangular to truncated hexagonal by preferred siting of Co at the sulfur edge site of MoS_2.[20,71] STM observation on the thiophene adsorbed model of MoS_2 provided information on the adsorption site, which was suggested to be the metallic edge site of MoS_2. Such an approach is strongly expected to accelerate in-situ structural analysis of the practical catalyst. It must be noted that dynamic natures of catalyst structure and substrate conversion are important targets.

TEM observation of HDS catalysts was widely applied to evaluate the stacking degree and width of each stack of MoS_2. It must be recognized that TEM can not detect the stacking of MoS_2 when its C axis is perpendicular to the surface of alumina. A number of stacks observed under TEM are placed to direct their C axis parallel to the surface. Detailed design of Co(Ni)MoS_2 can be achieved by molecular design of Co(Ni)M clusters with definite structure. Interaction of clusters with the surface of the support must be further clarified for complete sophistication.[68] The present authors believe now that most MoS_2 sits on its edge on the active support while weak interaction may allow the flat sitting of MoS_2 on an inactive support.

14. CATALYTIC ACTIVE SITES FOR HDS AND HYDROGENATION

Co(Ni)MoS supported on alumina shows catalytic activity for hydrogenation as well as HDS. These catalysts include activation of hydrogen to substitute the counterpart of C-S bond or saturate the C-C double bond, which occur simultaneously. However, some features of these catalysts suggest that there are different active sites on Co(Ni)MoS/Al_2O_3. It is good to design catalysts of HDS with less hydrogenation. NiMoS is believed more active for hydrogenation than CoMoS.[1,2] Very low concentrations of H_2S appear to retard hydrodesulfurization while it accelerates hydrogenation, although high concentration prohibits both reactions.[72,73] Acidic supports accelerate hydrogenation and hydrodesulfurization through the hydrogenation of refractory sulfur species. Acidity strengthens resistance to H_2S inhibition of hydrodesulfurization. Such results suggest that the active sites for these catalysts are more coordinatively unsaturated for HDS than for hydrogenation. HDS requires two open valences to insert hydrogen into a C-S bond as illustrated in Fig. 6. In contrast, π-coordination of an aromatic ring or unsaturated bond in the aromatic ring to one of the active sites is followed by the addition of hydrogen from S-H on the sulfide for the first stage of hydrogenation. Strong adsorption of a partially hydrogenated aromatic ring continues the successive hydrogenation of other unsaturated bonds to complete the aromatic hydrogenation. An acidic support moderates the electron density of active metals to be more acidic, activating S-H or Ni-H bonds to transfer the proton for hydrogenation. Nickel is certainly more active for hydrogenation than cobalt.

Other metals, including iron or noble metals, are worthwhile for examination to compare the selectivity between hydrodesulfurization and hydrogenation, although a series of metals are compared in the relationship between strength of metal-S and -H bonds and catalytic activity to confirm the Sabatier principle.[74]

Another important point not much discussed yet is the chemistry of π-coordination in heterogeneous catalysis.[75,76,77] The authors are particularly interested in the contribution of heteroatoms, especially sulfur, in the same or adjacent rings of the π-coordination. Fig. 18 shows the possible coordination geometry of thiophene. The catalytic sites must be clarified in such π-coordination. It may be important to distinguish carbon and S atoms in the aromatic ring for the selective hydrogenation of DBT against pure aromatic hydrocarbons as found in LCO and HCO from FCC the process. Roles of alkyl groups on the DBT ring are also considered. It is necessary to define the desulfurization mechanism of the target species such as thiols, thiophene and benzothiophene in the hydrodesulfurization of cracked gasoline.

Selective poisoning of hydrogenation has been patented to demonstrate selectivity for hydrodesulfurization. Sulfur compounds are postulated to adsorb on the support to reduce hydrogenation activity more than hydrodesulfurization as describe above. It is in line with a conclusion that the acidic support accelerates the hydrogenation. Unfortunately, such selective poisoning is still not very selective, as it also reduces hydrodesulfurization activity. More details and deeper understanding of the active sites and influential factors in the mechanism of hydrodesulfurization and hydrogenation are still being explored. The authors believe that the detailed description of the molecular structures of the catalyst, support, substrate, intermediate and then dynamic intermediates are logically established to build up catalysts frameworks.

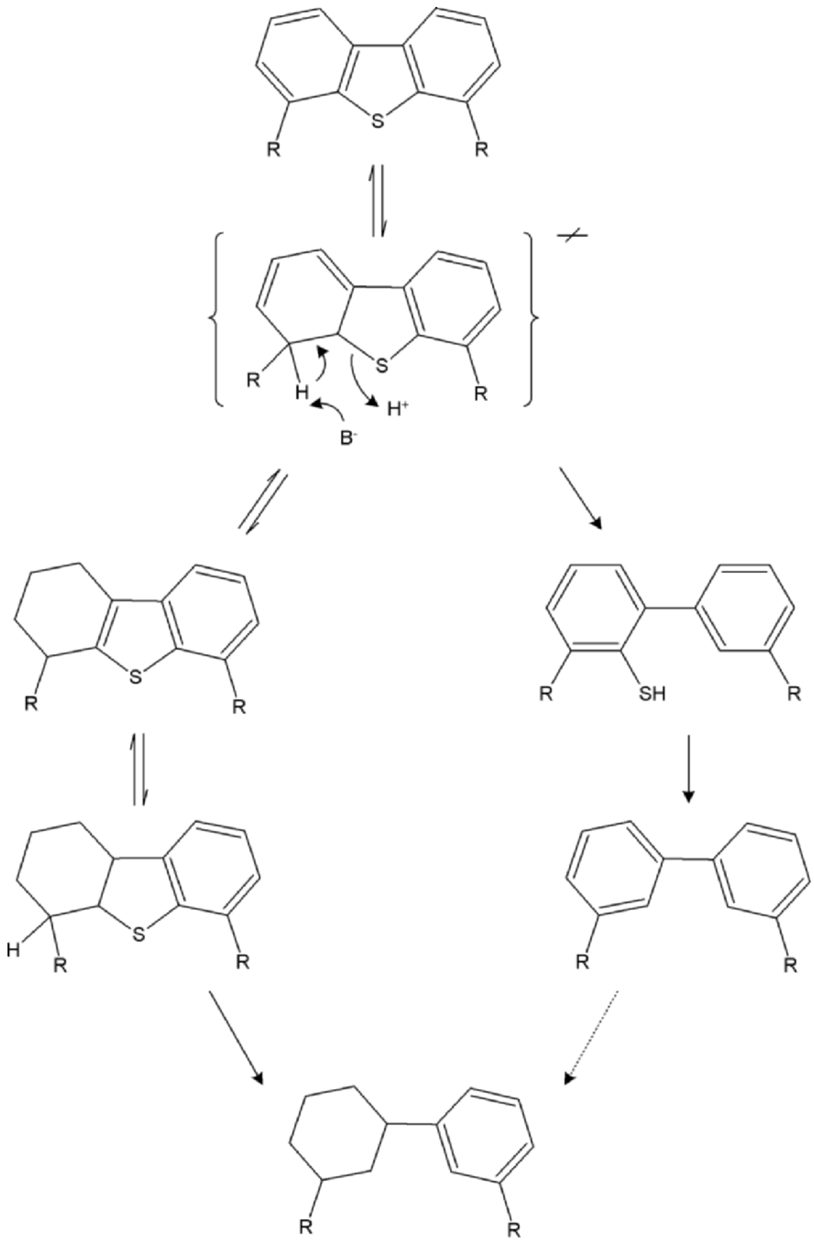


Figure 18. Reaction mechanism of HDS of 4,6-dialkylDBT, assuming the formation of dihydro intermediate [5]

15. ROLES OF STERIC HINDRANCE IN ADSORPTION AND KINETIC PROCESSES OF HDS

It is definitely recognized that the deep hydrodesulfurization of gas oil relies upon the deep hydrodesulfurization of refractory sulfur species, which tend to stay almost exclusively at a significant level in conventional hydrodesulfurization processes. The refractory sulfur species are of low reactivity and suffer high inhibition by H_2S, nitrogen compounds including NH_3, and even aromatic compounds. The refractory sulfur species carry alkyl groups at the 4 and 6 positions on the DBT ring. The influence of 1 and 9 positions have not been examined yet. Other positions – 2, 3, 7, and 8 – do not deactivate but accelerate the hydrodesulfurization. Refractory sulfur species have been recognized to be desulfurized mainly through the hydrogenation of at least one phenyl ring prior to sulfur elimination. Hydrodesulfurization of hydrogenated intermediates is very rapid under typical hydrodesulfurization conditions.[78] In contrast, the reactive sulfur species are mainly desulfurized through direct elimination of sulfur atoms without hydrogenation of any phenyl ring, even if the hydrogenated intermediate could be desulfurized more rapidly. Thus, hydrogenation of one phenyl ring in refractory sulfur species is the rate-determining step. At higher temperature than 360°C, direct hydrodesulfurization becomes dominant even with the refractory sulfur species because higher temperature under the constant hydrogen pressure very sharply reduces obstacles against the direct elimination.[78] Such results indicate steric hindrance of alkyl groups at 4 and 6 positions on the DBT ring. The question is, which step is sterically hindered? Sulfur species can be adsorbed onto a sulfide catalyst first through π-coordination of the DBT ring. It is not clear how much and which place on the catalyst π-electrons of S atoms are coordinated at this stage. The π-coordinated species is transformed into σ-coordination of the sulfur atom on an active site of probably Co or Ni of coordinative unsaturation. This leads to the insertion of the active metal between aromatic C and S atoms as described above. The C-active site and C-S bonds are hydrogenatively fissioned, probably in a successive manner with two hydrogen atoms coming from the catalyst surface for S extraction. The SH group on the active site is further hydrogenated and desorbed eventually as H_2S. The steric hindrance can work during σ-coordination, at insertion, and during the hydrogenative fission steps.

The σ-coordinating step is often considered to be the most sensitive to steric effects. Strong inhibition against refractory sulfur species, especially at concentrations less than 300 ppm, favors steric hindrance at this stage. Inhibition is basically competition for active sites among the substrates, including inhibitors. σ-coordination of aromatic rings may not be probable. π-coordination to an active site, a σ-coordination site or a hydrogenation site may hinder hydrodesulfurization. In the latter case, only the hydrogenation route is inhibited and no inhibition can be observed with direct elimination of sulfur atoms. Detailed kinetic analyses are still needed to clarify the true features. High measured heat of adsorption suggests strong adsorption of refractory sulfur species. The measured heat is consistent with π-coordination adsorption. Hence, steric hindrance at σ-coordination sites is not excluded by this result. Kinetic analyses are necessary to estimate the heat of adsorption of real intermediates.

It is necessary to clarify more details of π-coordination on the catalyst in terms of its relation with the hydrogenation of aromatic species and which sites of sulfided catalysts are involved. Selectivity among aromatic species of pure hydrocarbons and of nitrogen, sulfur or oxygen containing rings can be discussed by clarifying such questions. Steric hindrance of alkyl groups on hydrogenation has been discussed for lower temperature.[16] However, no evidence has been observed in HDS above 300ºC.

The hydrogenative bond fission step can be also postulated to suffer steric hindrance.[2] Alkyl groups at other locations may be involved in this stage. In this sense, reactivities of 1,9-dialkyl DBTs are interesting to discuss at these stages. The same questions have been posed in the HDN of aromatic nitrogen species. So far, in depth discussion has not been attempted.

Perot et al.[5] proposed the formation of dihydro intermediates during the HDS of DBT and dialkyl-DBT, regardless of whether the route involves hydrogenolysis or direct desulfurization as seen in Fig. 19. They ascribed the inertness of 4,6-DMDBT to hindered β-elimination by substituted methyl groups.

In conclusion, we believe that steric hindrance plays its role dominantly at the σ-coordination stage. Details of π-coordination must be involved in competition for the catalyst surface even if the step may not be rate-determining. Even so, participation of π-coordination may be influential in some petroleum refining reactions.

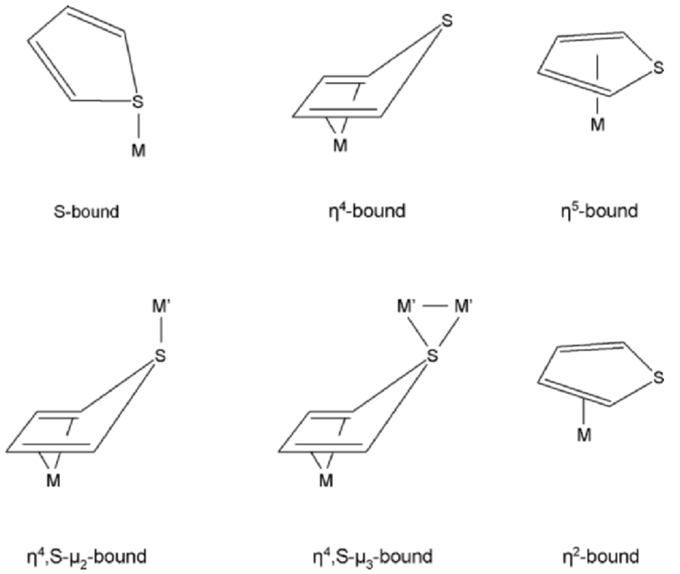


Figure 19. Coordination of thiophen in organometallic complexes [77]

16. FURTHER SCOPE AND ACKNOWLEDGMENTS

The present authors intended to cover the overall chemistry of hydrotreating processes in terms of feed and intermediates. The authors are grateful to the editors for giving us a chance to summarize our current research in hydrotreating catalysis and catalysts. One of the present authors (IM) has been involved in hydrotreating research for two decades. It is now time to establish the feeds and products, as well as the nature of catalysts, at the molecular level, including both structures and dynamics. Contributions of steric hindrance must be considered when discussing π-coordination. The authors believe that the present days are the turning point in catalytic research. Past assumptions must be deeply reviewed, based on modern techniques of analysis and the testing of more catalytic species, with due respect for the past 50 years of research, to establish current refining technologies.

The present review did not include the hydrotreatment of very heavy oils such as bitumen which must become very competitive resources in the near future.

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