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Catalysis science and technology for cleaner transportation fuels

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Abstract

The production of liquid transportation fuels such as gasoline, diesel and jet fuel from petroleum involves the use of a variety of catalytic processes. Although the petroleum refining industry is quite mature, fuel composition requirements continue to evolve with time in response to environmental legislation and changes in engine design. In addition, petroleum feedstocks are becoming heavier and more sour with time. New technology is emerging that allows efficient conversion of natural gas to liquid hydrocarbon fuels. Taken together, these changes pose considerable challenges to the refining industry and significant advances in catalysis are needed to meet the challenge. © 2000 Published by Elsevier Science B.V.

Keywords: Transportation fuels; Catalytic process; Refining industry; Petroleum feedstocks

1. Introduction

Over 80 million barrels of petroleum are processed every day in refineries around the world to meet the demand for liquid transportation fuels such as gasoline, diesel fuel and jet fuel. Despite the advances made in improving fuel economy of automobiles and trucks, worldwide consumption of transportation fuels has continued to grow and is expected to remain strong well into the next millennium.

Catalysis plays a key role in petroleum refining. A variety of processes are required to transform raw petroleum crude oil into finished products. These processes may be based on acid catalysis as in Fluid Catalytic Cracking and Alkylation or on transition metal catalysis as in hydrotreating. In some cases, the catalysis is bifunctional relying on a combination of acid and metal catalysis.

For a number of years, the oil and auto industry have worked in a cooperative effort called the Auto-Oil Air Quality Research Program to understand the relationships between fuel composition and vehicle emissions. The intent of this effort is to make cost-effective improvements to transportation vehicles and fuels to minimize the adverse impacts on the environment resulting from the combustion of fossil fuels. Regulatory changes being enacted over the next 10 years will require dramatic changes in fuel composition. Both gasoline and diesel fuel will likely be required to have an ultra-low sulfur content. The hydrocarbon composition of the fuel will shift away from aromatics and olefins to hydrocarbon types such as naphthenes and paraffins that burn more cleanly. As engine technology advances are made to high efficiency engines that more effectively mix air and fuel in the combustion chamber, changes in fuel composition will be driven by the need to match fuel volatility and viscosity with the fuel injection design of the engine. Hydrocarbon based fuels for fuel cell powered vehicles will have a completely different set of composition requirements as characteristics such as octane or cetane number will no longer be relevant.

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In addition to changes in fuel composition, the petroleum feedstocks coming into the refinery are changing with time. The recent decline in crude oil prices notwithstanding, future crude oil supplies are expected to become heavier and to contain higher concentrations of sulfur, or be more “sour”. Emerging technology for the conversion of natural gas to pristine hydrocarbon fuels will also become important in the future. Thus, against this backdrop of constant change, the technology challenge for the petroleum industry will be to provide cleaner fuels from more difficult feedstocks at the lowest cost to the consumer. Significant advances in catalysis science and technology are needed to meet this challenge.

2. Regulatory outlook

Environmentally driven regulations are requiring significant improvement in the quality of diesel and gasoline in many parts of the world. Reducing the concentration of organic sulfur species in gasoline has been recognized as one way of reducing emissions, most notably nitrogen oxides (NO_x). In the US, reformulated gasoline has since January 1998 been governed by the EPA’s Phase I Complex Model. This has resulted in lowering the average sulfur content of reformulated gasoline to about 320 ppm. In the year 2000, the EPA Phase II Complex Model will require about 150 ppm S, with the possibility of reductions to as low as 30 ppm by 2005. California introduced more severe California Air Resources Board (CARB) Phase II gasoline regulations in 1996, placing limits (avg.) on gasoline of 30 ppm sulfur, 22% aromatics, 4% olefins, 0.8% benzene, and 1.8% oxygen. Automobile manufacturers have asked CARB to reduce sulfur to 5 ppm by 2005 in order to enable them to meet new stringent exhaust emission standards. Due to the concerns of groundwater contamination, high octane oxygenates such as MTBE which are prevalent in the US, are under increasing pressure to be eliminated from gasoline. Canada has recently outlined regulations involving a two-step plan which mandates 150 ppm sulfur in gasoline by 2002, with further reduction to a 30 ppm average by 2005. In addition, Canada cut benzene content in gasoline to 1% effective 1 January 1999. In the European Union, sulfur levels in gasoline will be reduced to 150 ppm in the year 2000, and then to 50 ppm in 2005. Further restrictions on gasoline composition in Europe include 18% olefins, 1% benzene, 42% aromatics, and 2.7% oxygen (maximum) in the year 2000 with aromatics being reduced to 35% in the year 2005.

Automotive diesel fuels are also throughout the world facing significant limits on a number of specifications. In Europe, sulfur is the primary target since its connection with particulate emissions is generally accepted. Sulfur levels will drop to 350 ppm in the year 2000 and then to 50 ppm in 2005. Other diesel fuel specifications include 845 kg/m^3 density, 360°C T95, 51 cetane number, and 11% polyaromatic hydrocarbons in the year 2000. There is the potential that these specifications could be further reduced to 825 kg/m^3 density, 340°C T95, 58 cetane number, and 1% polyaromatics. In the US, the 1990 Clean Air Act specified that all on-road diesel fuels must meet a 500 ppm sulfur limit with a minimum cetane index of 40 and a maximum aromatics content of 35%. In California, CARB implemented a more stringent specification of 500 ppm sulfur, 10% aromatics, and 48 cetane number. Beginning in 1997, Canada set limits of all on-road diesel fuel at 500 ppm sulfur and cetane specifications of 45 by the year 2000. In Japan diesel sulfur specifications are 500 ppm sulfur and 45 cetane number. Further reductions in diesel sulfur content in the future are very possible.

3. A typical refinery

Fig. 1 provides a simplified schematic of a typical petroleum refinery and highlights the processes involved in making liquid transportation fuels in which catalysis plays a key role. Crude oil entering the refinery is first fractionated into different boiling ranges in a series of atmospheric pipestills (APS) and vacuum pipestills (VPS). The lighter liquid petroleum fraction in the gasoline boiling range is called naphtha; this can be processed in several ways, including isomerization, hydrotreating and/or reforming. Isomerization is a process that utilizes a bifunctional acidic and metal containing catalyst in the presence of hydrogen to isomerize low octane paraffins into branched paraffins that have improved octane. Hydrotreating is a process that utilizes a supported metal sulfide catalyst in the presence of hydrogen to remove sulfur and nitrogen

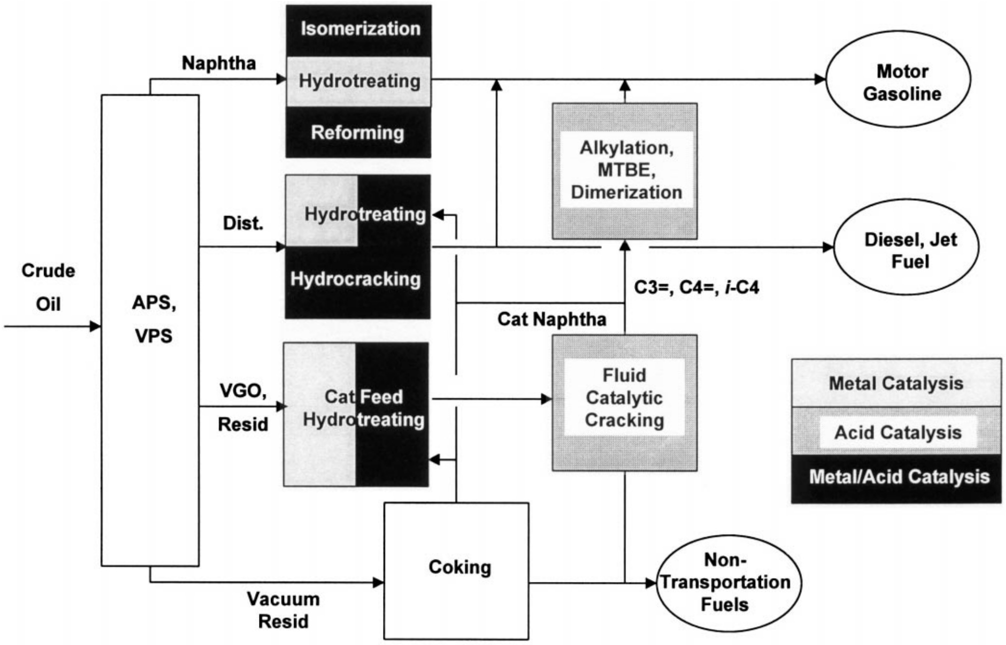


Fig. 1. Simplified flow scheme for a typical refinery.

from the naphtha. Reforming is a process that uses a catalyst with noble metal on a support having some acidity. Reforming converts cycloparaffins, known as naphthenes, and paraffins into single ring aromatics having high octane. Reforming is also an important source of hydrogen for use in other refinery processes that consume hydrogen.

The distillate fraction, which boils in the range needed for making diesel and jet fuel, is typically either hydrotreated to remove heteroatoms such as sulfur and nitrogen or hydrocracked to both remove sulfur/nitrogen and to crack some of the distillate into gasoline. These hydrotreating and hydrocracking processes also help to remove heteroatoms from cracked distillate streams produced in other units such as coking or fluid catalytic cracking. As with the naphtha processes, these involve either metal based or bifunctional metal/acid catalysis.

The next boiling fraction is called vacuum gas oil (VGO). The VGO is often sent directly to a fluid catalytic cracker (FCC), sometimes referred to as a “cat unit” for short. However, hydrotreating of the VGO fraction prior to FCC in order to reduce sulfur content in the final products is becoming more and more common. Sometimes, part or all of the highest boiling crude oil fraction, called resid, is also converted in FCC. The FCC is based on an acid catalyst containing crystalline aluminosilicates known as zeolites. The FCC process is very effective at cracking these higher boiling streams into “cat naphtha” as well as into lighter olefins such as propylene and butylenes. A significant amount of *iso*-butane is also produced. These light streams can be further processed over acid based catalysts via alkylation or dimerization to make high octane gasoline blendstock. The *iso*-butylene is often used for reaction with methanol to make methyl-tertiary-butylether (MBTE) which has high octane and is an important source of oxygen for gasoline formulations where oxygen is required to help to reduce CO emissions from automobiles. The heaviest resid fraction is the most challenging feedstock of all as it typically contains the highest concentrations of heteroatoms and significant amounts of highly aromatic, polar molecules that readily poison catalysts in catalytic processes. Thus, the vacuum resid is most often converted via a non-catalytic thermal process known as coking which generates lighter liquid streams and a solid coke by-product. However, even

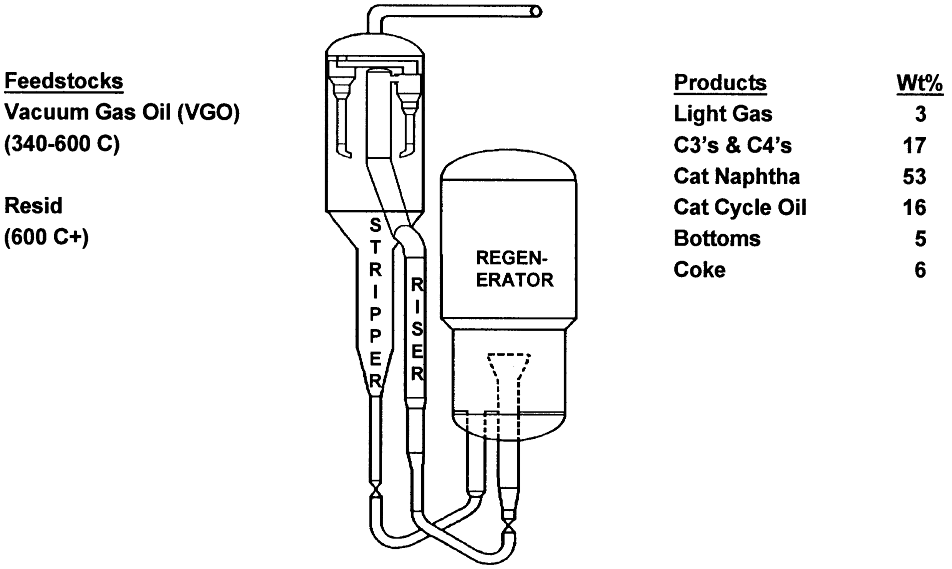


Fig. 2. Fluid catalytic cracking is a key conversion unit.

for this fraction, catalytic processes relying on metal catalysts and high hydrogen pressure are sometimes used to convert the resid to lighter products.

The net effect of petroleum refining is an extensive redistribution of atoms in order to meet fuel composition requirements. Some refinery processes, such as coking, "reject" carbon from the petroleum in the form of coke. Reforming "rejects" hydrogen from gasoline range molecules to increase the octane through aromatic molecules. Hydrotreating adds hydrogen back to other molecules to reduce aromatic content in diesel and jet fuel.

4. Fluid catalytic cracking

Fluid catalytic cracking is the key conversion unit for many modern refineries. Fig. 2 shows a schematic drawing of the FCC unit along with typical feedstocks and products. VGO (and sometimes resid) is cracked over a fluidized catalyst in a riser reactor converting the high boiling hydrocarbons primarily to cat naphtha. The cracking reaction is highly endothermic consuming a large amount of heat. During the cracking step, coke is deposited on the powdered solid acid catalyst, quickly deactivating it. The residence time in the riser is usually 5 s or less. Converted products are stripped from the catalyst surface in the stripper using steam and the coke-deactivated catalyst is then transferred to the regenerator where the coke is burned off the catalyst with air. This regeneration step is highly exothermic and heats up the catalyst as well as reactivating the acid sites. The heat from regeneration then supplies the heat of cracking in the riser as the circulating fluidized catalyst connects the two reactions.

The catalyst design is critical in fluid catalytic cracking (Fig. 3). The catalyst consists of microspheres about 60 μm in diameter that can be fluidized with a stream of vapor. Y-zeolite crystals, about 1 μm in diameter, are dispersed in a porous aluminosilicate

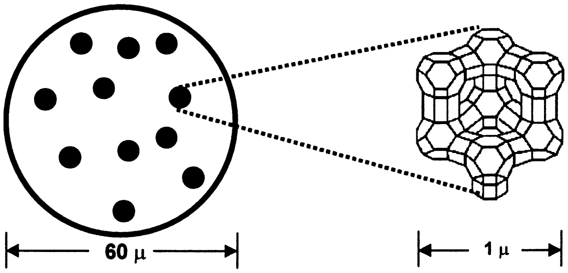


Fig. 3. Design of an FCC catalyst.

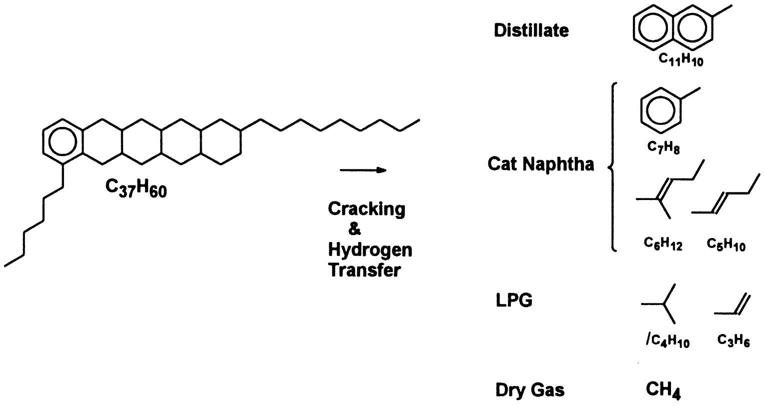


Fig. 4. Typical FCC feed and product molecules.

matrix. Bronsted and Lewis acid sites are distributed throughout the catalyst in both the matrix and the zeolite. The larger feed molecules crack initially on the matrix where the pore sizes are relatively large (20–250 Å). Smaller molecules and cracked intermediate products are then cracked in the zeolite, this having a pore opening a little larger than 7 Å. Thus, cracking is initiated on the matrix and completed in the zeolite. Since current FCC riser designs with short contact time provide less than 5 s residence time, the catalyst pore structure must provide rapid access of the molecules to the acid sites. A good balance between matrix and zeolite activity is therefore crucial. In addition to the Y-zeolite based catalyst, other additives are often included in the catalyst mixture, these having special functionalities such as trapping trace metal feed contaminants like vanadium, CO combustion promoters for the regenerator, and re-cracking naphtha olefins to propylene and butylenes.

FCC presents many catalytic challenges. Fig. 4 shows one possible distribution of product molecules from cracking and hydrogen transfer reactions for a large naphthenoaromatic molecule having the molecular structure $C_{37}H_{60}$. The majority of the distillate molecules produced from modern high conversion FCC units are aromatic as illustrated by methylnaphthalene in the figure. These molecules have relatively low value for diesel and jet fuel. The cat naphtha is highly olefinic and aromatic. This is desirable from a standpoint of providing high octane molecules to the gasoline pool. The light petroleum gas (LPG) consists largely of propylene, butylenes and *iso*-butane. Propylene is a high value precursor to the production of chemicals such as polypropylene. The butylenes and *iso*-butane are useful components for making high octane gasoline or MTBE.

The trace nickel and vanadium contaminants, present in resid in the form of metalloporphyrins and other organo-metal species, offer additional catalytic challenges. Vanadium deposits on the catalyst and accelerates the destruction of the active acid sites in the zeolite, this leading to a loss in crystallinity and activity of the zeolite. Nickel also deposits on the catalyst where it catalyzes undesirable side reactions (dehydrogenation), this resulting in increased coke and hydrogen formation.

Some of the key catalytic challenges for the FCC area include developing super active catalysts that will enable operation at ultra-short contact times at which the selectivities to high value light products are improved. This will require advances in both the zeolitic and matrix components of the catalyst. New catalyst materials will be needed that are resistant to other heavy feed components such as nickel, vanadium and nitrogen. Improved additives for re-cracking naphtha olefins to propylene will increase in importance as the demand for propylene increases in the future. Further, reducing the sulfur content of cat naphtha will be a high priority to meet lower gasoline sulfur specifications.

Additives containing ZSM-5 zeolite are commonly used to increase the yield of light olefins in FCC [1]. As shown in Fig. 5, ZSM-5 re-cracks olefins in the naphtha boiling range to lighter olefins such as

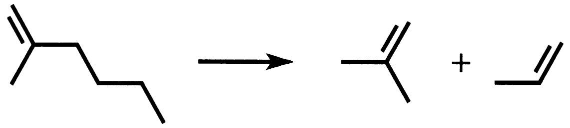


Fig. 5. ZSM-5 re-cracks naphtha olefins.

propylene and *iso*-butylene. Some *iso*-butane is also formed as a result of hydrogen transfer reactions from other hydrogen donor molecules. Smaller amounts of even lighter gas products are also formed.

Conventional FCC units produce about 4 wt.% propylene. Some modern FCC units have been revamped so that they currently achieve up to about twice the propylene yield of conventional units. Further, as indicated in Fig. 6, new advances in catalyst and process technology are emerging [2–4] which deliver substantially higher amounts of propylene. Theoretically, there is additional room for further improvements to be made. Thus, there is significant potential for even higher yields of propylene through the use of improved catalysts. Additionally, with hydrotreated or highly paraffinic feedstocks [5], even higher yields of propylene can be achieved. Exxon has a strong technology capability in this area and has an active research and development program targeted at achieving the full potential.

5. Reducing the sulfur content of gasoline

Future changes in gasoline composition, especially sulfur content, will dramatically affect FCC operations and associated processes that treat FCC feed and products. FCC is the largest contributor to the gasoline pool and, as shown in Table 1, the sulfur content of cat naphtha can be very high compared to future gasoline specifications. FCC is the primary contributor to sulfur in gasoline contributing over 90% of the sulfur [6]. Further, the high olefin content of cat naphtha could also become a challenge in the future. Thus, technology options that crack gasoline range olefins to high value light olefins will become more important in the future. Technology options that lower the sulfur content of gasoline from FCC will also grow in importance.

Table 1
Cat naphtha composition vs. current and future gasoline composition

	Cat naphtha	Current gasoline	Future gasoline
Sulfur (ppm)	50–2500	350	30–50
Olefins (wt.%)	20–35	15	4–18
Aromatics (wt.%)	20–30	35	35

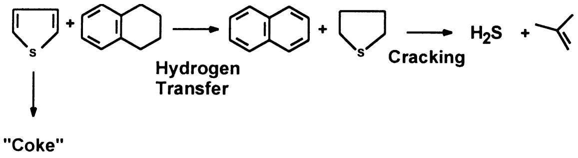


Fig. 7. Opportunities for cat naphtha sulfur management.

There are three primary commercial alternatives for reducing the sulfur in gasoline that comes from FCC. One option is to discover improved FCC catalysts and additives so that the cat naphtha sulfur content is reduced. A second option is to use cat feed hydrotreating to reduce the sulfur content of the feed to the FCC unit. The third option is to hydrotreat the cat naphtha to remove the sulfur from it.

In the FCC unit, catalysis opportunities exist to help reduce the sulfur content of cat naphtha. Much of the sulfur in cat naphtha is thiophenic and cannot be cracked directly to remove the sulfur. However, catalysts or additives that promote hydrogen transfer from a donor molecule to thiophene, as shown in Fig. 7, can transform thiophene into a crackable species

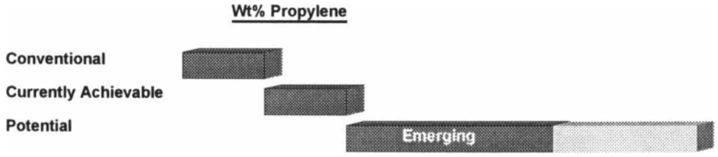


Fig. 6. Propylene production from FCC.

enabling removal of the sulfur as hydrogen sulfide, which can be readily recovered from the FCC product gases [7,8]. Additives are emerging that can reduce cat naphtha sulfur by up to 30% [9]. An alternative option is to design catalysts that selectively adsorb thiophenes and transport them to the regenerator where they are burned. This approach requires effective removal of the sulfur oxides formed from the regenerator flue gas.

Although a very capital intensive process, cat feed hydrotreating (CFHT) provides significant improvements in cat cracking yields, reduces sulfur in FCC naphtha, distillate and fuel oil products, decreases coke make, and lowers regenerator sulfur oxide (SO_x) emissions. In addition, CFHT provides the refinery with added flexibility in that heavier, sulfur-laden feeds can be converted profitably in the FCC unit.

Proper catalyst selection is critical for CFHT. In many cases, a staged catalyst bed is utilized, this being designed to remove specific contaminants (Fig. 8). Typically, wider pore diameter (150–200 Å) NiMo or CoMo based catalysts are used as guard beds and placed in the lead reactor to remove the Ni- and V-containing porphyrins present in heavier feeds. If not controlled, these metals will poison CFHT catalysts. The use of larger pore catalysts is important to minimize pore mouth plugging since Ni and V are deposited into catalyst pores. Operating conditions in the demetallation zone must be carefully chosen as high demetallation rates can quickly lead to pore mouth plugging and reduce the metals-holding capacity of the catalyst. In the main reactor, moderate pore NiMo and NiCoMo catalysts are designed to maximize denitrogenation (HDN) and desulfurization (HDS) activity and to be tolerant of small amounts of Ni and V that slip through the lead reactor. Nitrogen reduction is important as it is not only a poison for CFHT catalysts, but is also a significant poison for the acidic, zeolite-based FCC catalysts. The saturation of large aromatic hydrocarbons in the CFHT unit is valuable for improving the feed quality to the FCC unit. High activity NiMo and NiCoMo catalysts are employed in the tail reactor of the CFHT unit to optimize the saturation of polynuclear aromatic components.

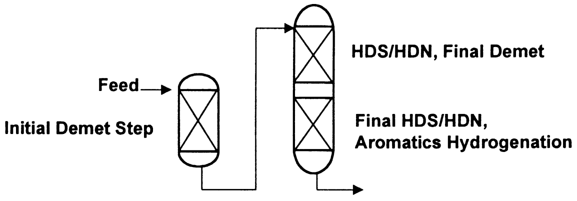


Fig. 8. CFHT process.

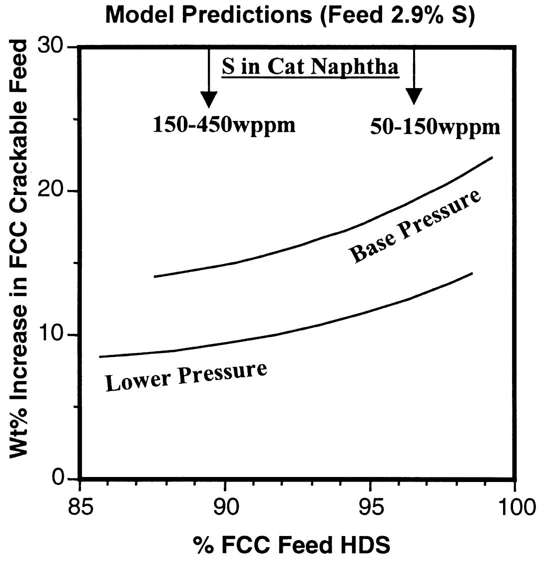


Fig. 9. CFHT performance.

The performance of CFHT on FCC feed quality as a function of % HDS is shown in Fig. 9. The impact of pressure is quite dramatic. At base pressure, FCC feed crackability (to cat naphtha and LPG) increases by 15–20 wt.% with respect to the feed. As sulfur reduction in gasoline becomes more stringent, CFHT leads to lower concentrations of sulfur in the FCC naphtha (gasoline) products. For example, at CFHT desulfurization levels of >95% HDS, the resultant product naphtha sulfur levels from the FCC unit can be reduced to as low as 50 ppm. A lower cost, lower pressure CFHT process is nearly as effective at reducing the sulfur in the FCC naphtha product but it does not have the same impact on FCC feed crackability. Because CFHT is a very capital investment intensive process, catalysts with higher performance for demetallation, HDS, HDN, and aromatics saturation are needed to maximize the feed upgrade to the FCC unit at the lowest possible reaction pressures.

In most refineries, the prime contributor to sulfur in the gasoline pool is FCC naphtha. In contrast to CFHT, hydrodesulfurization of FCC naphtha is a

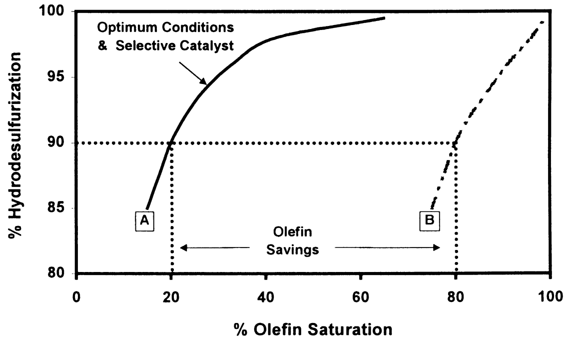


Fig. 10. SCANfining, selective cat naphtha hydrodesulfurization.

low pressure process and consequently, a lower cost process. Hydrotreating naphtha to very deep levels of HDS (<1 ppm S) is possible, for example, with NiMo catalysts. However, FCC naphtha also contains a considerable proportion of valuable, high octane C_5–C_8+ olefins which are completely saturated to paraffins under these severe hydrotreating conditions. Octane reductions of up to 7–10 in research octane number (RON) and 3–4 in motor octane number (MON) would occur [10]. Because of the need to minimize octane loss, new technology has recently been introduced to selectively reduce the sulfur in FCC naphtha while minimizing the hydrogenation of the high octane olefins. Selective desulfurization has an added benefit in that hydrogen consumption is also minimized.

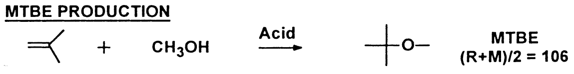
Due to an improved understanding of the inherent compositional characteristics of cat naphtha, it is generally accepted that sulfur compounds concentrate in the higher boiling fractions while olefins concentrate in the lighter fraction. Consequently, fractionating these streams and hydrotreating only the higher boiling fraction enables deep desulfurization while minimizing olefin saturation. However, due to the more stringent gasoline sulfur specs, it may be necessary also to desulfurize the lighter cat naphtha fractions. Exxon Research & Engineering (ER&E) has developed a technology called SCANfining and has jointly commercialized, with Akzo Nobel, a catalyst which provides a highly selective approach for reducing sulfur in cat naphtha [11].

As shown in Fig. 10, two operating curves display the impact of % hydrodesulfurization vs. olefin saturation in a typical FCC naphtha. Curve (A) uses the most selective catalyst and process conditions (i.e. SCANfining); curve (B) uses a non-selective catalyst and non-selective process conditions. Case B shows that a substantial amount of olefin saturation, about 80%, will occur at about 90% HDS. On the other hand, under selective (SCANfining) conditions, case A shows that only 20% olefin saturation occurs at similar levels of HDS. Using SCANfining, octane losses, $\frac{1}{2}(R+M)$, can be minimized to about 1–1.5 at 95% HDS for typical FCC naphtha feeds.

SCANfining takes advantage of a unique CoMo catalyst with low metals content and high dispersion which is specially designed to achieve high HDS/olefin saturation selectivity with excellent maintenance of activity. The development of new catalyst preparation procedures were required because of the importance of the support–metals interaction and support design features. Further advances in selectivity are possible by taking advantage of the different sites [12] (e.g. rim vs. edge) on the catalyst surface (Fig. 11).

6. Improved octane components in gasoline

Reducing the sulfur content of gasoline is not the only challenge facing petroleum refiners in which catalysis plays a major role. Legislative requirements for oxygenated gasoline to help to reduce carbon monoxide emissions has resulted in widespread use of MTBE as a gasoline additive. MTBE is produced from the reaction of methanol and *iso*-butylene over an acid catalyst, typically an ion exchange resin. Besides contributing oxygen to the gasoline composition, MTBE has a high octane blending number (106). The octane blending number is often expressed as the average of the Research Octane (*R*) and the Motor Octane (*M*), i.e. as $\frac{1}{2}(R + M)$. Growing concerns about the use of MTBE in gasoline due to the contamination of groundwater has put the use of MTBE under increasing environmental pressure. Thus, highly branched paraffins, which also have high octane, are expected to grow in importance as environmentally friendly gasoline components.



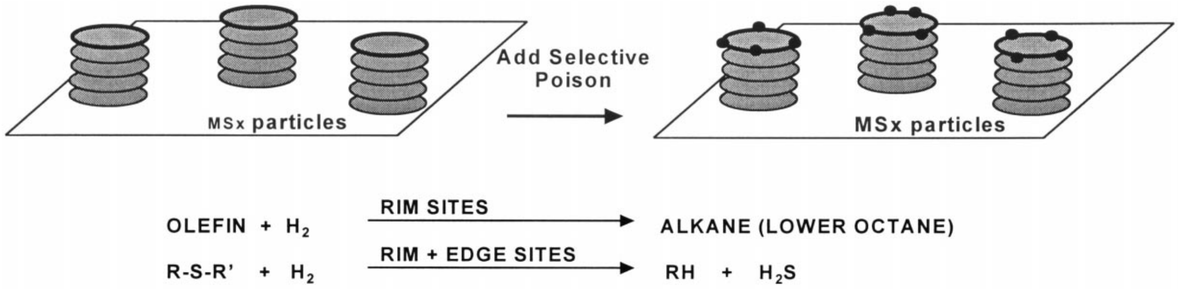
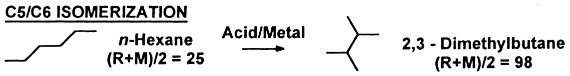
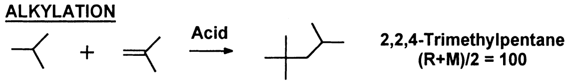


Fig. 11. Catalytic sites on hydrodesulfurization catalysts.

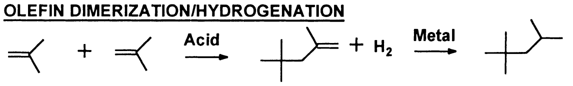
Linear paraffins, typically found in crude oil, have very low octane numbers. For example, *n*-hexane has an octane blending number $\frac{1}{2}(R+M)$ of 25. Catalytic processes are commercially available that isomerize pentanes and hexanes over bifunctional acid/metal catalysts to produce branched paraffins with increased octane. For example 2,3-dimethylbutane, one of the products obtained from hexane isomerization, has an octane number of 98.



Alkylation is another commercial process available to produce highly branched paraffins. In alkylation, a light paraffin such as *iso*-butane is reacted with a light olefin, such as *iso*-butylene, over an acid catalyst to produce branched paraffins like 2,2,4-trimethylpentane which has an octane number $\frac{1}{2}(R+M)$ of 100. Historically, alkylation processes have utilized either hydrofluoric or sulfuric acid as catalysts. However, new alkylation processes are emerging that utilize solid acids to avoid the hazards associated with handling hydrofluoric acid and could save on costs for reprocessing sulfuric acid.



Another approach to making branched, high octane paraffins is to dimerize light olefins such as *iso*-butylene over an acid catalyst, and then hydrogenate the intermediate product in the presence of a metal catalyst to make 2,2,4-trimethylpentane. New technology options are emerging for this type of catalysis as well. Nonetheless, there will be a continuing need for advances in both acid and metal catalysis to make the branched paraffins with the highest octane numbers more selectively and from the lowest-value starting molecules possible.



7. Hydroprocessing technology for diesel fuel

While it has been widely recognized that deep desulfurization of middle distillates can be achieved by conventional single-stage hydrotreating, the key to the design of a low cost, efficient process lies in a thorough understanding of the catalyst and process. The detailed characterization of the catalysts and the kinetics of the process for sulfur-containing species have been an active area of interest for many years [13,14]. Until recently, most integral HDS models have assumed a single reaction order to be applicable for all sulfur-containing molecules. Since sulfur species have widely differing reactivities, such models would show higher reaction orders than 1.0 for data obtained over a wide range of conditions. However, extrapolating mild to moderate severity data to much deeper desulfurization can seriously underestimate reactor volume requirements. Other factors such as co-processing of cracked distillate feedstocks, heat release, and hydrogen partial pressure profiles along the reactor make additional knowledge of the process as well as model sophistication and enhanced molecular characterization methods necessary to meet present and future processing needs.

Since hundreds of distinct sulfur-containing molecular species can be effectively separated and identified with a capillary GC and sulfur specific detector, some “lumping” is required to simplify the modeling task. The relative rates of reaction of different sulfur “lumps” have been found to differ as much as tenfold. The sulfur-containing molecular classes also differ in boiling point and include non-aromatic non-thiophenes (e.g. sulfides, disulfides, mercaptans), aromatic thiophenes, and three-ring aromatic dibenzothiophenes (DBTs). Depending on the location of the alkyl substituents, DBTs can vary greatly in reactivity. For example, DBT itself or DBTs with substitutions in non-beta positions relative to the sulfur atom are relatively reactive. A methyl or ethyl substituent in the beta position relative to the sulfur atom sterically hinders reactivity and molecules with such substituents are moderately reactive. DBTs with alkyl substitution in both beta positions are very difficult molecules to desulfurize. A separate category, unassigned 3- and 4-aromatic ring sulfur types, includes molecules which are difficult to identify due to their complexity and typically low concentrations. These are classified as moderate to difficult to react. In addition, an unassigned 1- and 2-ring-aromatic sulfur category was applied to a class of poorly resolved compounds which elutes over a wide range of retention times. This category of molecule is also moderately reactive.

It has also been recognized that in addition to exhibiting differences in reactivity the various sulfur types are not evenly distributed across the boiling range of distillate feeds. This effect is illustrated in work carried out by Exxon on a straight-run distillate derived from Arab Medium crude [14]. The feed was fractionated into 11 cuts and the sulfur lumps determined as shown in Fig. 12. The lighter cuts contain easy to moderately reactive sulfur types (e.g. benzothiophenes, non-beta substituted DBTs, etc.) that undergo rapid HDS. The heavier cuts contain the most difficult sulfur types such as di-beta-substituted DBTs. Difficulty converting these species is a key reason why hydrotreating unit performance suffers as the distillation endpoint rises. An extensive database on cracked and virgin feeds has been assembled from pilot plant data at over 400 combinations of operating conditions/feed. These data were used to regress rate constants, activation energies, hydrogen partial pressure constants, etc. for the various sulfur types. The final kinetic model has proven to be highly effective in designing and predicting the performance of ER&E’s diesel oil deep desulfurization (DODD) units [15].

To maximize the productivity of diesel desulfurization units, catalyst vendors and oil companies have focused research on discovering catalysts with high HDS activity. Advances in HDS activity have generally kept pace with the trend to lower sulfur distillates mandated by regulations to meet the 500 ppm S specification (Fig. 13). Several approaches have been used to advance high activity distillate HDS catalysts. One method is to load high levels of Co and Mo oxides on high-density supports. An alternative approach is to

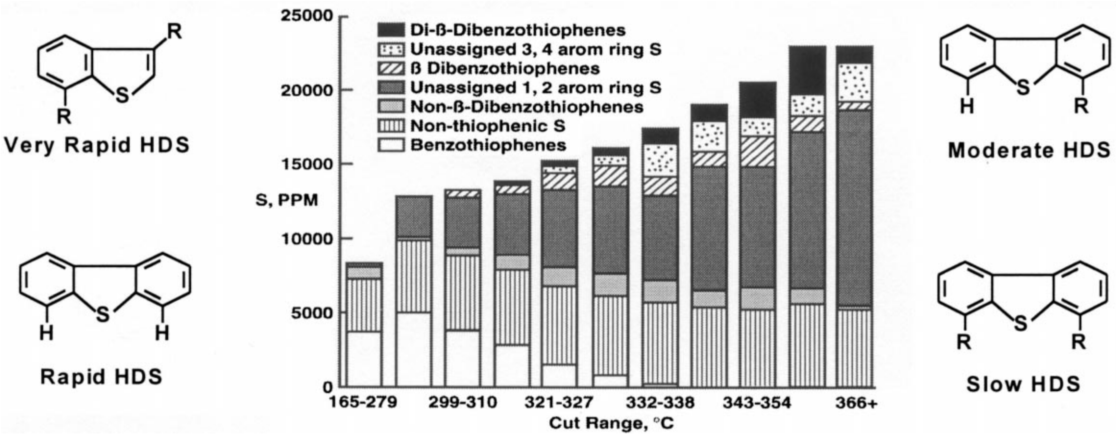


Fig. 12. Sulfur types in Arab Medium distillate.

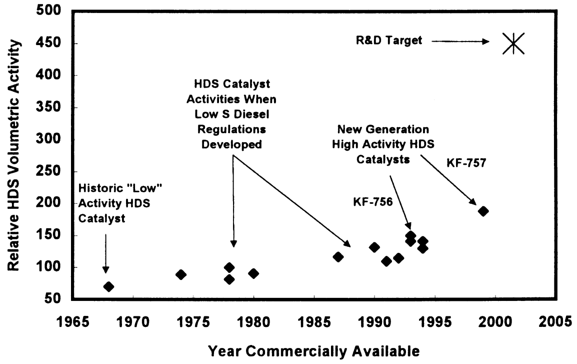


Fig. 13. Advances in HDS catalyst activity.

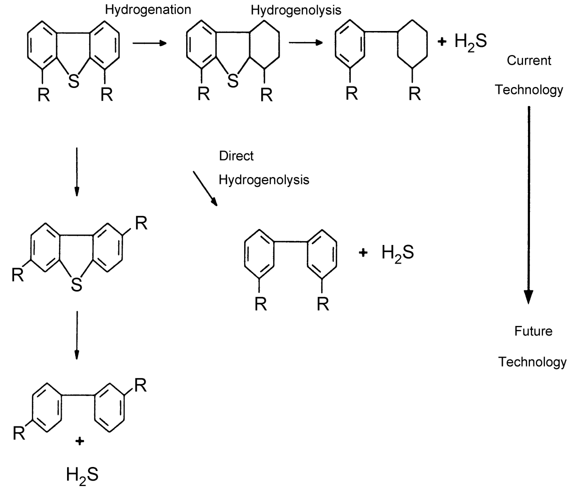


Fig. 14. HDS reaction pathways.

maximize dispersion of the high levels of active metal on supports with moderate density. ER&E took the second approach and focused on catalyst formulations that would target the sulfur species that are hard to desulfurize. One of these catalyst formulations, designated KF-756, was commercialized in collaboration with Akzo Nobel [16]. The increased HDS activity of this catalyst is the result of two complementary achievements: (1) application of a new alumina-based carrier technology, and (2) a specially developed promoter impregnation technique to allow high and uniform dispersion of the metals.

Recently, more advanced HDS catalyst systems have emerged which are driven by the European requirements to reduce distillate sulfur levels to 350 ppm by 2000 and to 50 ppm by 2005. For example, in 1998 Akzo Nobel announced a new high activity HDS catalyst, KF-757, which shows an additional 25% higher HDS activity relative to KF-756. Although the relative activities will differ depending on specific feed and unit operating conditions, a very significant challenge remains in order for catalysts to meet ultra-low sulfur levels (i.e. <50 ppm S). As shown in Fig. 13, in order to utilize the existing reactor, a step-change increase of the order 3–5× in HDS activity would be required relative to commercially available catalysts. This situation reflects the significant differences in kinetic rates of the di-beta-DBTs, which become the predominant remaining sulfur species in the distillate stream when the easier to more moderate sulfur species have been converted.

Advances in both metal sulfide and acid catalysis are required in order to increase the reaction rates of the more difficult sulfur species. Fig. 14 shows three reaction pathways that could lead to desulfurized species. With conventional HDS catalysts, for example $CoMo/Al_2O_3$, the reaction of di-beta-dibenzothiophene (DB-DBT) can proceed via a two-step sequence: partial hydrogenation of one of the aromatic rings followed by hydrogenolysis to form di-beta-phenyl-cyclohexane; or in a single step reaction producing di-beta-biphenyl species and H_2S. Some transition metal sulfides (TMS) have been shown to bring about direct hydrogenolysis to form di-beta-biphenyl derivatives and H_2S. A “volcano” plot was developed which indicated that strong electronic effects occur which might be attributable to the high HDS activity of certain TMS [17]. An additional factor is the crystal structure or “geometric effect” of certain TMS. A linear correlation has been observed between certain isotropic TMS (e.g. RuS_2) with HDS activity in contrast to the more conventional anisotropic metal sulfides (e.g. MoS_2) which do not correlate with activity. It has also been recognized that a strong but reversible metal–sulfur bond interaction is an important feature for high activity [18].

An alternative approach is to isomerize or transalkylate the alkyl groups on the DB-DBT away from the sulfur atom. This reduces steric hindrance and transforms the more difficult DB-DBT to a more moderate to convert species. Catalysts used to effect this transformation require an acidic function, as found, for

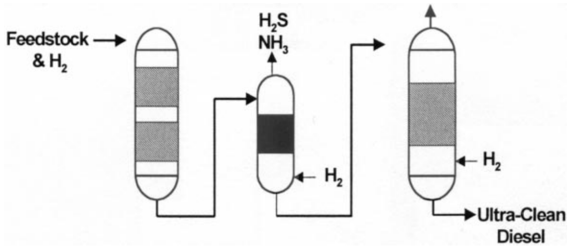


Fig. 15. Aromatics saturation process.

example, in zeolites. The challenge is to balance the level of metal and acid catalysis. For example, Isoda et al. [19] showed that a stacked bed of Ni-supported Y-zeolite (first stage) and a conventional $CoMo/Al_2O_3$ catalyst (second stage) increased the conversion of 4,6-dimethyldibenzothiophene by a factor of 2.

Continued pressure on other diesel properties such as aromatics, cetane index/number, gravity, and distillation endpoint will require further upgrading. Generally, a two-stage process is required; deep desulfurization/denitrogenation followed by aromatics saturation. In the first stage, sulfur and nitrogen are reduced to low levels by severe hydrotreating with CoMo or NiMo catalysts, and then a noble metal catalyst is used in the second stage to achieve saturation of any aromatics. An interstage stripper can be used to remove H_2S and NH_3 produced in the first stage in order to reduce the poisoning impact on the noble metal catalysts in the second stage (Fig. 15). Recent improvements have focused on minimizing the pressure requirements, the application of new, more sulfur/nitrogen tolerant noble metal catalysts, and use of novel process configurations to minimize the poisoning effects of H_2S and NH_3.

The Synsat process [20] operates the first stage (HDS/HDN) in a conventional downflow co-current mode, but employs a countercurrent flow reactor with fresh hydrogen entering at the bottom of the second stage (aromatics saturation) reactor. This process, developed jointly by ABB Lummus Crest and Criterion Catalyst, minimizes the H_2S and NH_3 concentration and maximizes the hydrogen partial pressure at the reactor liquid outlet. This optimizes both the kinetics and the thermodynamic equilibrium for aromatics saturation.

8. Pristine fuel components from natural gas

Another source of low aromatic, high hydrogen content diesel is gas-to-liquids conversion, an area receiving much interest recently [21]. In this case, diesel is derived from natural gas rather than petroleum in catalytic processing equipment most likely located at a gas reserve rather than at a refinery.

An example of Fischer–Tropsch (F–T) diesel is that produced by the advanced gas conversion process, AGC-21, developed by Exxon for converting natural gas to liquid *iso*-paraffins virtually free of typical emission-causing impurities. The AGC-21 process, as shown in Fig. 16, contains multiple new technologies within three main process blocks: synthesis gas generation, hydrocarbon synthesis and hydroisomerization.

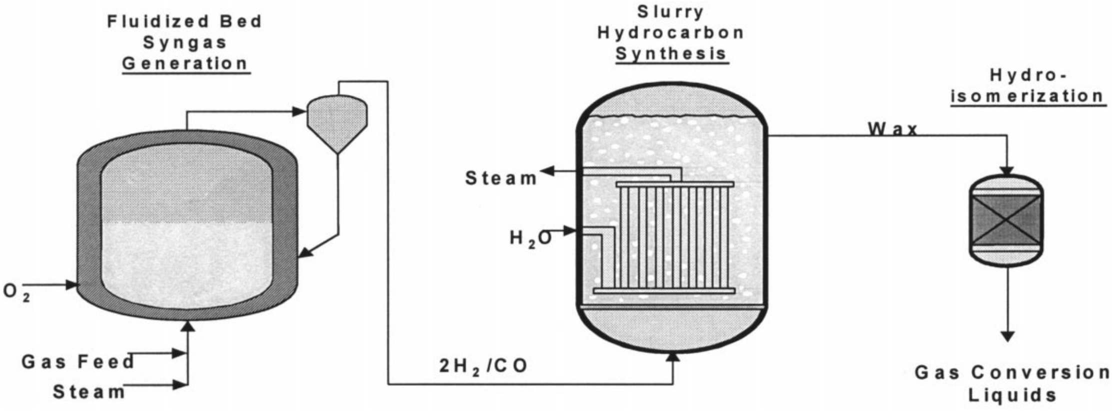


Fig. 16. Exxon's AGC-21 process.

This process, which has been described previously [22], first brings about the conversion of natural gas or methane to hydrogen and carbon monoxide. This is accomplished by contacting methane with steam and limited oxygen in a catalyzed fluid bed reactor where steam reforming and catalytic partial oxidation occur in a single vessel.

The hydrogen–carbon monoxide syngas is then converted almost exclusively to linear paraffins in a novel slurry reactor using a high productivity, cobalt-based hydrocarbon synthesis catalyst. These hydrocarbons are produced at high alpha as determined by Shultz–Flory distributions at high levels of syngas conversion. The full-range, primarily normal paraffin product contains significant 650°F+ waxy material which is a solid at room temperature and melts above 250°F and which is unsuitable for pipelining or transporting in conventional crude carriers. The final step, accomplished with proprietary catalysts in a fixed or trickle bed reactor, mildly isomerizes any normal paraffins to slightly branched molecules which make excellent feeds for refineries and chemical plants. This step along with hydrocarbon synthesis can be altered to control the selectivity and yield of liquids from the process. An AGC-21 plant could be configured to produce a variety of products; one scheme of particular interest produces only light, clean products with diesel yield approaching 80% with the balance as naphtha [23].

The AGC-21 process utilizes major new catalysts, reactor advances, heat and stream integration enhancements and tailored chemistry, thus providing a technological step-out over first generation gas-to-liquids conversion technology. Hydrocarbon synthesis is an especially interesting area to highlight for catalysis advances. Synthesis reactions take place within a three-phase, slurry reactor that enables very high catalyst utilization and productivity. Heat from the very exothermic hydrocarbon synthesis reaction is effectively and efficiently removed with this uniquely designed reactor. The fine particle catalyst, a cobalt-based system, is specifically formulated for slurry operations from a stable of high performance catalysts that enhance slurry reactor features and capacities.

Fundamental studies of the cobalt catalyst system has led to deeper understanding of the relationship between catalyst structure and product selectivity as shown in Fig. 17. The electron micrographs depict individual catalyst particles with active cobalt preferentially placed on a thin outer layer or rim of the support. Catalysts prepared in this manner produce less C_1–C_4 gas than a catalyst with more uniform cobalt distribution into the core of the particle.

An explanation for this behavior is shown on the right-hand side of Fig. 17 which indicates that hydrogen enrichment occurs within the core of a catalyst particle with more uniform cobalt dispersion. This hydrogen-rich synthesis gas is more prone to preferential production of methane. This diffusion-related selectivity debit can be overcome by limiting access by the cobalt to the outer regions of the particle before diffusion and enrichment become significant. Moreover, gases diffusing to the center of the particle remain virtually unreacted until they re-equilibrate with fresh syngas nearer the surface. As an additional benefit, this exothermic synthesis reaction is highly controlled within the particle interior thereby decreasing

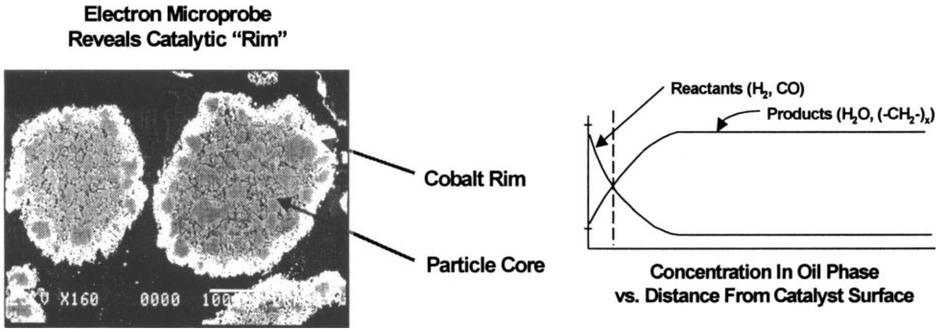


Fig. 17. AGC-21 hydrocarbon synthesis catalyst.

catalyst particle overheating. Consequently, the Exxon slurry process exhibits very high productivity to the preferred liquid products. This is one aspect within the AGC-21 process which is protected by multiple patents covering both catalyst and process innovations. The AGC-21 process is a good example of how advances in catalysis science and technology are providing entirely new options for meeting future clean fuels requirements.

9. Summary

In summary, both acid and metal catalysis play a key role in petroleum refining. Although the petroleum refining industry is very mature, ongoing changes in legislative requirements and engine design will continue to challenge the industry to make changes in fuel composition. Significant advances in catalysis science and technology will be needed to meet the challenge. This provides room to obtain competitive advantage through the development of superior technology options and, as a result, there is intense industry activity to meet the clean fuels challenge of providing cleaner fuels to the consumer from more difficult feedstocks at the lowest cost.

References

[1] J.S. Buchanan, Y.G. Adewuyi, Appl. Catal. A 134 (1996) 247–262.

[2] P.K. Niccum, R.B. Miller, A.M. Claude, M.A. Silverman, N.A. Bhore, K. Liu, G.K. Chitnis, S.J. McCarthy, 1998 NPRA Meeting, Paper AM-18, 1998.

[3] T.Y. Chan, K.M. Sundaram, SCC: advanced FCCU technology for maximum propylene production, AIChE 1999 Spring Meeting, 1999.

[4] C.H. Hemler, L.L. Upson, Maximize propylene production, in: Proceedings of the European Refining Technology Conference, November 16–18, 1998.

[5] A. Fu, D. Hunt, J.A. Bonilla, A. Batachari, Oil Gas J. 96 (2) 1998.

[6] L.L. Upson, M.W. Schnaith, Oil Gas J. 95 (49) (1997) 47–51.

[7] R.H. Harding, R.R. Gatte, J.A. Whitecavage, R.F. Wormsbecher, ACE Symp. Ser. 552 (1994) 286–296.

[8] R.R. Gatte, R.H. Harding, T.G. Albro, D.S. Chin, R.F. Wormsbecher, Prep. Pap. — Am. Chem. Soc., Div. Fuel Chem. 37 (1) (1992) 33–40.

[9] U. Alkemade, T.J. Dougan, Stud. Surf. Sci. Catal. 100 (1996) 303–311.

[10] A.K. Rhodes, Oil Gas J. (1994) 16–20.

[11] K.L. Riley, J.L. Kaufman, S. Zaczepinski, P.H. Desai, S.W. Mayo, Akzo Nobel Catalyst Symposium, Vol. G-3, June 1998, pp. 1–8.

[12] M. Daage, R.R. Chianelli, A.F. Ruppert, Stud. Surf. Sci. Catal. 75 (1993) 571–584.

[13] M.J. Girgis, B.C. Gates, Ind. Eng. Chem. Res. 30 (1991) 2021.

[14] T. Halbert, G. Anderson, G. Markley, R. Gupta, A. Feinberg, C. Darnell, in: Proceedings of the 15th World Petroleum Congress, 1998, pp. 681–693.

[15] T.A. Cavanaugh, D.S. McCaffrey, W.H. Gregory, Hydrocarbon Tech. Int. (1994) 23.

[16] K.L. Riley, G.H. Anderson, K.D. Chomyn, J.W.M. Sonneemans, Akzo Nobel Catalysts Symposium, Noordwijk, the Netherlands, 1994, pp. 69–76.

[17] T.A. Pecararo, R.R. Chianelli, J. Catal. 67 (1981) 430–445.

[18] R.R. Chianelli, M. Daage, M.J. Ledoux, Adv. Catal. 40 (1994) 177–232.

[19] T. Isoda, Y. Takase, H. Takagi, K. Kusakabe, S. Morooka, Proc. Petr. Div. Am. Chem. Soc. 43 (4) (1998) 547–549.

[20] D. Dave, A. Gupta, K. Karlsson, A. Suchanek, H. van Stralen, Paper AM-93-24, NPRA, March 1993.

[21] P.B. Ting, A Report by SalomonSmithBarney, November 11, 1998.

[22] C.M. Eidt Jr., R.F. Bauman, B. Eisenberg, J.M. Hochman, G.C. Lahn, in: Proceedings of the 14th World Petroleum Congress, June 1994.

[23] L.L. Ansell, R.F. Bauman, B. Eisenberg, B.M. Everett, in: Proceedings of the World Petroleum Conference on Refining Technology and Reformulated Fuels, March 1997.