KF 787 PULSAR™: THE NEW BREAKTHROUGH CATALYST FOR LOW- AND MEDIUM-PRESSURE MIDDLE DISTILLATES HYDROTREATING

Bringing high returns in applications with limited hydrogen, difficult feedstocks and severe operating conditions

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Over the last years, improved hydrotreating (HT) catalysts have been introduced in the market primarily to serve operations with high pressure and hydrogen availability. However, catalyst innovation for operations limited by hydrogen, such as low- and medium-pressure middle distillates HT (MD HT), has been slower and less groundbreaking. The challenge is being able to deliver both premium activity and stability in applications with limited hydrogen, difficult feedstocks and severe operating conditions.

To improve catalyst stability for hydrogen-constrained MD HT operations, suppliers followed a defensive approach and sought to develop moderately active catalyst systems with low selectivity for nitrogen removal. The drawback in adopting such catalysts is that, while benefitting from their stability in operation, refiners still cannot maximize activity and thereby extract the full operating potential and profit from their critical units.

Albemarle responded first to the need for low- and medium-pressure higher-performance catalysts by introducing KF 780 STARS®, a highly active, stable and versatile CoMo grade developed for fluidized catalytic cracking pretreatment (FCC-PT) and MD HT applications. KF 780 delivers enhanced metals efficiency for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) activity and higher robustness in operation. The acceptance of KF 780 by refiners for both applications has been overwhelmingly positive.

Research into novel, alternative approaches to HT catalyst design has now led Albemarle to introduce a new and superior generation of catalysts: PULSAR™. PULSAR is a breakthrough technology that effectively controls the morphology and the dispersion of the metal active phase.

The first grade of this new class is KF 787 PULSAR. This catalyst delivers superior activity without compromising stability, even in operations with challenging feedstocks and constrained by low hydrogen availability.

Challenges in low- and medium-pressure MD HT

A premium ultra-low-sulfur-diesel (ULSD) catalyst for low- and medium-pressure HT applications that process difficult feedstocks requires a perfectly balanced combination of superior activity, stability and robustness against operational upsets.

Performance in these challenging operations is constrained by both kinetics and thermodynamics.

Figure 1 shows the simplified reaction pathway for the HDS reaction and the response of its different routes to operating hydrogen pressure under thermodynamically favorable conditions. The HDS reaction consists of two routes. The direct desulfurization route (DDS) is a single-step reaction in which sulfur is converted via direct hydrogenation (HYD) to hydrogen sulfide. DDS is typically the fastest HDS pathway at very low pressure, especially for easy sulfur removal, and the one that requires the lowest hydrogen consumption. HYD-assisted HDS (HYD-HDS) occurs in parallel with DDS and is a more complex reaction requiring HYD (of at least one aromatic

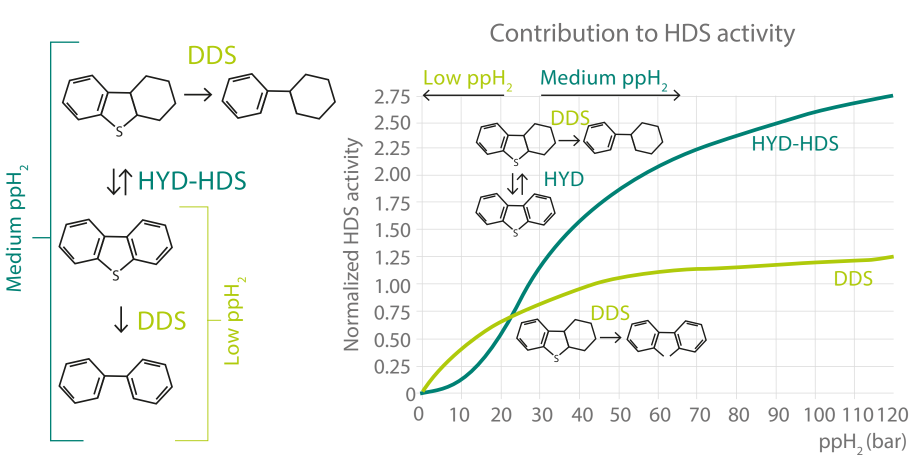

Figure 1: Response to ppH_2: DDS compared with HYD-HDS.

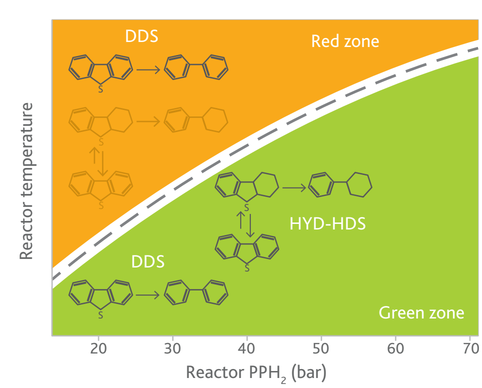

Figure 2: Operating regions in an MD HT unit.

ring) as a first step and DDS as the final one. Therefore, DDS is also necessary in the HYD-HDS route, particularly at low and medium pressure (ppH_2 <35–40 bar) where HYD reactions are slow and DDS is needed to shift the equilibrium of the first HYD step. At a very low pressure, pure DDS is the dominant reaction; at low-to-medium pressure (25 bar < ppH_2 < 40 bar), the DDS and the HYD-HDS routes are both potentially important. The more refractory the sulfur species to be converted, the more important the contribution of the HYD-HDS route.

Note that the HDN reaction also proceeds via a HYD step. Hence, its response to hydrogen pressure and thermodynamics is similar to that of the HYD-HDS route.

For the HYD-HDS and HDN routes to be effective in an HT reactor though, additional conditions are required:

a) a sufficiently high hydrogen coverage to preserve a high enough ppH_2 at the bottom of the reactor

b) a sufficiently high temperature-to-ppH_2 ratio to avoid thermodynamic limitation of the HYD step

c) limited inhibition effects by refractory feed nitrogen, especially basic nitrogen, which adsorbs on the catalyst's HYD sites and inhibits the HYD-assisted reactions.

Based on the considerations above, it is possible to identify three typical operating regimes, or regions, for an HT reactor. These regions are illustrated in Figure 2.

The effectiveness of the different reaction routes varies by region:

a) In the green operating region, which is characterized by a low temperature-to-ppH_2 ratio, all three reactions, DDS, HYD-HDS and HDN, are effective, with DDS being dominant for HDS at low pressure and HDN and HYD-HDS becoming increasingly more important at higher pressures.

b) In the intermediate region (depicted in yellow), the rate of HDN, HYD-HDS and hydrodearomatization start to slow down because of limitations on the HYD steps by the thermodynamics.

c) In the red region, the one with the highest temperature-to-ppH_2 ratio, all the HYD-assisted reaction routes are severely hindered. In this zone, the rates of removal of sulfur and nitrogen are significantly lower and HDS has to proceed almost exclusively via the DDS route.

Low- and medium-pressure HT units processing difficult feedstocks often operate totally or partially in the intermediate or in the red region already at the beginning of their cycles. This is particularly true for units with very low ppH_2, low hydrogen coverage and/or a high space velocity, which are all conditions that lead to higher operating temperatures.

In the red operating region, not only are the HDS and HDN reaction rates slower, but other phenomena are also favored that can negatively affect the performance of a catalyst. Depending on a catalyst's properties, dehydrogenation and condensation of (nitrogen-containing) polyaromatics leading to coke formation that can block the catalyst's active sites can occur. In addition, high temperatures can cause metals migration from the active metal slabs into larger agglomerates with significantly lower activity.

When designing a premium catalyst for low and medium pressure for upgrading difficult feedstocks to high-value diesel, all these aspects must be considered. The optimal catalyst would be the one that can maximize DDS activity without compromising the potential of the HYD reactions for HDS and HDN, and that can still provide high robustness and full operating stability.

Developing such a catalyst has been the focus of Albemarle's catalyst research over the last years and has required a fundamentally new approach to catalyst design.

KF 787 PULSAR: A breakthrough innovation in MD HT catalysts

PULSAR is a new catalyst technology developed at Albemarle's catalyst research center in Amsterdam, the Netherlands.

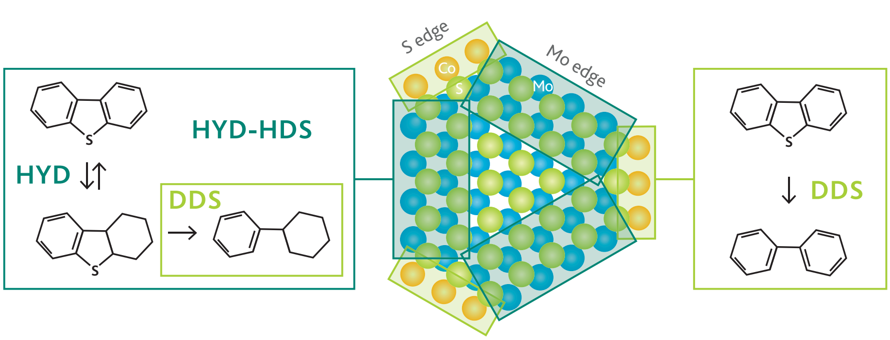

Figure 3: Model of the metal active slabs in CoMo hydrotreating catalysts and of the DDS (light-green frames) and the HYD-HDS active sites (dark-green frames).

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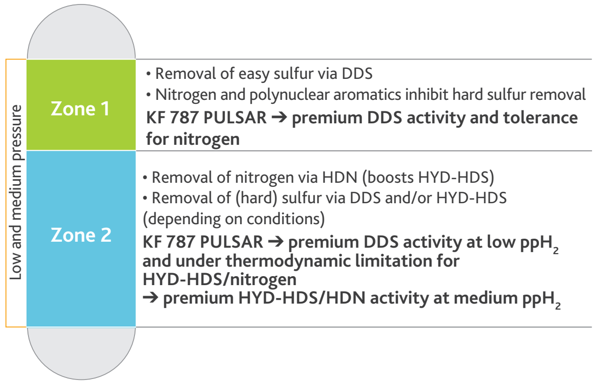

Figure 4: KF 787 PULSAR's advantages in MD HT applications.

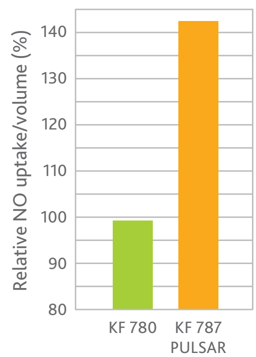

Figure 5: Comparison between the concentration of DDS sites/reactor volume of KF 787 PULSAR and KF 780.

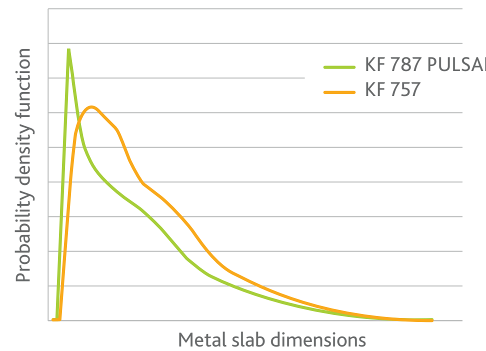

Figure 6: 3D HR-STEM analysis of the metal active slabs in spent KF 787 PULSAR and KF 757.

The first new grade with this technology is KF 787 PULSAR, a supported CoMo catalyst that is specifically designed for low- and medium-pressure MD HT. This catalyst can deliver both premium activity and stability, even in operations with challenging feedstocks and constrained by low hydrogen availability.

Thanks to its special design, KF 787 PULSAR has an extremely wide hydrogen pressure application range that stretches from very low to medium-to-high pressure (10–55 bar ppH_2).

In terms of handling and sulfidation, KF 787 PULSAR can be treated exactly like the previous STARS catalyst generation and, like STARS catalysts, PULSAR catalysts can also be rejuvenated to over 90% of their fresh relative volume activity (RVA) HDS activity through REACT™ treatment.

Specific features of the PULSAR technology are the tightly controlled morphology and size of its active metal phase. These result in very high metals dispersion, thereby boosting metal efficiency and specific activity per reactor volume.

Figure 3 depicts the most widely accepted model for the HYD CoMo metal active phase: hexagonal imperfect molybdenum disulfide (MoS_2) slabs decorated at the sulfur edges with cobalt (Co) as the promoter.

The HYD step of the HYD-HDS reaction pathway takes place on the molybdenum (Mo) edge and on the first ring of Mo atoms adjacent to the slabs' edges (Mo atoms in the dark-green frames). In contrast, the DDS step occurs only on the Co atoms at the sulfur edge (atoms in the light-green frames).

When the metal slabs are larger, the ratio between the number of HYD-HDS and DDS sites also increases according to their geometrical constraints; hence, larger metal active slabs have a higher selectivity for HYD.

KF 787 PULSAR's advantages

Reducing the size of the metal slabs, as achieved with the PULSAR technology, increases selectivity for the DDS reaction, which brings several advantages in operation at low and medium pressures:

a) HDS activity increases, even in the intermediate and red operating zones (see Figure 2).

b) Nitrogen tolerance is enhanced, which enables treating of feeds with higher end points, more cracked stock intake and more basic nitrogen.

c) Stability is improved thanks to the lower tendency to form coke on the catalyst's surface, particularly when operating in the intermediate and red zones.

KF 787 PULSAR's advantages in applications are summarized in Figure 4, depending on its position in an HT reactor and on its operating mode.

KF 787 PULSAR has great flexibility in application with respect to both the type of operation and the loading zone in a reactor. Its higher nitrogen tolerance enables it to be loaded in the reactor top (or Zone 1); the higher stability makes it suited for the reactor's middle and bottom section in any (U)LSD application (Zone 2).

Equally important is that KF 787 PULSAR's metal active phase is bound to the support in a way that helps to prevent the metal agglomeration that is typical of extended use and exposure to high temperatures. This adds to the stability advantage already provided by its high metal dispersion and DDS selectivity.

The special morphology and the high presence of DDS sites in KF 787 PULSAR's active phase have been demonstrated by nitrogen monoxide (NO) chemisorption and by 3D high-resolution scanning transmission electron microscopy (3D HR-STEM) measurements.

NO adsorbs preferentially on the Co atoms at the edge of the metal slabs and can be used to measure the concentration of a catalyst's DDS sites. As shown in Figure 5, NO chemisorption tests have confirmed that KF 787 PULSAR has an exceptionally high concentration of DDS sites, i.e., almost 50% more per reactor volume than the already highly DDS selective KF 780.

In addition, 3D HR-STEM analysis has shown that the active metal slabs are significantly smaller than in KF 780 and KF 757 (Figure 6), which is in line with KF 787 PULSAR's high DDS selectivity and stability. The

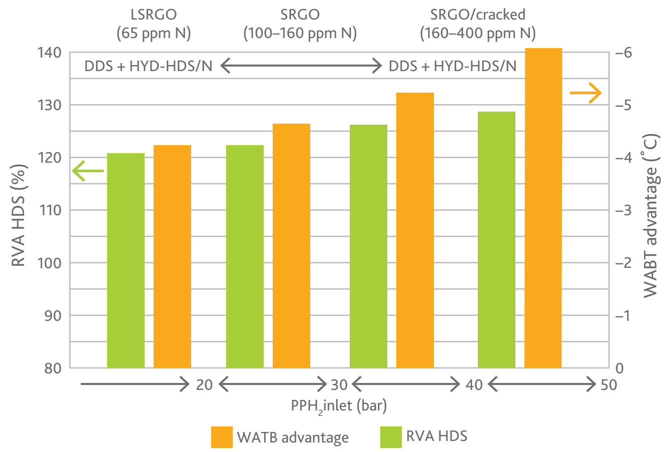

Figure 7: Relative advantage in performance of KF 787 PULSAR compared with KF 780 in various MD HT ULSD applications.

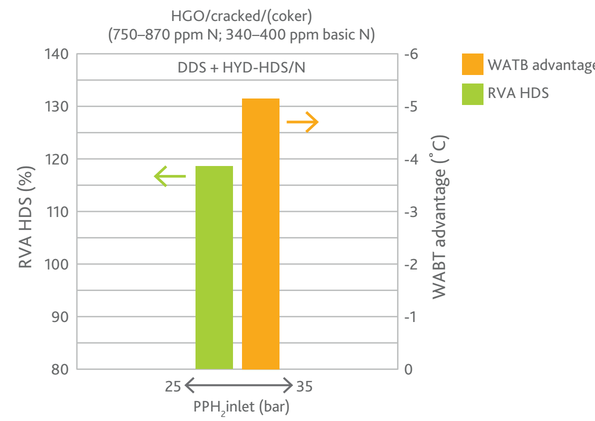

Figure 8: Relative advantage in performance of KF 787 PULSAR compared with KF 780 for heating oil production.

microscopy analysis was carried out on the spent catalysts after they had been tested side by side in a pilot plant unit for 40 d. The test was run at low hydrogen pressure (15–35 bar) with various feedstocks, including SRGO–FCC LCO blends and HGO, and included a final stress condition of 5 d with LGO (1.1 wt% sulfur; 240 ppm nitrogen; 410°C final boiling point; density = 0.861 g/ml) at 380°C at 15 bar ppH_2 outlet. The objective of this final condition was to apply additional stress to the catalysts that would simulate metal agglomeration before analyzing the active phase.

Figure 6 shows the size distribution of the active metal slabs of KF 757 and KF 787 PULSAR after the activity test. The active metals slabs in KF 787 PULSAR are smaller, with a significantly narrower size distribution, and are, thus, better dispersed. These features are the direct result of the PULSAR technology and are preserved even after use in demanding operating conditions, thanks to a reduced tendency for metal agglomeration.

These observations are remarkable when considering that the reference grade is KF 757, a catalyst very well known in the market for the stability of its active phase and its robustness in operation.

KF 787 PULSAR was tested extensively in pilot plant units with different types of feedstocks and in a large range of conditions to assess its applicability and performance advantage fully. The results confirmed that it is a premium and fully flexible catalyst by design and suited for any ULSD MD application at low and medium pressures (Figure 7), and for heating oil (50 ppmw target product sulfur) production at low and medium pressures (Figure 8). The RVA HDS typically ranges from 120 to 130%, or up to 6°C weighted average bed temperature (WABT) advantage compared with KF 780, which is among the most active and widely applied catalyst in the low- and medium-pressure MD segments today.

Remarkably, KF 787 PULSAR's superior performance is delivered consistently across the whole MD application segment, from light SRGO applications below 20 bar ppH_2, to heating oil production in the 25–35-bar ppH_2 range, to cracked stock upgrading to high-quality diesel at 50 bar ppH_2. This flexibility is one of the advantages of the PULSAR technology and the result of the catalyst-specific design that combines high HDS activity with moderate selectivity for HYD.

The performance advantage by KF 787 PULSAR can be monetized by refiners in different ways, depending on their technical needs and the economics at play.

The most obvious utilization would be to increase upgrading of distressed feedstock to ULSD, with higher density uplift as an additional benefit. Considering KF 787 PULSAR's moderate selectivity towards HYD, the higher activity would not come at the cost of significantly higher hydrogen consumption. The high HDS-activity-to-hydrogen-consumption ratio lowers the specific hydrogen consumption at equal sulfur removal compared with more hydrogenating catalysts. In addition, KF 787 PULSAR provides higher stability that, in combination with a lower start-of-run WABT, leads to longer cycles and thus lower changeout and downtime costs.

Another tangible economic advantage is KF 787 PULSAR's flexibility in operation: by fitting all the reactor zones in the most diverse applications, it can be utilized in any low- and medium-pressure MD HT unit with significant advantages for refiners' catalyst pool management and logistics.

Other important economic advantages are the catalyst's high robustness in case of operational upsets, the energy savings in view of the potentially lowered WABT and delayed capital investments for revamping units that are potentially constrained by catalyst activity.

The main key features and advantages in application of KF 787 PULSAR are summarized in Figure 9.

Although KF 787 PULSAR has just been launched in the market and is already operating in its first commercial reference, research at Albemarle on the new PULSAR technology is continuing at full speed.

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As new applications are being explored, future PULSAR grades are being perfected and will be introduced shortly to accompany KF 787 PULSAR.

Conclusions

In recent years, Albemarle has made significant progress in developing catalysts for low- and medium-pressure MD HT.

Research into alternative approaches to HT catalyst design and production has now led to the introduction of a new and superior generation of catalysts: PULSAR. This is a breakthrough technology that, among other things, enables precise control of the morphology of the metal active phase and its dispersion. The active metals slabs in PULSAR catalysts are smaller and better dispersed, and have an extremely narrow size distribution.

The first grade of this new generation is KF 787 PULSAR. This catalyst was developed to bring high returns primarily for refiners that process high nitrogen and cracked feedstock, including operations constrained by low operating pressure and limited hydrogen availability.

KF 787 PULSAR is a fully flexible MD HT catalyst by design. The typical activity advantage with difficult feedstocks is 6°C WABT compared with KF 780 STARS. Remarkably, KF 787 PULSAR performs consistently across the whole MD application segment, from light SRGO applications at well below 20 bar ppH_2, to heating oil production in the 25–35-bar ppH_2 range, to cracked stock upgrading to high-quality diesel at 50 bar ppH_2.

The performance advantage of KF 787 PULSAR can be monetized by refiners in different ways, depending on their technical needs and the economics at play, starting from increased upgrading of distressed feedstock to ULSD, with higher density uplift as an additional benefit, to longer operating cycles leading to lower changeout and downtime costs.

Another tangible economic advantage derives from the catalyst's full flexibility in operation. KF 787 PULSAR fits all low- and medium-pressure MD HT operations and all reactor zones, from the top to the bottom, which greatly simplifies refiners' catalyst pool management and logistics. It also offers high robustness in case of operational upsets.

Although KF 787 PULSAR is already operating in its first commercial reference, future PULSAR grades are being perfected and will shortly be introduced in the market.

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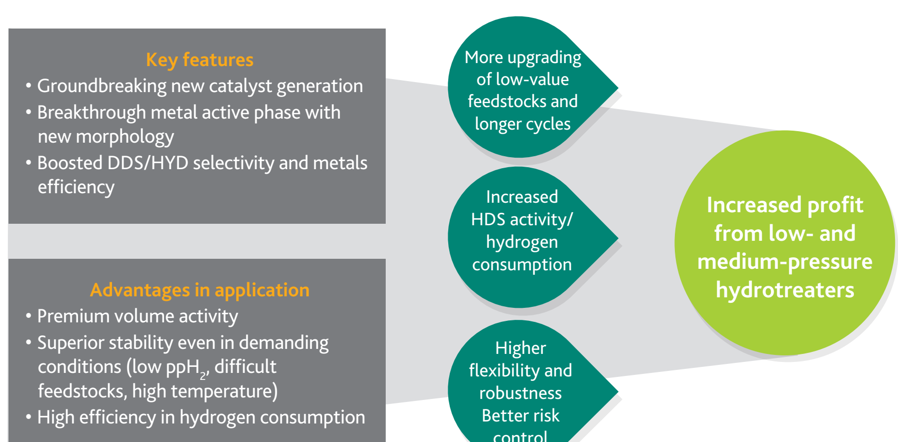

Figure 9: Key features and advantages in application.