



Catalysis

Part Two of a Two-Part Series

The Challenging Chemistry of Ultra-Low-Sulfur Diesel

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This is the second article of a two-part series discussing the chemistry and catalysis involved in producing ultra-low-sulfur diesel (ULSD). In the first article (December 2002 WR, page 24), we reviewed the chemistry of ULSD and the challenges it poses compared with refiners' current hydroprocessing capabilities. This segment examines how new hydrotreating catalysts are designed to more effectively exploit the ULSD chemistry and thus provide more cost-effective solutions to ULSD production.

If altering the feed mix or reducing the endpoint are not practical or are not sufficient to achieve ULSD, then catalyst and process alternatives must be considered to meet the specifications. In this section, we focus on the impact that an ultra-high-activity catalyst can have in achieving ULSD targets.

Recent advances in hydroprocessing catalyst development by Criterion Catalysts & Technologies (CC&T) have resulted in a step change in performance compared with historical improvements made over the past few decades (Figure 1). This has been achieved by the fast-track development of a new way of producing hydroprocessing catalysts, resulting in CC&T's CENTINEL technology. The combination of this new technology and the knowledge already built upon conventional catalysts has yielded an unparalleled series of catalysts with optimized pore structure, metals dispersion, and active-phase selectivity.

In September 2000, CC&T introduced its new CENTINEL catalyst technology for refinery hydroprocessing applications. Both CoMo (cobalt-molybdenum) and NiMo (nickel-molybdenum) catalysts were launched simultaneously in distillate hydrotreating, vacuum gasoil (VGO) desulfurization, first-stage hydrocracking (FSHC), cat-feed hydrotreating (CFH), and lube hydroprocessing application areas. Within the first two years, more than 50 units have been started-up with CENTINEL products, including more than 20 distillate units.

Fundamentals of the Technology

Conventional hydrotreating catalysts are manufactured in a process where metal precursors are impregnated onto a support material and converted to the oxide form by means of high-temperature calcination. The metal oxides are then converted into the active sulfide phase through a sulfiding process, which takes place in a hydrotreating reactor. As a consequence of the strong interactions formed between

the metal oxides and the support material during the calcination process, Mo and Ni (Co) retain some metal-oxygen interactions and are not fully sulfided. Also, some of the Ni (Co) become intercalated in the alumina support and are unavailable for distribution onto the active "edge sites" of the MoS₂ crystallites.

Catalyst Improvements

The optimized pore structure of CENTINEL catalysts emerged from our long-standing experience in VGO hydrodesulfurization (HDS): CC&T's catalyst series DN-200/DC-200 has been highly successful in the market and is the industry standard. The catalysts in this series have also been applied in distillate and naphtha hydrotreating services.

As a result of the novel manufacturing process used for CENTINEL catalysts (Figure 2), metal complexes, MX_n, physically absorbed on the surface react directly with sulfur compounds to form highly dispersed metal sulfide species, M—S_x. These highly dispersed metal sulfide crystallites are "locked in place" during the activation process. This results in the active sulfide phase of the catalyst, MS_y. As a result, all of the metals placed on the catalyst are fully sulfided while maintaining high dispersion and better metals utilization than conventional catalysts.¹

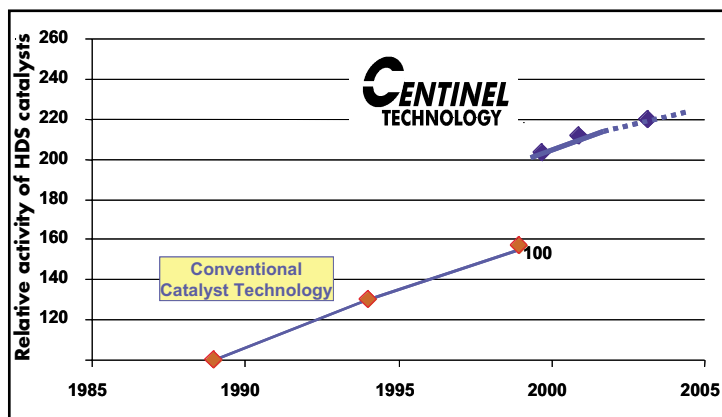


Figure 1. Recent advances in hydroprocessing catalyst development.

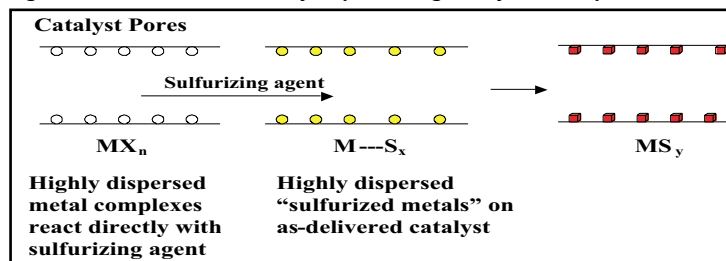


Figure 2. CENTINEL technology.

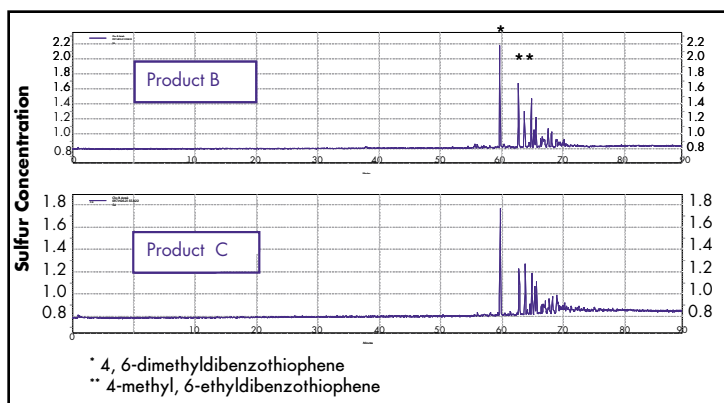


Figure 3. Sulfur distributions of two liquid products at 75-ppm sulfur.

Using x-ray photoelectron spectroscopy (XPS), the extent of sulfiding of an as-produced CENTINEL NiMo catalyst was shown to be substantial. All the nickel and half the molybdenum in the manufactured CENTINEL catalyst is sulfided. After activation, XPS shows that the remainder of the molybdenum has become fully sulfided. Conversely, XPS indicates that sulfiding of a conventional NiMo catalyst leaves a significant portion of the molybdenum and nickel unsulfided.

Using high-resolution transmission electron microscopy (HRTEM) to investigate the MoS₂ morphology of conventional and CENTINEL NiMo catalysts confirms the high dispersion of the fully sulfided active sites on the CENTINEL catalyst and indicates less stacking overall (higher dispersion). This higher dispersion for CENTINEL NiMo and exclusive presence of the fully sulfided active sites combine to give the catalysts their high-activity performance.

The optimized active-phase selectivity of CENTINEL catalysts is the result of a long-standing study on the dependence of the different HDS reaction pathways on catalyst type, feed properties, and process conditions. Feedstocks with completely different sulfur distributions can yield highly comparable product sulfur distributions at deep HDS conversion levels. Figure 3 shows the sulfur distributions of the liquid products of two feedstocks (Feeds B and C from Figure 3 in Part 1 of our series) after HDS down to about 75-ppm sulfur. While at first glance the resulting sulfur distributions look similar, they have a much different reactivity due to the relative concentrations of each of the remaining species.

Much can be learned from tracer molecules within and between each class of sulfur compounds. For example, for the class of the substituted dibenzothiophenes, the ratio of highly refractive sulfur species (such as 4-ethyl,6-methyldibenzothiophene and 4-methyl,6-ethyl dibenzothiophene) to less-refractive species (4-methyldibenzothiophene) can be monitored to gain insight into which pathways are followed preferentially. In this way, the selectivity of the active phase can be optimized for the preferred level of desulfurization with minimized H₂ consumption. This will become increasingly more important as the sulfur specification tightens to 15 ppm in the U.S. and 10 ppm in the European Union.

An example of the change in the reactivity ratios of sulfur compounds is demonstrated by the results from two tests, which differed only by a minor change in the catalyst formulation (without a change in the metals content). In the first test, using catalyst formulation A, the ratio of highly refractive dibenzothiophene to

less-refractive dibenzothiophene was 5.2:1. In the second test, using catalyst formulation B, the ratio was 11.1:1.

In addition to improving selectivity toward refractory sulfur removal, improvement of hydrodenitriding (HDN) functionality has been integral to enhancing CENTINEL catalysts' ULSD performance. In particular, DC-2118 offers HDN performance far exceeding that of all CoMo catalysts in its class and comparable to that of many NiMo catalysts. DC-2118 achieves much lower product nitrogen values than prior-generation CoMo catalysts (Figure 4), with HDN activity as much as twice as high. This improved performance also translates into higher HDS activity, which is especially important when treating streams like LCO (light cycle oil), LCGO (light coker gasoil), and synthetic crude-derived distillate streams that contain fairly high nitrogen levels.

Application of CENTINEL Catalysts for ULSD

Installing a new high-activity catalyst is a drop-in change that can have a large impact on sulfur reduction. CENTINEL catalysts offer a substantial increase in performance to produce ULSD over the catalysts being used today to produce 350- to 500-ppm diesel fuels. Depending on the feedstock and operating conditions, the activity level can range 30%–70% higher, especially at ultra-low product sulfur levels.

One benefit of CENTINEL catalysts (CoMo DC-2118 or NiMo DN-3110) is that their performance advantage relative to conventional catalysts increases as the sulfur-slip decreases (Figure 5). The increased activity comes from a higher level of dispersion of active sites and improved hydrogenation functionality. The improved hydrogenation allows the catalyst to work more effectively on the most refractory sulfurs.

The question of when to apply DC-2118 or DN-3110 is dependent on a number of different variables: feedstock, product sulfur level, operating pressure, and other product quality targets. In general, DC-2118 is used at low to medium pressures, while DN-3110 is applied at higher pressures (Figure 6). Since it has demonstrated a much higher HDN and hydrogenation activity than typical CoMo catalysts, DC-2118 can be used in the moderate-pressure range where others apply NiMo catalysts. The benefit of using the DC-2118 at these pressures is the improved stability of a CoMo catalyst: in this region, NiMo catalysts typically deactivate more rapidly.

Stacked CoMo/NiMo CENTINEL catalyst systems provide fewer HDS advantages than stacking of conventional catalysts. The enhanced HDN and hydrogenation power of DC-2118 diminishes the need to stack CENTINEL CoMo and NiMo to enhance ultra-deep HDS performance. However, a stacked CENTINEL system might be attractive when additional product quality improvements (cetane, density) are desired, particularly when trying to squeeze as many lower-value LCO or LCGO barrels as possible into the ULSD pool. CENTINEL catalyst systems can also be tailored to match the hydrogen demands or restrictions for a given set of circumstances. It is important to satisfy HDS requirements with high-activity systems; however, it is essential not to waste hydrogen by overtreating the feed if the upgrading benefits cannot be realized.²

Commercial Diesel Experience

CENTINEL CoMo and NiMo catalyst systems have been in

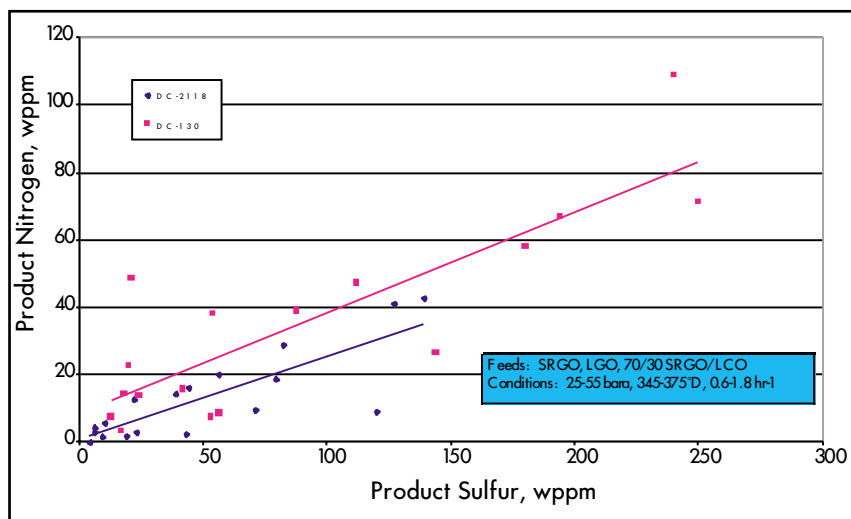


Figure 4. DC-2118 offers better nitrogen removal at constant sulfur slip.

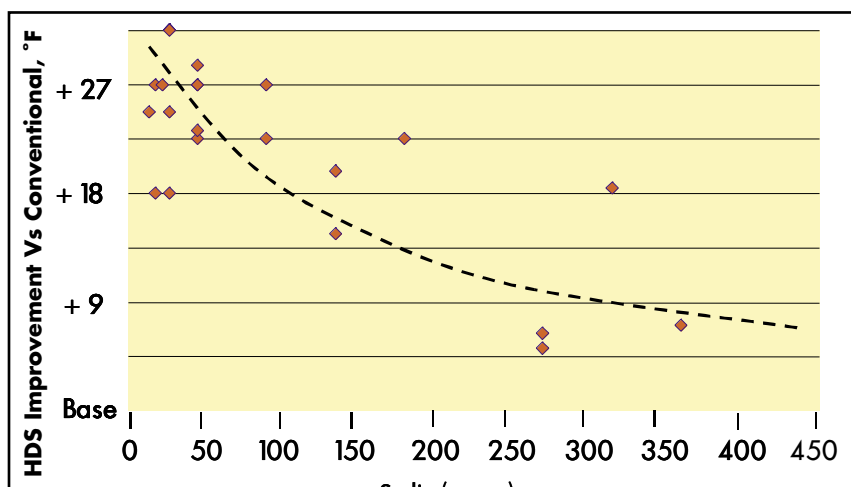


Figure 5. CENTINEL performance improves with increasing HDS level.



Figure 6. Application area for conventional vs. CENTINEL catalyst in distillate HDS.

commercial operation since the latter part of 2000. More than 20 units are using either DC-2118 or DN-3110 to treat mid-distillate streams to both conventional and ultra-low (10- to 50-ppm) product sulfur levels. In a normal low-sulfur environment (300–500 ppm), refiners have taken advantage of the improved activity and performance of CENTINEL catalysts to raise throughput, increase cracked feed content, increase the endpoint of the existing feeds, process more sour feeds, or overtreat the feed to balance the overall refinery diesel pool. Most of these changes have been made without a measurable penalty in cycle life, owing to the stability of the catalysts.

In Europe, several customers have used CENTINEL catalysts along with other feed or process changes to achieve ULSD, with product sulfur in the 10- to 50-ppm range.³

One client (Customer A) has used a drop-in catalyst solution while simultaneously increasing throughput to maximize the returns available for producing zero-sulfur middle distillates for the German market. The refiner took advantage of low-sulfur straight-run gasoil (SRGO), a medium boiling-range feed without a significant tail, and exclusion of cracked feeds in order to produce this ULSD product. The unit started up in the third quarter of 2001. An overview of the feed quality and operating conditions is shown in Table 1, and a plot showing the stable catalyst performance represented by normalized WABT (weighted-average bed temperature) is shown in Figure 7.

A second European refiner (Customer B) revamped an existing unit to produce predominantly <50-ppm sulfur product while periodically pushing the unit to make <10-ppm sulfur product. The unit typically operates at <500 psia H₂ partial pressure, with a feed 90% point at 645°F. However, this refinery has been able to take advantage of the high activity and stability of DC-2118 to periodically process heavier feeds to meet their ULSD specifications (Figure 8), despite the fact that a leaking exchanger caused some operational headaches at the beginning of the cycle.

Conclusions

This two-part article has presented the challenges of treating different types of middle-distillate feeds by analyzing and identifying the refractory sulfur compounds to be removed in order to reach the ULSD sulfur standards of 10–50 ppm. In essence, ULSD processing requires the removal of more-refractory sulfur species than is possible in current operations. Nitrogen removal plays a significant role in determining the ability to remove refractory sulfur, too.

In production of ULSD, one needs to be cautious in determining the processability of the

TABLE 1. OVERVIEW OF PROCESSING FACTORS—EUROPEAN REFINER A		
	Units	Value
Feed Quality Factors		
Straight Run	%	100
Cracked Stock	%	0
Sulfur	wt%	0.23
Density	°API	35.0
Total Aromatics	wt%	28.2
D86 IBP	°F	410
50%	°F	545
90%	°F	608
FBP	°F	657
Main Operating Conditions		
Catalyst	—	DC-2118
H ₂ partial pressure	psia	<600
SOR Treq	°F	<650
Product Sulfur	ppm	10-30
Expected Cycle Length	months	>24

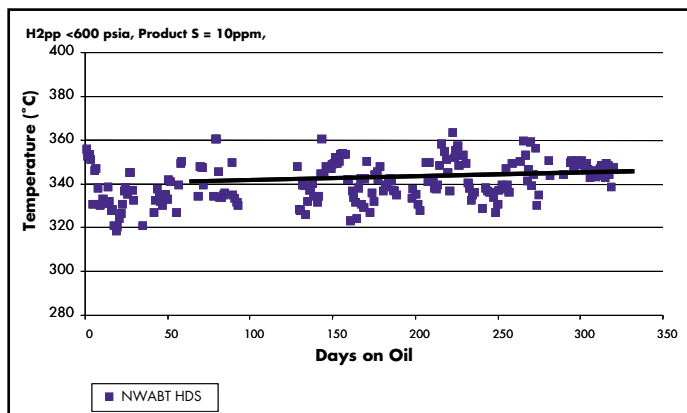


Figure 7. Customer A—catalyst stability to achieve 10-ppm sulfur.

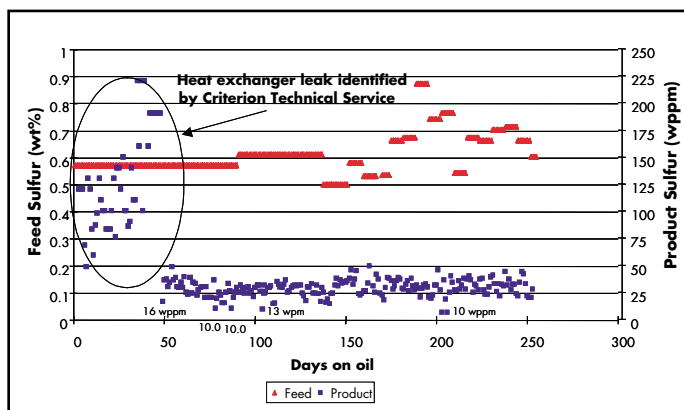


Figure 8. Customer B—consistently producing ULSD at <50-ppm sulfur.

feed. Unlike 500-ppm sulfur production, it is difficult to assess reactivity by reviewing conventional properties, such as total sulfur and distillation. We now know that the concentration and type of sulfur compounds present, as well as the nitrogen content, help determine the feed reactivity.

Once feed processability has been evaluated properly, refiners can examine what it will take to achieve ULSD in their units. New-generation catalysts, such as CENTINEL DC-2118 and DN-3110, are essential elements in producing ULSD. These catalysts have been specifically designed to eliminate the refractory sulfur species and the nitrogen compounds that inhibit HDS reactions, making them instrumental in minimizing reactor size and capital investment when ULSD units are designed. In some cases, no-capital solutions involving catalyst and feed adjustment may be enough to achieve ULSD, but in many cases this will not be the total solution. ●

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