

Developments in hydrotreating catalyst

How a second generation hydrotreating catalyst was developed for high pressure ultra-low sulphur diesel units and hydrocracker pretreaters

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The worldwide market demand for more active NiMo hydrotreating catalysts is extraordinary. Despite tremendous improvements in catalyst technology for the past 20-30 years, ultra-low sulphur fuel legislation and the shift towards VGO hydrocracking to maximise diesel production are more than ever forcing refiners to search for the absolute top tier NiMo catalyst for their ultra-low sulphur diesel (ULSD) or hydrocracker pretreat reactor.

The dramatic drop in natural gas prices observed particularly in the US has resulted in a low production cost for hydrogen. The low cost of hydrogen makes it very profitable to add hydrogen catalytically to middle distillate fractions, thereby increasing the liquid volume swell, resulting in higher yields of valuable diesel.

To address these requirements, refineries continuously need better, yet cost-efficient, alumina based catalysts with the highest possible activity in order to obtain the desired boost in performance and hydrogen consumption. Furthermore, alumina based hydrotreating catalysts will help minimise the operating cost when targeting volume swell in comparison with higher cost unsupported catalyst formulations.

Continuously improving alumina based catalysts

Topsoe has been at the forefront of important technological breakthroughs in the hydroprocessing industry for decades and continuously explores the possibilities within this area. In the 1970s, Topsoe discovered the active CoMoS phase in hydrotreating catalyst, which revolutionised the catalyst world by applying fundamental research in the catalyst development approach. In the 1980s, Topsoe

researchers, headed by Dr Henrik Topsøe, discovered the difference between Type I and Type II hydrotreating catalysts and gave them the names that are known throughout the industry today. With this breakthrough, the hydroprocessing catalyst development entered the nanotechnology era, and the Type II hydrotreating catalysts became the industry standard for high-activity catalysts. In the early 2000s, Topsoe's research in surface science paid off again, and a new activity site was discovered: the BRIM site. With this finding, Topsoe developed BRIM technology within both the CoMo and NiMo type catalysts, which fuelled Topsoe's unparalleled growth in market share globally due to a top tier catalyst portfolio.

From BRIM to HyBRIM

Topsoe's latest catalyst technology, HyBRIM, involves an improved production technique for both NiMo and CoNiMo hydrotreating catalysts. It combines the BRIM technology with a proprietary catalyst preparation step. The synergistic effect of merging the two technologies has enabled Topsoe to design an advanced metal slab structure that is characterised by an optimal interaction between the active metal structures and the catalyst carrier. The activity of the Type II sites is positively influenced to a high degree by this interaction between the metal slab and the carrier. HyBRIM technology exploits this interaction and substantially increases the activity of both the direct sites and the hydrogenation sites without compromising the catalyst stability.

Topsoe's NiMo catalysts that are developed today are around three times more active than the catalysts produced in the 1990s. **Figure 1** illustrates the development of the company's

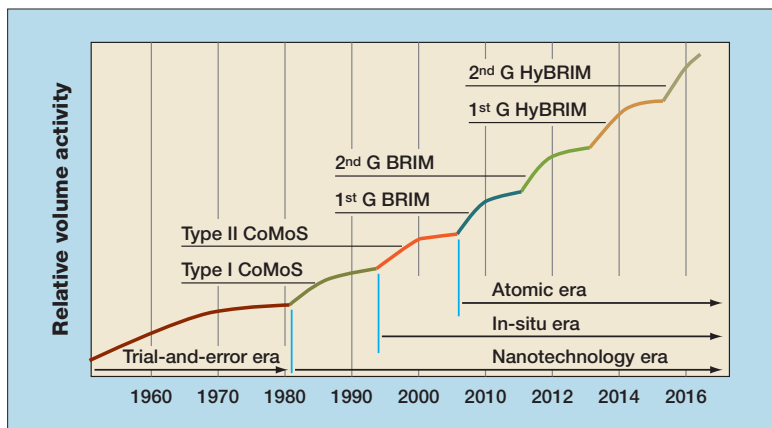


Figure 1 Topsoe's catalyst development progress – from Type I through second generation HyBRIM

many catalyst generations. Since Topsoe's scientists employed tools such as electron microscopes, in situ monitoring, and high throughput screening in their research programmes, we have made considerable progress within hydrotreating and hydrocracking catalyst development. The BRIM and HyBRIM catalyst technologies are the direct outcomes of this scientific approach.

HyBRIM technology was originally introduced with Topsoe's TK-609 HyBRIM in 2013 and has since been extended to include several different hydrotreating catalysts covering medium to high pressure refinery applications. As mentioned above, the need for ULSD production from low quality crudes and higher severity hydrocracking is creating a need for even better catalysts.

During the past three years, HyBRIM technology has been broadly recognised by the industry to be at the forefront of what is possible within



Figure 2 Image of TK-611 HyBRIM

hydrotreating. In addition, more than 100 hydrotreating units around the globe have a HyBRIM catalyst installed right now. However, Topsoe's researchers recently discovered even more potential within the HyBRIM method – a potential utilising the active metals to an even higher extent and securing a dispersion of active sites to a level never seen before. Therefore, Topsoe is launching the second generation of HyBRIM technology – the TK-611 HyBRIM catalyst with 25% higher activity for both sulphur and nitrogen removal.

Higher activity, same stability

When applying the TK-611 HyBRIM catalyst in either ULSD or hydrocracker pretreatment service, the improved activity can be exploited in several ways. Obviously, a higher activity is often used to operate the unit as in previous cycles, only at a lower reactor temperature, which then yields longer cycle lengths. However, the new high activity can also be utilised in terms of

increasing unit throughput or, in the case of a hydrocracker, to lower the nitrogen slip from the pretreat section to the cracking section, resulting in higher conversion and better yields. In addition, TK-611 HyBRIM will increase the volume swell due to better hydrogenation functionality. Refiners also benefit from purchasing more opportunity crudes or processing more LCO and they will have a stronger and robust catalyst candidate to handle these more challenging

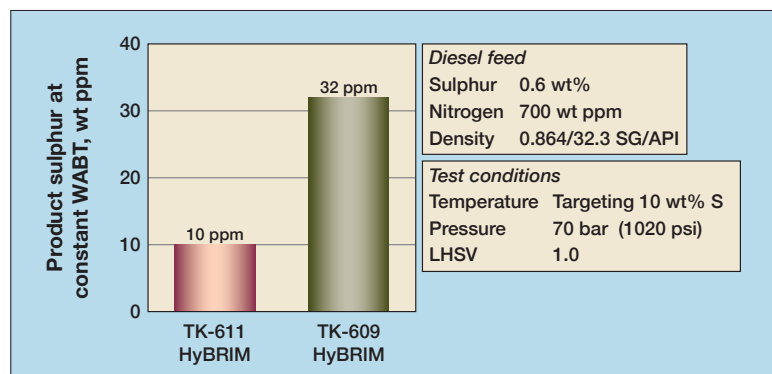


Figure 3 Comparing TK-611 HyBRIM with TK-609 HyBRIM in ultra-low sulphur diesel service

feedstocks. In any case, TK-611 HyBRIM will significantly improve the profitability of refinery assets.

Figure 3 shows ULSD pilot plant testing and compares TK-611 HyBRIM with TK-609 HyBRIM side-by-side. It is seen that if the two catalysts are operated at exactly the same conditions and at a reactor temperature giving 10 wt ppm product sulphur for TK-611 HyBRIM, then TK-609 HyBRIM will simultaneously deliver a product with 32 wt ppm sulphur. Hence the activity advantage of TK-611 HyBRIM corresponds to a delta product sulphur of 22 wt ppm at ULSD conditions, which is a remarkable step-change in activity.

The same type of experiment is illustrated in Figure 4 for vacuum gas oil (VGO) at hydrocracker pretreatment conditions. While 62 wt ppm product nitrogen slip is achieved with TK-609 HyBRIM, TK-611 HyBRIM, at exactly the same conditions, is able to deliver a product nitrogen slip of only 26 wt ppm. Such a difference is a substantial improvement for a hydrocracker pretreating unit.

High start-of-run activity is obviously important; however, activity has no real meaning unless it is accompanied by high catalytic stability, ensuring that improved performance is maintained over the projected cycle. Some catalyst formulations on the market display an impressive fresh activity; however, due to the nature of these catalysts, there is an initial line-out deactivation caused by the nitrogen species present in the feed passivating the most active sites. When these types of catalysts are installed, they will typically have lost their activity benefits after four to six weeks on-stream.

During the development of BRIM and subsequent HyBRIM technologies, Topsoe has

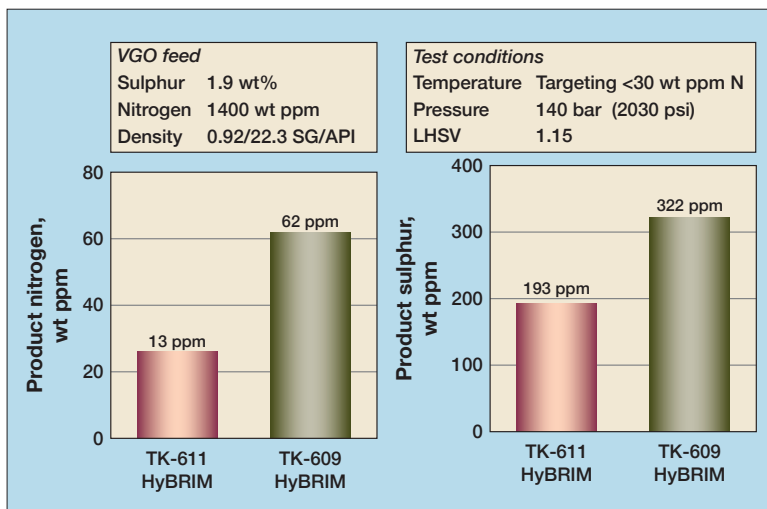


Figure 4 Data for hydrocracker pretreatment service for TK-611 HyBRIM versus TK-609 HyBRIM

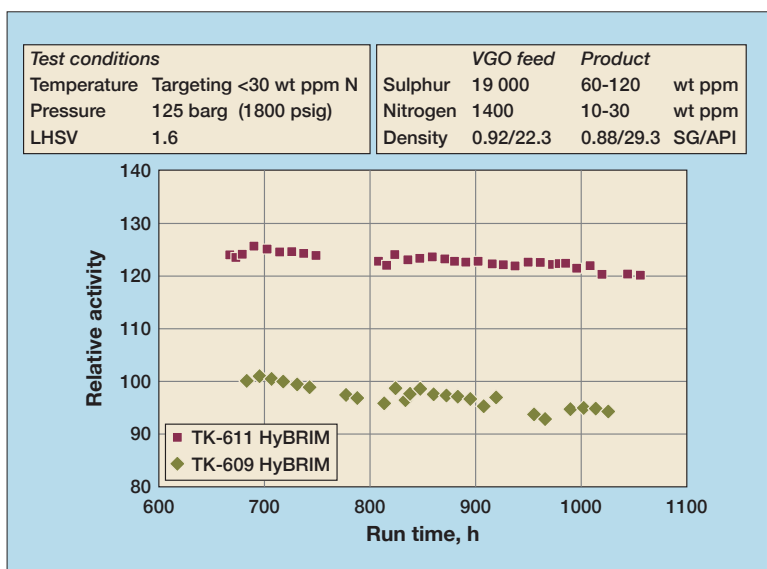


Figure 5 Catalyst stability for TK-611 HyBRIM versus TK-609 HyBRIM in hydrocracking pretreat service

successfully been able to modify the alumina structure and catalytic surface. By employing scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques, Topsoe's researchers have observed how the catalyst preparation steps influence the catalyst functions. This knowledge has led to an improved alumina pore structure and an optimised interaction with the alumina support, providing very active and stable CoMoS/NiMoS catalyst formulations. The data shown in Figure 5 compares the stability of the new TK-611 HyBRIM with TK-609

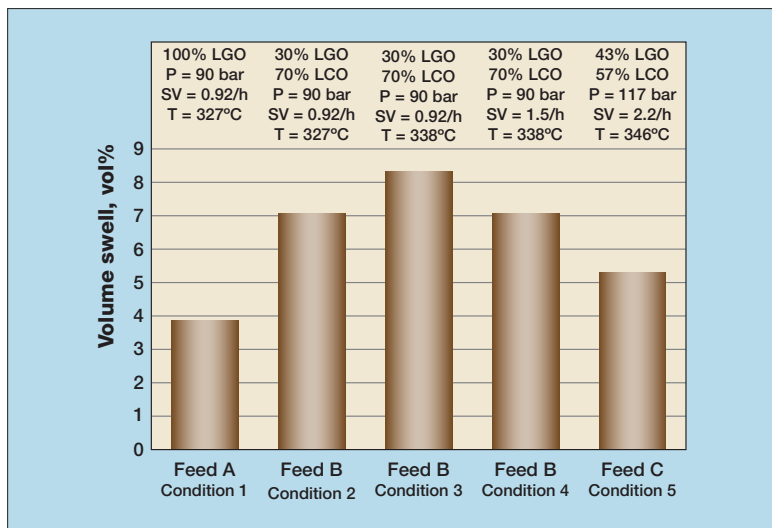


Figure 6 Obtained volume swell with HyBRIM catalyst in a LCO hydrocracker

HyBRIM in VGO hydrocracker pretreat service at the same operating conditions. The testing reveals that even though TK-611 HyBRIM is operated at higher sulphur and nitrogen conversion levels, due to its higher activity, the two catalysts exhibit exactly the same performance stability.

More volume swell

Introducing as much hydrogen into the distillate fractions as possible can, as previously mentioned, be very profitable when excess hydrogen is available. The term ‘volume swell’ refers to the increase in the liquid volume when the product density and distillation are lowered by hydrotreating. This includes contributions from removing sulphur, nitrogen (only a very small contribution), and hydrogenation of olefins. However, the main contributor is without doubt the saturation of poly-, di-, and mono-aromatics.

Topsoe has previously demonstrated that there is a strong correlation between the observed density improvement and the degree of aromatic saturation (%HDA). Aromatics saturation is controlled by the catalyst’s hydrogenation activity, the presence of inhibitors, such as nitrogen species, and by thermodynamic equilibrium. The overall amount of hydrogen consumed by hydrodearomatization (HDA) reactions is of course also dependent on the actual amount of aromatics present in the feed (see **Figure 6**).

A simple way to quantify the volume swell is to compare the liquid product density with the feed

density. This is an easy approach and is based on available data; however, it does not take the yield losses into account. The correct way is therefore to compare the increase in the C_5+ volume yield with the fresh feed. This method is accurate; however, these data are not always readily available from commercial units or from simple pilot tests, as it requires fractionation and the ability to close the mass balance.

Topsoe’s researchers have previously published that the presence of nitrogen and, in particular, basic nitrogen compounds strongly inhibits HDA reactions. Therefore it is beneficial to remove nitrogen to very low levels, lower than 2–3 wt ppm N, in order to increase HDA and the associated volume swell. Consequently, TK-611 HyBRIM with maximum activity for nitrogen removal (HDN) will also provide the highest volume swell.

Figure 6 illustrates the effect on volume swell when changing the operating conditions and feed blend. The pilot plant test was conducted simulating a LCO hydrocracker pretreat unit using a HyBRIM catalyst as the main treating catalyst. It included five different conditions, where pressure, temperature, space velocity, and LCO amount in the feed blend were varied. The results show that the HyBRIM catalyst removed the nitrogen to very low levels, below 0.2 wt ppm N, which is the detection limit. Consequently, this indicates that saturation of aromatics and, in particular, monoaromatics should take place in the last part of the reactor. In this pilot plant test, the temperature has been kept in the low range in order to avoid thermal cracking. As expected, Feed B, being very rich in aromatics due to the high LCO content, obtained the highest volume swells at test conditions 2, 3, and 4.

In **Figure 7**, the corresponding aromatics content from Feed B is plotted. It is seen that test condition 3, where the highest volume swell is reached, is also where the most aromatics are saturated. This can be explained by the higher reactor temperature and low space velocity. Monoaromatics especially are saturated the most

at condition 3, and there is actually a correlation between the obtained volume swell and the residual content of monoaromatics. In refinery terms, the highest volume swell observed with Feed B corresponds to gaining more than 3300 b/d of additional liquid out of a 40 000 b/d unit. This is remarkably high in conventional hydrotreating without any cracking catalyst and is the result of a high degree of aromatic saturation. This volume swell represents an additional profit of about \$40 million per year even after subtracting the cost of the extra hydrogen that is consumed in the hydrotreater. The value is based on an oil price of \$45/bbl, and profitability will obviously increase with the increasing cost of crude oil.

As part of the data shown in Figure 3, we also obtained volume swell data for the two catalysts, enabling a direct comparison of the hydrogenation and hydrodearomatisation difference between first and second generation HyBRIM catalysts at the same reactor conditions. In Figure 8, the difference in volume swell based on density reduction is depicted. Despite a quite low feed aromatic content, TK-611 HyBRIM delivers 20% higher volume swell compared to TK-609 HyBRIM at ULSD conditions. This is a significant difference, and the improvement is remarkable because TK-609 HyBRIM is already a high volume swell catalyst.

Figure 9 reveals the main reason for the 20% higher volume swell. At ULSD conditions, the product nitrogen for both catalysts is low and actually below the detection limit. This means that the 'mono-aro-

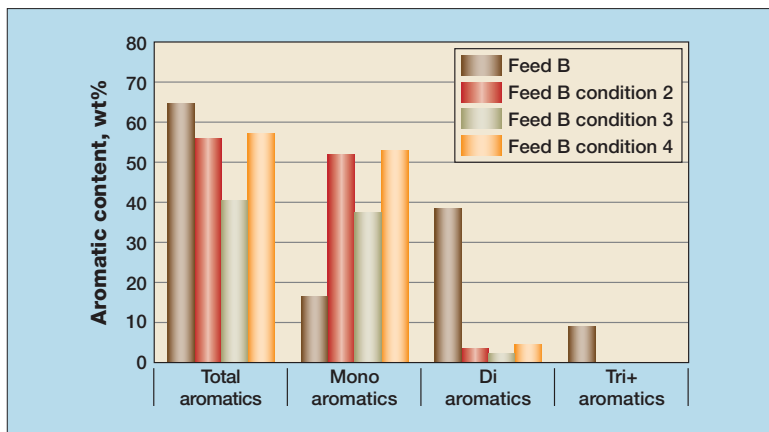


Figure 7 Aromatics content in feed and products in Feed B case

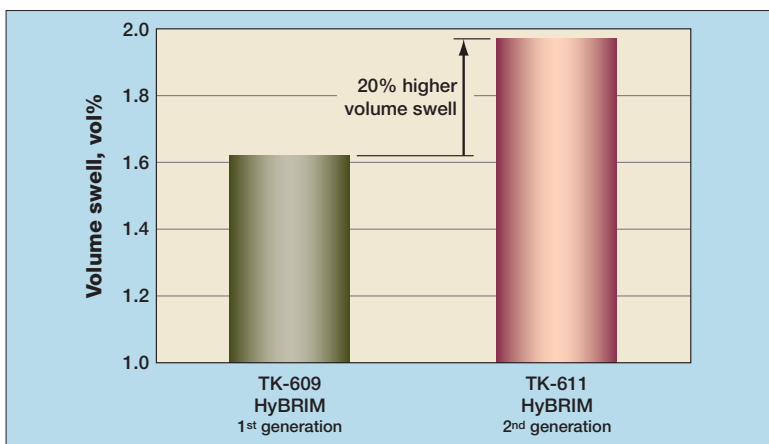


Figure 8 Volume swell comparison of TK-611 HyBRIM versus TK-609 HyBRIM at ULSD conditions

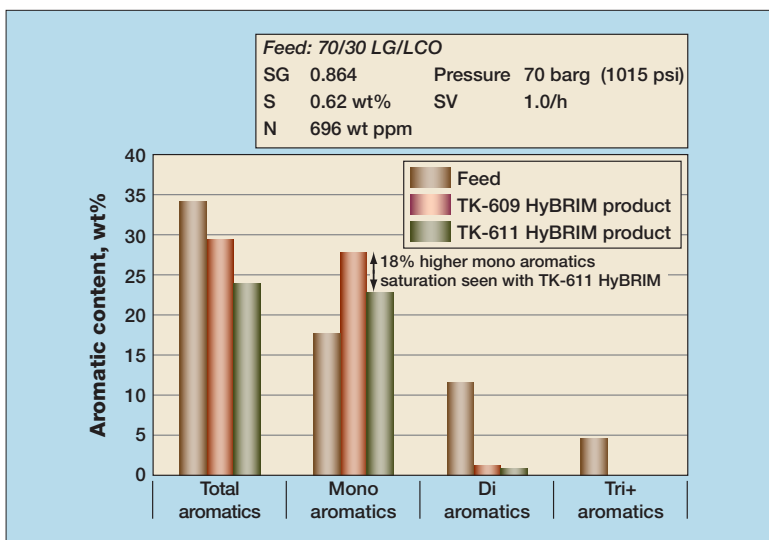


Figure 9 Aromatics content before and after ULSD hydrotreating with TK-611 HyBRIM and TK-609 HyBRIM

matics saturation high-way' is fully open with the nitrogen inhibitors removed. At such conditions, the hydrogenation potential of the catalyst is providing the volume swell, and it is therefore observed that TK-611 HyBRIM is saturating 18% more monoaromatics than TK-609 HyBRIM.

Conclusion

The second generation of HyBRIM technology is now available with the introduction of TK-611 HyBRIM catalyst. The 25% higher activity of TK-611 HyBRIM compared to first generation TK-609 HyBRIM catalyst unlocks additional flexibility to obtain longer catalyst cycles, more throughput, better product qualities or even processing of more severe feedstocks. The activity boost can be translated into lowering the reactor temperature significantly in hydrocracker pretreating and ULSD units, while simultaneously obtaining the same conversion of sulphur and nitrogen. Equally important, it is established that second generation HyBRIM technology exhibits the same high stability that refiners have come to expect from the BRIM and HyBRIM catalyst series. It has been demonstrated that TK-611 HyBRIM catalyst has

significantly higher hydrogenation activity than TK-609 HyBRIM catalyst due to its higher activity for nitrogen removal, an ability that will provide higher volume swells at similar conditions, resulting in substantially increased profitability for the refinery asset. In conclusion, the advantages of the new TK-611 HyBRIM can be utilised to improve the overall profitability and economy of all hydrocracker pretreating and ULSD units in multiple ways.

HyBRIM and BRIM are trademarks of Haldor Topsoe.

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