

Desulfurization

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INTRODUCTION

Desulfurization of hydrocarbon streams is an important process used in a petroleum refinery to reduce the sulfur concentration in fuels such as gasoline, jet fuel, kerosene, diesel, and heating oil so that the resulting fuels meet environmental protection standards.^[1–7] Hydro-treating is one of the most popular and widely practiced desulfurization processes and refers to the catalytic removal of sulfur [hydrodesulfurization (HDS)], nitrogen [hydrodenitrogenation (HDN)], oxygen [hydrodeoxygenation (HDO)], and metals [hydrodemetallation (HDM)] from petroleum distillates in the presence of hydrogen. Hydrotreating first appeared in petroleum refineries as a finishing process in the 1930s.^[2] Hydro-treating operates at conditions milder than those typically used in fluidized catalytic cracking (FCC) or hydrocracking. Typical hydrotreating process conditions vary with feedstock and are summarized in Table 1.

In the past two decades petroleum refining has changed extensively and the fortunes of hydrotreating, in particular, have witnessed a sea change. Hydro-treaters now occupy a central role in modern refineries and more than 50% of all refinery streams now pass through hydrotreaters for conversion, finishing, and pretreatment purposes.^[2] Hydrodesulfurization is the largest application of catalytic technology in terms of the volume of material processed.^[8] On the basis of usage volume, HDS catalysts are ranked third behind catalysts used for automobile emission control and FCC.^[8]

Commercial hydrotreating catalysts are, typically, sulfides of Mo or tungsten (W) supported on $\gamma\text{-Al}_2\text{O}_3$ and promoted by either Co or Ni. Nickel, known for its high hydrogenation activities, is preferred as a promoter when feedstocks containing high amounts of nitrogen and aromatics need to be processed. Table 2 provides the compositional range and physical properties of typical hydrotreating catalysts in the oxidic phase.

GROWING DEMAND FOR DESULFURIZATION

The challenge of fulfilling the world's growing transportation energy needs is no longer a simple issue of

producing enough liquid hydrocarbon fuels. This challenge is instead accentuated by a complex interplay of environmental and operational issues. Environmental issues include societal demands that liquid hydrocarbon fuels be clean and less polluting. The emergence of new refining processes and the increasing use of new forms of energy production, e.g., fuel cells, exemplify operational issues. Together, these trends are driving the need for deep desulfurization of diesel and jet fuels.

As an example of the kind of regulations that are being specified and contemplated for hydrocarbon fuels, Table 3 lists the compositional and performance properties for diesel. The United States Environmental Protection Agency (USEPA) has mandated that diesel—whose automotive use is now growing at a pace faster than that of gasoline—have no more than 15 parts per million by weight (ppmw) of sulfur by 2006.^[9,10] This represents a 97% reduction in the allowable sulfur concentration in diesel from 500 to 15 wppm. The United States now allows up to 3000 wppm of sulfur in jet fuel.^[11] With the European Union now demanding no more than 1000 wppm of sulfur in jet fuel, a reduction in the permissible sulfur content of U.S. jet fuel can be expected.^[12] New gasoline sulfur regulations will require most refiners to meet a 30 ppmw sulfur average with an 80 ppmw cap for both conventional and reformulated gasoline by January 1, 2006.

Initially, fuel sulfur was regulated to reduce emissions of the oxides of sulfur, which contribute to acid rain, ozone, and smog. The recent and stricter round of sulfur specifications, however, are an effort to reduce automobile emissions of the oxides of nitrogen (NO_x) and particulate matter (PM). For example, the 15 ppmw diesel sulfur limit follows from the USEPA's parallel program of rule making that seeks to reduce automobile NO_x and PM emissions by 95% and 90%, respectively, by 2007. Automobile manufacturers are demanding ultra-low-sulfur fuels because only then would their advanced, sulfur-sensitive after-treatment technologies achieve such drastic reductions in NO_x and PM emissions.^[13,14]

Sulfur specifications are the more visible drivers for desulfurization research. Fig. 1 presents a qualitative

Table 1 Typical hydrotreating process conditions for various feedstocks

Feedstock	Temperature (°C)	Hydrogen pressure (atm)	LHSV ^a (hr ⁻¹)
Naphtha	320	15–30	3–8
Kerosene	330	30–45	2–5
Atmospheric gas oil	340	38–60	1.5–4
Vacuum gas oil	360	75–135	1–2
Atmospheric residue	370–410	120–195	0.2–0.5
Vacuum residue	400–440	150–225	0.2–0.5

^aLHSV, liquid hourly space velocity.
(From Ref.^[2].)

relationship between the type and size of sulfur molecules in various distillate fuel fractions and their relative reactivities.^[5] Various refinery streams are used to produce three major types of transportation fuels, gasoline, jet fuels, and diesel fuels, that differ in composition and properties. Other fuel specifications are equally important, albeit less visible, reasons for continued research and development in desulfurization. For example, European countries typically require diesel fuel with sulfur less than 50 wppm, cetane number of 48–51, and density less than 0.825 g/cm³. These fuel specifications are more stringent than those enforced in the United States (see Table 3). To be active in the European diesel fuels market—larger than that in the United States—oil refiners will have to produce ultraclean, high-quality, premium diesel fuel through sophisticated refining

processes such as the selective ring opening (SRO) of naphthenes.^[15]

Ring opening is commonly observed in the hydrocracking process where one or more carbon–carbon (C–C) bonds are broken. Selective ring opening, in contrast, breaks only one C–C bond open, thus preventing extensive reduction in molecular weight.^[16] This process, shown for a model diaromatic molecule in Fig. 2, leads to extensive improvement in the quality of diesel fuel by increasing cetane number and decreasing fuel density simultaneously.^[16]

Hydrodesulfurization is important for the SRO process because the most effective SRO catalysts are based on noble metals such as iridium, which are highly sensitive to sulfur. Therefore, all SRO feedstocks will have to be extensively desulfurized and hydrogenated before being sent to an SRO reactor. Selective ring opening, while fulfilling important nonsulfur fuel specifications, is an emerging refining process that symbolizes a compelling operational issue that could require more active HDS catalysts.

In recent times, there has been tremendous interest in fuel cells. This interest is set to intensify with the U.S. government's new Freedom Cooperative Automotive Research (Freedom CAR) program that seeks to develop cars based on hydrogen-powered fuel cells.^[17] Enough hydrogen to satisfy a fuel cell-based transportation system will have to be produced by processing hydrocarbon fuels through reforming and related processes all of which are sensitive to sulfur. While most fuel cells are also sulfur sensitive, some are intolerant to as little as 0.1 wppm sulfur, e.g., polymer electrolyte membrane fuel cell (PEMFC).^[7] As the sulfur compounds in liquid hydrocarbon fuels and the H₂S produced from these sulfur compounds in the hydrocarbon reforming process are poisonous to both the catalysts in hydrocarbon fuel processor and the electrode catalysts in fuel cell stack, the sulfur content in the liquid hydrocarbon fuels has to be reduced to a very low level [<10 ppmw for solid oxide fuel cell and <0.1 ppmw for PEMFC].^[7] Consequently, desulfurization will continue to be one of the most important processes in oil refineries.

Table 2 Composition and properties of typical hydrotreating catalysts

Composition and properties ^a	Range	Typical values
Active phase precursors (wt%)		
MoO ₃	13–20	15
CoO	2.5–3.5	3.0
NiO	2.5–3.5	3.0
Promoters (wt%)		
SiO ₂	0.5–1	0.5
B, P	0.5–1	0.5
Physical properties		
Surface area (m ² /g)	150–500	180–300
Pore volume (cm ³ /g)	0.25–0.8	0.5–0.6
Pore diameter (nm)		
Mesopores	3–50	7–20
Macropores	100–5000	600–1000
Extrudate diameter (mm)	0.8–4	3
Extrudate length/diameter	2–4	3
Bulk density (g/ml)	0.5–1.0	0.75
Average crush strength/length (kg/mm)	1.0–2.5	1.9

^aActive phase precursors and promoters are supported on a γ -Al₂O₃ carrier.

Table 3 Specifications for diesel fuel

Parameter	U.S.A.		Europe		World Fuels Charter
	EPA 2006	CARB ^a average	Current	2005	
Sulfur (ppmw)	15	15	350	50 ^b	30
Density (g/cm ³)			<0.845	(<0.825)	<0.84
T 90% (°C)	338	321			
T 95% (°C)		349	360	(<340)	340
Cetane number		48	51	(>56)	55
Cetane index	40				
Polyaromatics (%) ^c		1.4	11	(<1)	2
Total aromatics (%)	35	10			15

Values in parentheses have been proposed, and are not mandated yet.

^aCalifornia Air Resources Board.

^bSulfur content in some European countries is much lower, e.g., Germany requires diesel to have sulfur no more than 10 ppmw.

^cIn this article, unless indicated otherwise, percentage compositions are weight based.

SULFUR COMPOSITION OF KEY HYDROCARBON FUEL

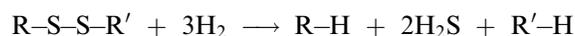
The major organic sulfur compounds in petroleum fractions are thiols (mercaptans), sulfides, disulfides, thiophenes, benzothiophenes (BTs), dibenzothiophenes (DBTs), naphthothiophenes (NTs), benzonaphthothiophenes (BNTs), phenanthro[4,5-b,c,d]thiophenes (PTs), and their alkyl-substituted derivatives, as shown in Table 4. There are three major types of transportation fuels, gasoline, diesel, and jet fuels, which differ in composition and properties (Fig. 1, Table 4). The major sulfur compounds existing in commercial gasoline are thiophene, 2-methylthiophene, 3-methylthiophene, dimethylthiophenes, and benzothiophenes, indicating that most sulfur compounds with higher HDS reactivity, including thiols, disulfides, and sulfides, have been removed from the commercial gasoline in conventional petroleum refining processes such as FCC. The major sulfur compounds in the jet fuels such as, JP-8 are dimethylbenzothiophenes and trimethylbenzothiophenes. Most of them have two methyl groups at the 2- and 3-positions, respectively, implying that these alkyl benzothiophenes are more difficult to be removed than others. The sulfur compounds in commercial diesel fuel include alkyl benzothiophenes and alkyl dibenzothiophenes. Of these compounds, alkyl dibenzothiophenes with alkyl groups at the 4- and/or 6-positions are the most difficult to remove by conventional HDS processes.

REACTIVITY AND REACTION MECHANISM OF VARIOUS SULFUR COMPOUNDS

The major fundamental approaches of the numerous theoretical and experimental studies conducted on desulfurization since the 1980s can be grouped into

four general areas: 1) determining reaction kinetics and inhibition, over existing and new catalysts; 2) catalyst characterization using spectroscopy; 3) studying coordination chemistry of organometallic complexes; and 4) employing molecular simulation and computational analysis.

The kinetics and poisoning investigations indicate that the sulfur compounds present in hydrocarbon fuels usually show different reactivities and mechanisms for undergoing desulfurization. The HDS reactivity of various sulfur compounds decreases in the order of disulfides > sulfides, thiols > thiophenes > BTs, NTs > BNTs, DBTs without any alkyl group at the 4- and/or 6-position > DBTs with one or two alkyl group(s) at the 4- and/or 6-position(s). For the sulfur compounds without a conjugation structure between the lone pairs on S atom and the π -electrons on the aromatic ring, including disulfides, sulfides, thiols, and tetrahydrothiophene, HDS occurs directly through the hydrogenolysis pathway:



These sulfur compounds exhibit higher HDS reactivity than that of thiophenic compounds, because they have higher electron density on the S atom and a weaker C-S bond. For the thiophenic compounds, in which the lone pairs on the S atom conjugate with the π -electrons on the ring, including thiophenes, BTs, DBTs, NTs, PTs, and BNTs, HDS over the commercial catalysts usually proceeds through two pathways, the hydrogenation pathway (hydrogenation followed by hydrogenolysis) and the direct hydrogenolysis pathway (direct elimination of S atom via C-S bond cleavage), as shown below.

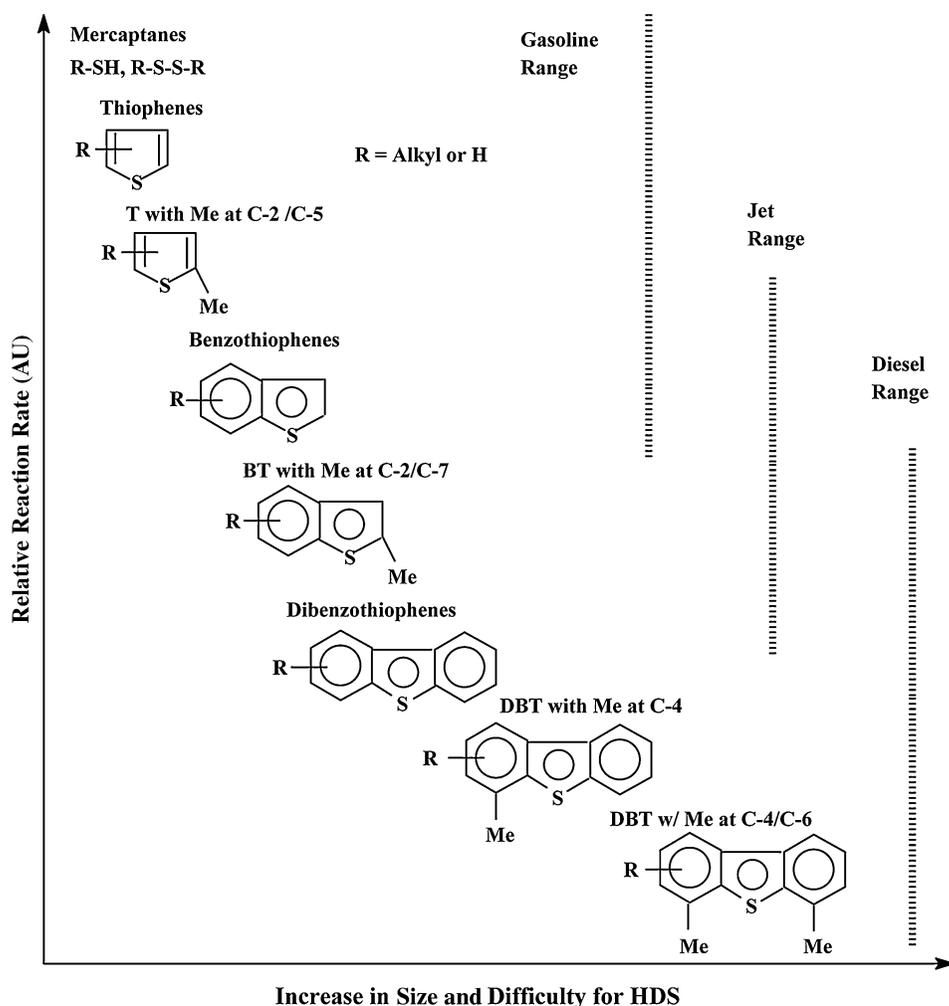


Fig. 1 Reactivity of various organic sulfur compounds in HDS vs. their ring sizes and positions of alkyl substitutions on the ring.

The HDS reactivity of the thiophenic compounds is dominantly dependent on both the electron structure and the steric hindrance of alkyl groups. For thiophene and BT, the total HDS reactivity is greater than that of DBT by about an order of magnitude because there is higher π -electron density at the C(2)–C(3) and C(4)–C(5) bonds in thiophene and at the C(2)–C(3) bond in BT, leading to their greater HDS reactivity through the hydrogenation pathway.^[18] The π -electron distribution

on dibenzothiophene is more uniform, as on a benzene ring, resulting in its lower hydrogenation reactivity. Thus, HDS of DBT over commercial Co–Mo catalysts proceeds dominantly through the hydrogenolysis pathway (see Scheme 1). However, if one or two alkyl groups are attached at the 4- or/and 6-positions of DBT, the hydrogenolysis pathway will be hindered strongly and the hydrogenation pathway becomes dominant.^[3] In this case, the HDS reactivity will

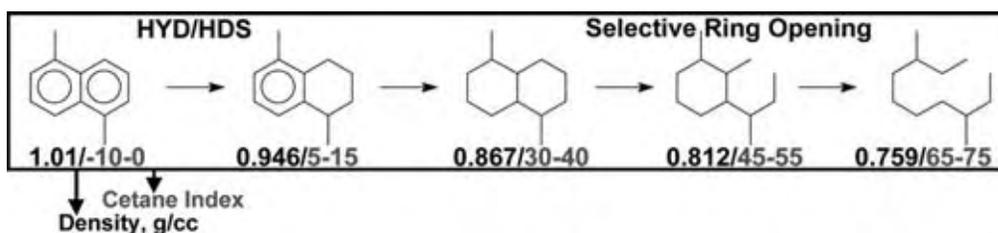
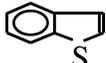
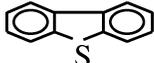
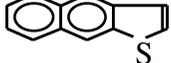


Fig. 2 Selective ring opening of a model diaromatic molecule. (From Ref.^[16].) (View this art in color at www.dekker.com.)

Table 4 Some typical sulfur compounds in petroleum fractions

Thiols (mercaptans)	R-S-H
Sulfides	R-S-R
Disulfides	R-S-S-R
Thiophenes	
Benzothiophenes (BTs)	
Dibenzothiophenes (DBTs)	
Naphthothiophenes (NTs)	
Benzonaphthothiophenes (BNTs)	
Phenanthro[4,5-b,c,d]thiophenes (PTs)	

decrease significantly. These sulfur compounds are called as the refractory sulfur compounds.

Some coexisting compounds in petroleum fractions and in the products during the HDS process exhibit a strong effect on HDS. H₂S was found to be one of the main inhibitors of the hydrogenolysis pathway, while polyaromatic compounds were found to be the main inhibitors of the hydrogenation pathway.^[3] Basic nitrogen compounds affect both the hydrogenolysis pathway and the hydrogenation pathway. Some excellent reviews of this aspect of HDS research are available in the literature.^[1-6]

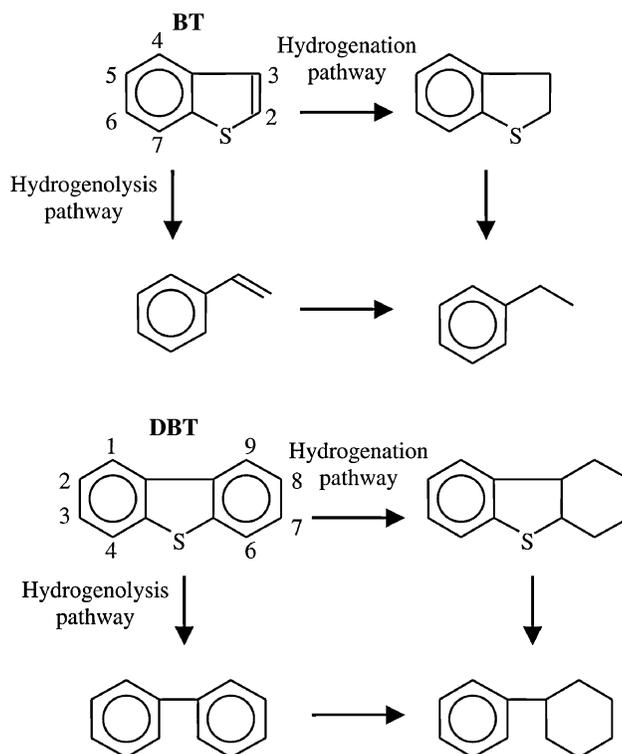
CHALLENGES IN ULTRADEEP DESULFURIZATION PROCESSES

Reactivity of Sulfur Compounds

Recently, investigations demonstrated that sulfur compounds remaining in diesel fuels at sulfur level lower than 500 ppm are dominantly the DBTs with alkyl substituents at the 4- and/or 6-position, and are lower in HDS reactivity.^[3-6] These species are termed refractory sulfur compounds. Both steric hindrance and electronic factor are responsible for the observed low reactivity of 4- and 6-substituted DBTs.^[19]

Based on HDS reactivity of sulfur compounds in a gas oil, the sulfur compounds can be classified into four groups according to their HDS reactivities that were described by the pseudo-first-order rate constants.^[20] The first group is dominantly alkyl BTs; the second, DBT and alkyl DBTs without alkyl substituents at the 4- and 6-positions; the third, alkyl DBTs with only one alkyl substituent at either the 4- or the 6-position; the fourth, alkyl substituents at the 4- and 6-positions. The sulfur distribution in the gas oil is 39, 20, 26, and 15 wt%, respectively, and the relative rate constant of HDS for each of the four groups is 36, 8, 3, and 1, respectively.^[20] Fig. 3 shows the relative reactor volume requirements for various degrees of sulfur removal by conventional single-stage HDS of diesel fuel.^[6] According to this result, when the total sulfur content is reduced to 500 ppmw, the sulfur compounds remaining in the hydrotreated oil are the third and fourth group sulfur compounds. When the total sulfur content is reduced to 30 ppmw, the sulfur compounds remaining in the hydrotreated oil are only the fourth group sulfur compounds, indicating that the lower is the sulfur concentration the lower is the HDS reactivity of the remainder sulfur compounds.

For desulfurization of sulfur species in gasoline, it is not difficult to remove the sulfur compounds in the



Scheme 1 Mechanistic pathways (hydrogenolysis and hydrogenation) for the desulfurization of refractory polyaromatic sulfur compounds.

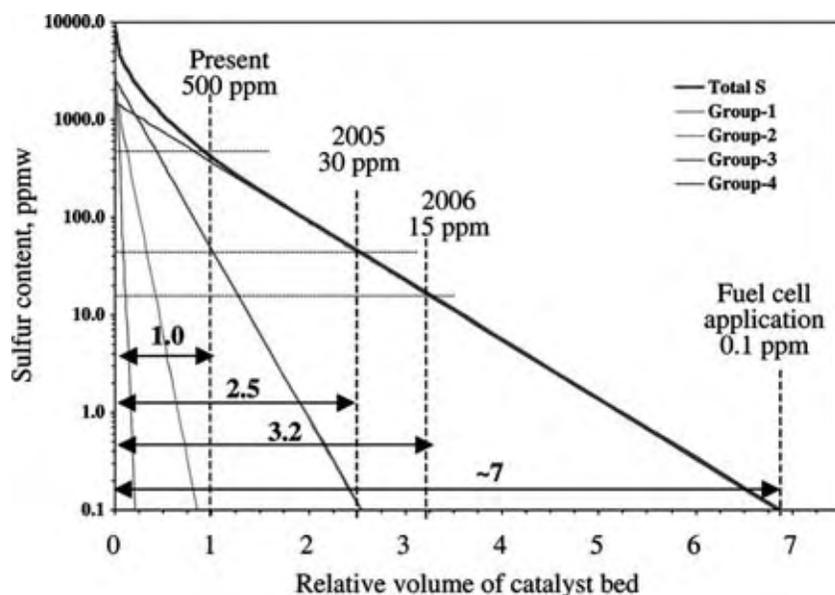


Fig. 3 Simulated HDS of diesel to meet 15 and 0.1 ppm levels on the basis of a conventional single-stage reactor, assuming 1.0 wt% S in the feed. HDS kinetic model: $C_{S,\text{total}} = C_{S10} e^{-k1t} + C_{S20} e^{-k2t} + C_{S30} e^{-k3t} + C_{S40} e^{-k4t}$. (View this art in color at www.dekker.com.)

naphtha range by current catalytic HDS processes. For the U.S. refineries, most of the sulfur in the gasoline pool is found in FCC naphtha. The challenge in deep desulfurization of FCC naphtha is selective conversion of sulfur compounds without saturation of olefinic compounds, which account for about 15–25 wt% in FCC naphtha and contribute to octane number enhancement. High hydrogen consumption in ultradeep HDS of FCC naphtha is another issue that needs to be considered. For straight-run kerosene, which is used for making jet fuels, the sulfur removal by HDS is more difficult than that from naphtha but less difficult compared to that from gas oil.

Inhibiting Effects of Fuel Components

A major challenge in the ultradeep desulfurization of hydrocarbon fuels is the inhibiting effects of fuel components (e.g., nitrogen compounds) and reaction products (e.g., hydrogen sulfide). While this area has been studied in catalysis literature, it is expected to gain increased attention because of the severity of the new sulfur specifications.^[1]

The difference in the catalytic activity between model compounds and real feedstocks is the most visible evidence for the influence of feedstock components on HDS catalysts. Some researchers have shown that an increase of 30–50°C in temperature is required for a commercial catalyst to achieve the same conversions of DBT, 4-MDBT, and 4,6-DMDBT in light gas oil as compared to the model compounds when dissolved in a hydrocarbon solvent.^[1,8] Inhibition of

HDS activity occurs predominantly through one of the following compounds:

1. Aromatic hydrocarbons
2. Nitrogen-containing compounds
3. Hydrogen sulfide
4. Ammonia, saturated hydrocarbons (solvents), and water.

The influence of these inhibitors is known to increase in the following order:^[21] saturated hydrocarbons, monoaromatics < condensed aromatics, oxygen compounds, hydrogen sulfide < organic sulfur compounds < basic nitrogen compounds. Three of these inhibitor classes are discussed here.

Aromatic compounds

Naphthalene and its derivatives are one of the more dominant aromatics present in various diesel and jet fuel feedstocks. Therefore, several investigators have reported the influence of naphthalene on HDS of model compounds. One of the first reports was by Lo who found naphthalene to weakly inhibit the conversion and selectivity of the HDS of DBT.^[22] Similarly, LaVopa and Satterfield found little effect of naphthalene and phenanthrene on the HDS of thiophene.^[23] Other researchers have, however, found naphthalene to be a stronger inhibitor of HDS activity.^[4] Nagai and Kabe, in fact, found naphthalene to significantly reduce catalyst selectivity for the hydrogenation pathway.^[24] Isoda et al., on the basis of similar selectivity inhibition, concluded that naphthalene severely inhibits the hydrogenation active sites in a

conventional HDS catalyst.^[25] While the inhibition of HDS by naphthalene and other aromatic hydrocarbons is significant, Girgis and Gates believe that it is weaker than inhibition caused by nitrogen-containing heterocyclic compounds.^[1]

Nitrogen-containing compounds

Among nonsulfur diesel fuel components, nitrogen-containing organic compounds have received significant attention because of their lower reactivity as compared to that of polyaromatic sulfur compounds (PASCs).^[8] Therefore, at very low sulfur levels, refractory nitrogen compounds could significantly influence the deep HDS of PASCs. Atmospheric gas oil, which is frequently used as a diesel feedstock, typically contains nitrogen compounds 70% of which are nonbasic (e.g., carbazole type) while the rest are basic (e.g., quinoline type). Light cycle oil (LCO), a feedstock used for diesel and thermally stable naphthenic jet fuels, contains much higher nitrogen, predominantly nonbasic in nature.^[8,11] Diesel and some jet fuel feedstocks, therefore, have enough nitrogen species to significantly influence deep HDS.

Several researchers have clearly established the inhibiting effect of basic nitrogen compounds on the HDS of thiophene and DBT.^[4] A much smaller body of work has dealt with the effect of nonbasic nitrogen on HDS and the results seem to be inconclusive. For example, La Vopa and Satterfield and, more recently, Furimsky and Massoth have reported on the inhibiting effects of carbazole and indole, respectively, for the HDS of DBT.^[23,26] Similarly, others found the inhibiting effects of carbazole and indole comparable to that of basic nitrogen compounds such as quinoline.^[4] However, a very recent study found carbazoles having little negative effect on the HDS of DBT and substituted DBTs found in their blend of gas oil and LCO.^[4] They, however, determined carbazoles and substituted carbazoles as the least reactive nitrogen compounds.

In addition to ambiguity on the effect of basic and nonbasic nitrogen, little is known about the exact mechanism of nitrogen poisoning. Kwak et al. found interesting influences of carbazole and quinoline on the HDS of DBT, 4-MDBT, and 4,6-DMDBT over a Co-Mo/ γ -Al₂O₃ catalyst.^[4] While both nitrogen compounds inhibited conversion of all three PASCs, the HDS of DBT was only mildly poisoned till at least 500 ppm of the nitrogen compound was present in the feedstock. More profoundly, the nitrogen compounds inhibited different types of sites on the catalyst. For example, the HDS of DBT occurred less through the hydrogenation route when poisoned with nitrogen compounds. Nagai and Kabe also

obtained similar results with the HDS of DBT on a sulfided Mo/ γ -Al₂O₃ catalyst.^[4] In the case of the substituted DBTs, however, Kwak et al. noticed that conversion was achieved mainly through the hydrogenation pathway, i.e., the hydrogenolysis route was inhibited.^[4]

Hydrogen sulfide

Several researchers have experimentally demonstrated the inhibiting influence of hydrogen sulfide (H₂S) on HDS.^[1,4] This inhibiting influence is expected from simple and kinetic and equilibrium considerations. Refiners take great care to keep H₂S in commercial hydrotreaters at an optimum level. For example, hydrogen—used in excess in a hydrotreater—is recirculated after scrubbing out the H₂S by-product carefully. The recycle stream needs to contain an optimum level of H₂S to keep the catalyst as a sulfide and thus maintain its activity and selectivity. Sie has described other process options to minimize inhibition effects by H₂S, e.g., countercurrent flow reactors and monolithic catalyst systems.^[27]

Hydrogen sulfide also inhibits HDS activity by modifying the catalyst surface. For example, high concentrations of H₂S are known to increase the density of Bronsted acid sites on a commercial catalyst.^[2] Several researchers have found H₂S to poison mainly hydrogenolysis sites on a sulfided Co-Mo/ γ -Al₂O₃ catalyst.^[2]

Therefore, the petroleum refining industry faces a major challenge to meet the new stricter sulfur specifications and the need for fuel cell applications in the early 21st century when the quality of the crude oils continue to decline in terms of increased sulfur content and decreased API gravity.

APPROACHES TO ULTRADEEP DESULFURIZATION PROCESS

Ultradeep desulfurization approaches include: 1) improving catalytic activity by new catalyst formulation for HDS of 4,6-DMDBT; 2) tailoring reaction and process conditions; 3) designing new reactor configurations; and 4) developing new processes. One or more approaches may be employed by a refinery to meet the challenges of producing ultraclean fuels at an affordable cost.

Improving Catalytic Activity by New Catalyst Formulations

Design approaches for improving catalytic activity for ultradeep HDS focus on how to remove 4,6-DMDBT

more effectively, by modifying catalyst formulations to 1) enhance hydrogenation of the aromatic ring in 4,6-DMDBT by increasing the hydrogenating ability of the catalyst; 2) incorporate acidic feature in the catalyst to induce isomerization of methyl groups away from the 4- and 6-positions; and 3) remove inhibiting substances (such as H_2S). The catalytic material formulations may be improved for better activity by using different supports (carbon, TiO_2 , $TiO_2-Al_2O_3$, HY, MCM-41, etc.) for conventional alumina-supported Co-Mo, Ni-Mo, and Ni-W catalysts; increasing the loading level of active metal (Mo, W, etc.); adding one more base metal (e.g., Ni to Co-Mo or Co to Ni-Mo); and incorporating a noble metal (Pt, Pd, Ru, etc.). Catalyst companies such as Akzo Nobel, Criterion, and Haldor Topsøe have developed more active catalysts for deep HDS.

One catalyst development approach, the inclusion of acidic functionality in HDS catalysts, is discussed briefly here as a case study. Turaga and Song hypothesized that molybdenum sulfide (MoS_2) supported on mesoporous molecular sieve MCM-41 and promoted by cobalt would have superior activity for deep HDS because of MCM-41's 1) high surface area and uniform mesopores and 2) superior acidity as compared to conventional supports such as γ -alumina ($\gamma-Al_2O_3$).^[28] They synthesized and screened a series of mesoporous aluminosilicate MCM-41 molecular sieves with different silica/alumina (SiO_2/Al_2O_3) ratios (the framework SiO_2/Al_2O_3 ratio determines support acidity) as catalyst supports for varying loadings of cobalt oxide (CoO) and molybdenum oxide (MoO_3).

The activity of the MCM-41-supported catalysts was found to depend on the CoO- MoO_3 loading. At CoO- MoO_3 loadings typical of commercially available HDS catalysts, MCM-41-supported catalysts were only slightly better. At higher loadings—27.0% (by weight) MoO_3 and 5.8% CoO—MCM-41-supported catalysts were twice more active than the commercial catalyst. This difference in activities is related to the degree of MoS_2 stacking as suggested by temperature-programmed reduction and X-ray photoelectron spectroscopy. Additional characterization studies, furthermore, suggest the presence of a different and more active catalytic phase on MCM-41-supported catalysts.

A remarkable increase in the conversion of 4,6-DMDBT was observed over MCM-41-supported catalysts with decreasing SiO_2/Al_2O_3 ratio (or increasing acidity). More significantly, the SiO_2/Al_2O_3 ratio of MCM-41 has a profound effect on product distribution and catalyst selectivity. Irrespective of CoO- MoO_3 loading, catalysts using MCM-41 with a SiO_2/Al_2O_3 ratio of 50 convert more of 4,6-DMDBT through the highly desirable hydrogenolysis pathway. In comparison, the $\gamma-Al_2O_3$ -supported commercial

catalyst relies on the hydrogenation pathway for catalytic conversion. The acidity of these catalysts was measured using temperature-programmed desorption of *n*-butylamine and aluminum magic angle spinning nuclear magnetic resonance and correlated to their selectivities for hydrogenolysis and hydrocracking.

Tailoring Reaction and Process Conditions

Tailoring process conditions aims at achieving deeper HDS with a given catalyst in an existing reactor without changing the processing scheme, with no or minimum capital investment. The parameters include those that can be tuned without any new capital investment (space velocity, temperature, pressure) and those that may involve some relatively minor change in processing scheme or some capital investment (expansion in catalyst volume or density, H_2S scrubber from recycle gas, improved vapor-liquid distributor). First, space velocity can be decreased to increase the reactant-catalyst contact time. More refractory sulfur compounds would require lower space velocity for achieving deeper HDS. Second, temperature can be increased, which increases the rate of HDS. Higher temperature facilitates more of the high activation energy reactions. Third, hydrogen pressure can be increased. Fourth, improvements can be made in vapor-liquid-solid contact, which effectively increases the surface area of the catalyst. Fifth, the concentration of hydrogen sulfide in the recycle stream can be removed by scrubbing. Because H_2S is an inhibitor to HDS, its buildup in high-pressure reactions through continuous recycling can become significant. Recent work on decreasing the concentration of hydrogen sulfide in gas phase has been discussed by Sie.^[27] Finally, more volume of catalyst can be used, through either catalyst bed volume expansion or more dense packing.

Designing New Reactor Configurations

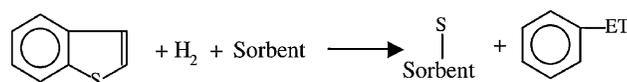
Industrial reactor configuration for deep HDS of gas oils in terms of reaction order, and the effects of the H_2S produced have been discussed by Sie.^[27] The reactor design and configuration involve both single-stage and two-stage desulfurization processes. Desulfurization processes in use today in the United States generally have only one reactor, because of the need to only desulfurize diesel fuel to 500 ppmw or lower. Hydrogen sulfide strongly suppresses the activity of the catalyst for converting the refractory sulfur compounds, which should occur in the major downstream part of a cocurrent trickle-bed reactor during deep desulfurization.

The normally applied cocurrent trickle-bed single reactor is, therefore, not the optimal technology for deep desulfurization. A second reactor can be used, particularly to meet the lower sulfur levels. Both desulfurization and hydrogenation in the second reactor can be improved by removing H_2S and NH_3 from the exit gas of the first reactor before entering the second reactor. This last technical change is to install a complete second stage to the existing one-stage hydrotreater. This second stage would consist of a second reactor, and a high-pressure hydrogen sulfide scrubber between the first and the second reactor. Assuming use of the most active catalysts available in both reactors, UOP projects that converting from a one-stage to a two-stage hydrotreater could produce 5 ppm sulfur relative to the current level of 500 ppm today.^[29]

A new way of reactor design is to have two or more catalyst beds, which are normally placed in separate reactors, within a single reactor shell and have both cocurrent and countercurrent flows. This new design was pioneered by ABB Lummus and Criterion, as represented by their SynSat process.^[30] Traditional reactors are cocurrent in nature. The hydrogen is mixed with the distillate at the entrance to the reactor and the mixture flows through the reactor. The advantage of cocurrent design is practical; it eases the control of gas-liquid mixing and contact with the catalyst. The disadvantage is that the concentration of H_2 is the highest in the front of the reactor and lowest at the outlet. The opposite is true for the concentration of H_2S . The novel solution to this problem is to design a countercurrent reactor, where the fresh H_2 is introduced from the bottom of the reactor and the liquid distillate from the top. Here, the hydrogen concentration is highest (and the hydrogen sulfide concentration is lowest) where the reactor is trying to desulfurize the most difficult (sterically hindered) compounds. The difficulty of countercurrent designs in the case of distillate hydrotreating is vapor-liquid contact and the prevention of liquid flooding and hot spots within the reactor. The SynAlliance (consisting of ABB Lummus, Criterion Catalyst Corp., and Shell Oil Co.) patented a countercurrent reactor design called SynTechnology. With this technology, in a single reactor design, the initial portion of the reactor will follow a cocurrent design, while the last portion of the reactor will be countercurrent.^[30]

Developing New Processes

Among the new process concepts, design approaches for ultradeep desulfurization focus on several different areas.^[1] Some researchers are looking at adsorption and sulfur atom extraction—removing sulfur by using



Scheme 2 Basic principle of the S Zorb Sulfur Removal Technology process developed by Phillips Petroleum for sulfur removal from liquid fuel at elevated temperatures under low H_2 pressure.

reduced metals to react with sulfur to form metal sulfides at elevated temperatures under H_2 atmosphere without hydrogenation of aromatics. For instance, Phillips Petroleum (now Conoco Phillips) studied its refineries and concluded the use of hydrotreating technologies to reach ultralow sulfur levels in gasoline to be a cost-prohibitive option. It developed a new process, S Zorb Sulfur Removal Technology for gasoline and diesel, in which the sulfur atom in the sulfur-containing compounds adsorbs onto a sorbent and reacts with the sorbent (see Scheme 2) at elevated temperatures under low H_2 pressure.^[31] On another front, researchers at Pennsylvania State University are investigating selective adsorption for removal of sulfur compounds (PSU-SARS) in which sulfur is removed under ambient or mild conditions without using hydrogen by selective interaction with sulfur compounds in the presence of aromatic hydrocarbons.^[6,7,32] Researchers at University of Michigan are using pi-complexation for adsorption of sulfur compounds.^[33] In other studies, sulfur compounds are oxidized by liquid-phase oxidation reactions with or without ultrasonic radiation, followed by separation of the oxidized sulfur compounds.^[34] Finally, biodesulfurization is a process that removes sulfur from fossil fuels using bacteria via microbial desulfurization. Several recent reviews outline the progress in the study of microbial desulfurization from the basic and practical point of view.^[35,36]

CONCLUSIONS

Heightened concerns for cleaner air and increasingly more stringent regulations on sulfur contents in transportation fuels will make desulfurization more and more important. The sulfur problem is becoming more serious in general, particularly for diesel fuels, as the regulated sulfur content is getting an order of magnitude lower, while the sulfur content of crude oils refined in the United States is becoming higher. The chemistries of gasoline and diesel fuel processing have evolved significantly around the central issue of how to produce cleaner fuels in a more efficient, environment friendly, and affordable fashion. New design approaches are necessary for making affordable ultraclean fuels.

REFERENCES

- Girgis, M.J.; Gates, B.C. Reactivities, reaction networks, and kinetics in high-pressure catalytic hydroprocessing. *Ind. Eng. Chem.* **1991**, *30*, 2021.
- Topsoe, H.; Clausen, B.S.; Massoth, F.E. Hydro-treating catalysis. In *Science and Technology*; Springer-Verlag: Berlin, 1996; 310 pp.
- Whitehurst, D.D.; Isoda, T.; Mochida, I. Present state of the art and future challenges in the hydrodesulfurization of polyaromatic sulfur compounds. *Adv. Catal.* **1998**, *42*, 345.
- Babich, I.V.; Moulijn, J.A. Science and technology of novel processes for deep desulfurization of oil refinery streams: a review. *Fuel* **2003**, *82* (6), 607–631.
- Song, C. An overview of new approaches to deep desulfurization for ultra-clean gasoline, diesel fuel and jet fuel. *Catal. Today* **2003**, *86* (1–4), 211–263.
- Song, C.; Ma, X. New design approaches to ultra-clean diesel fuels by deep desulfurization and deep dearomatization. *Appl. Catal. B Environ.* **2003**, *41* (1–2), 207–238.
- Song, C. Fuel processing for low-temperature and high-temperature fuel cells. Challenges, and opportunities for sustainable development in the 21st century. *Catal. Today* **2002**, *77* (1), 17–50.
- Prins, R. Catalytic hydrodenitrogenation. *Adv. Catal.* **2001**, *46*, 399–464.
- DeCicco, J.; Mark, J. Meeting the energy and climate challenge for transportation in the United States. *Energy Policy* **1998**, *26*, 395–412.
- EPA. Control of air pollution from new motor vehicles: heavy-duty engine and vehicle standards and highway diesel fuel sulfur control requirements. *Fed. Reg.* **2001**, *66*, 5101–5150.
- Song, C. Introduction to chemistry of diesel fuels. In *Chemistry of Diesel Fuels*; Song, C., Hsu, C.S., Mochida, I., Eds.; Taylor & Francis: New York, 2000; 1–60.
- National Petroleum Refiners Association. *Hydroprocessing—Fuel Quality, 1998 Q&A Minutes*; National Petroleum Refiners Association: Washington, DC, 1998.
- EPA. Control of diesel fuel quality. *Fed. Reg.* **1999**, *64*, 26142–26158.
- Manufacturers of Emission Controls Association. *The Impact of Sulfur in Diesel Fuel on Catalyst Emission Control Technology*; Manufacturers of Emissions Controls Association: Washington, DC.
- BP. *BP Statistical Review of World Energy 2001*; BP p.l.c.: London, U.K., 2001.
- Touville, M.S.; McVicker, G.; Daage, M.; Hudson, C.W.; Klein, D.P.; Cook, B.R.; Chen, J.G.; Hantzer, S.; Vaughan, D.E.W.; Ellis, E.S. Selective ring opening of naphthenic molecules. In 17th North American Catalysis Society Meeting, Toronto, Canada, 2001.
- Banerjee, N.; Hakim, D. U.S. ends car plan on gas efficiency; looks to fuel cells. *The New York Times* **2002**, Jan 9, A1.
- Nag, N.K.; Spare, A.V.; Broderick, D.H.; Gates, B.C. Hydrodesulfurization of polycyclic aromatics catalyzed by sulfided CoO–MoO₃/γ-Al₂O₃: the relative reactivities. *J. Catal.* **1979**, *57*, 509–512.
- Ma, X.; Sakanishi, K.; Isoda, T.; Mochida, I. Quantum chemical calculation on the desulfurization reactivities of heterocyclic sulfur compounds. *Energy Fuels* **1995**, *9*, 33–37.
- Ma, X.; Sakanishi, K.; Mochida, I. Hydrodesulfurization reactivities of various sulfur compounds in diesel fuel. *Ind. Eng. Chem. Res.* **1994**, *33*, 218–222.
- Schulz, H.; Bohringer, W.; Waller, P.; Ousmanov, F. Gas oil deep hydrodesulfurization: refractory compounds and retarded kinetics. *Catal. Today* **1991**, *49*, 87–97.
- Lo, H.S. Modeling of Hydrotreating. Ph.D. Thesis, Department of Chemical Engineering, University of Delaware, Newark, DE, **1981**.
- LaVopa, V.; Satterfield, C.N. Poisoning of thiophene hydrodesulfurization by nitrogen compounds. *J. Catal.* **1998**, *110*, 375–387.
- Nagai, M.; Kabe, T. Selectivity of molybdenum catalyst in hydrodesulfurization, hydrodenitrogenation, and hydrodeoxygenation: effect of additives on dibenzothiophene hydrodesulfurization. *J. Catal.* **1983**, *81*, 440–449.
- Isoda, T.; Nagao, S.; Ma, X.; Korai, Y.; Mochida, I. Hydrodesulfurization of refractory sulfur species. 1. Selective hydrodesulfurization of 4,6-dimethyldibenzothiophene in the major presence of naphthalene over CoMo/Al₂O₃ and Ru/Al₂O₃ blend catalysts. *Energy Fuels* **1996**, *10*, 482–486.
- Furimsky, E.; Massoth, F.E. Deactivation of hydroprocessing catalysts. *Catal. Today* **1999**, *52*, 381–495.
- Sie, S.T. Reaction order and role of hydrogen sulfide in deep hydrodesulfurization of gas oil: consequences for industrial reactor configuration. *Fuel Proc. Tech.* **1999**, *61*, 149–171.
- Turaga, U.T.; Song, C.; Turaga, T.; Song, C. MCM-41-supported Co–Mo Catalysts for deep hydrodesulfurization of light cycle oil. *Catal. Today* **2003**, *86* (1–4), 129–140.
- EPA-Diesel RIA. *Regulatory Impact Analysis: Heavy-Duty Engine and Vehicle Standards and Highway Diesel Fuel Sulfur Control Requirements*, Air and Radiation EPA420-R-00-026;

- United States Environmental Protection Agency, Dec. 2000.
30. Dautzenberg, F. A call for accelerating innovation. *Cattech* **1999**, 3 (1), 54–63.
 31. Gislason, J. Phillips sulfur-removal process nears commercialization. *Oil Gas J.* **2002**, 99 (47), 74–76.
 32. Ma, X.; Sun, L.; Song, C. A new approach to deep desulfurization of gasoline, diesel fuel and jet fuel by selective adsorption for ultra-clean fuels and for fuel cell applications. *Catal. Today* **2002**, 77 (1–2), 107–116.
 33. Hernandez-Maldonado, A.J.; Yang, R.T. Desulfurization of liquid fuels by adsorption via complexation with Cu(I)-Y and Ag-Y zeolites. *Ind. Eng. Chem. Res.* **2003**, 42 (1), 123–129.
 34. Aida, T.; Yamamoto, D.; Iwata, M.; Sakata, K. Development of oxidative desulfurization process for diesel fuel. *Rev. Heteroatom Chem.* **2000**, 22, 241–256.
 35. MacFarland, B.L.; Boron, D.J.; Deever, W.; Meyer, J.A.; Johnson, A.R.; Atlas, R.M. Biocatalytic sulfur removal from fuels: applicability for producing low sulfur gasoline. *Crit. Rev. Microbiol.* **1998**, 24 (2), 99–147.
 36. Ohshiro, T.; Izumi, Y. Microbial desulfurization of organic sulfur compounds in petroleum. *Biosci. Biotechnol. Biochem.* **1999**, 63 (1), 1–9.