

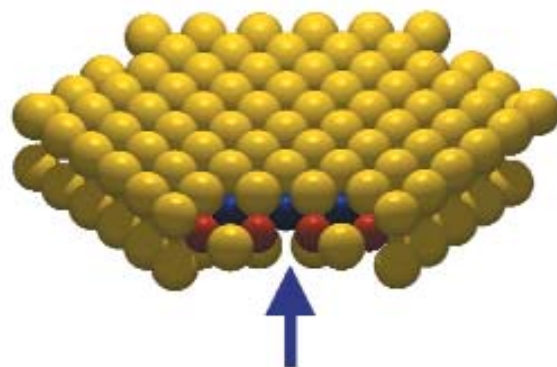
Brimming with activity

Per Zeuthen and Lars Skyum, Haldor Topsøe, Denmark, explain a new technology for high-activity hydroprocessing catalysts and present industrial experience highlighting their performance.

The need for high-activity hydroprocessing catalysts is more pronounced than ever. European refiners are ready to supply diesel and gasoline fuel with maximum 50 wt ppm sulfur from 2005 and maximum 10 wt ppm must be fully implemented from 2009. In a few countries, the near-zero level has already been introduced. As of June 2006, on-road diesel in the US must contain less than 15 wt ppm sulfur and gasoline less than 30 wt ppm sulfur.

Catalyst vendors respond to market demand by developing hydrotreating catalysts with significantly higher activity than previous generations of catalysts. With a trial-and-error catalyst development approach, it has been possible to achieve minor improvements, but obviously this is not the optimum way to develop high-activity catalysts. Topsøe's approach has therefore been to find a path from fundamental to applied research, and based on insight into HDS catalysis on the atomic scale, the company has in recent years succeeded in developing hydrotreating catalysts with considerably higher activities than previous generations of catalysts. In the 1980s and at the beginning of the 1990s, when hydrotreaters were operated at lower HDS conversion levels (up to 95 - 97%) than today (up to 99.95%), the sulfur removal primarily proceeded via the direct desulfurisation route. The primary objective of the research work at that time was to understand and develop catalysts with a high density of sites for direct desulfurisation. It was found that the activity correlated with the presence of Co-Mo-S (or Ni-Mo-S) structures on the alumina support. Also, it was shown that the sites responsible for the direct desulfurisation were sulfur vacancies located at the edges of the Co-Mo-S slabs (Figure 1). At the 9th Iberoamerican symposium on catalysis in Lisbon in 1984, Topsøe researchers published results from studies showing that there was a modified Co-Mo-S structure with substantially higher activity per

active site than the original Co-Mo-S structure. To differentiate between the two Co-Mo-S structures, these were



Type I and II – located at the sides of the CoMoS

Figure 1. Side view of CoMoS slabs showing type I and II sites.

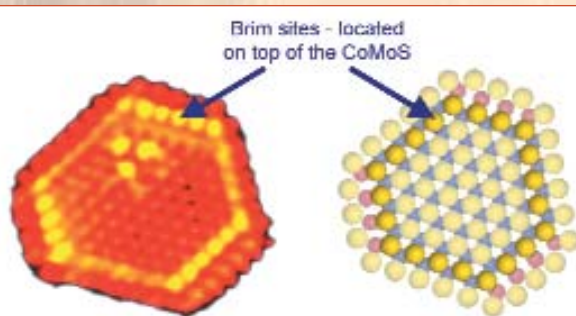


Figure 2. Top view of CoMoS slabs showing brim sites.

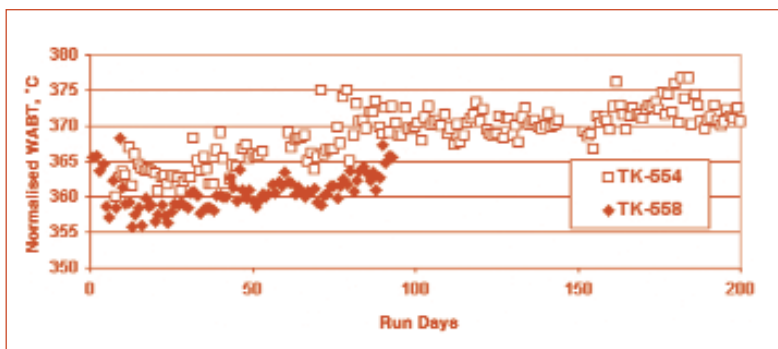


Figure 3. Run plot summary for refinery A, previous and current operation

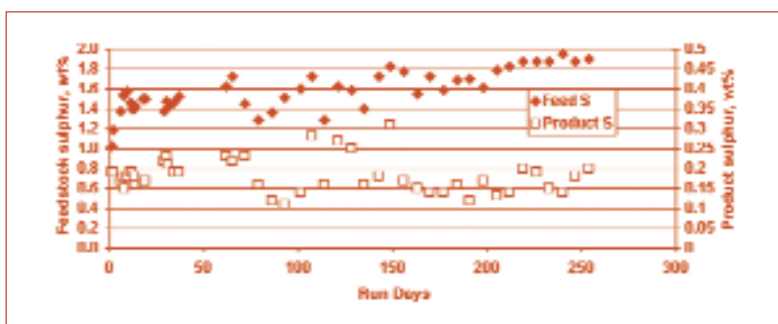


Figure 4. Run plot summary for refinery B, feed and product sulfur.

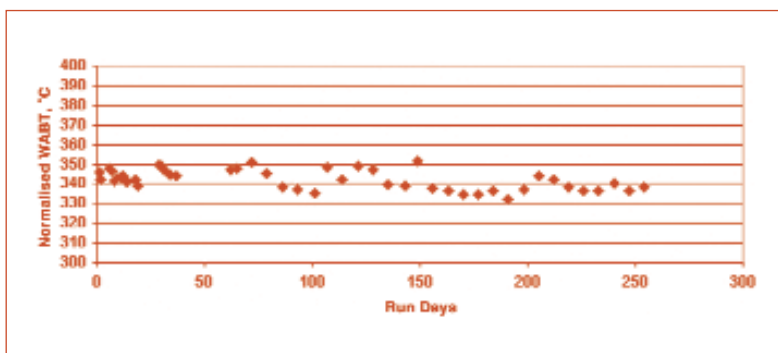


Figure 5. Run plot summary for refinery B, current operation with TK-558 BRIM™.

called Type I and Type II sites. Due to the higher activity of Type II versus Type I sites, catalysts commercialised in the 1990s had a higher concentration of the Type II reaction sites.

BRIM™ technology

With current and future sulfur specifications for transportation fuel, the sulfur conversion has increased, meaning the catalysts must be able to remove the most refractory sulfur species from diesel fractions and from feeds to be pretreated. It is generally understood and

Table 1. Feed characteristics and operating parameters for refinery A	
Feed characteristics	
Specific gravity,	0.9148
Sulfur content, wt%	1.5
Nitrogen content, wt ppm	1188
Ni + V, wt ppm	< 3
Distillation (5/50/95), °C	283/419/539 °C
Total aromatics, (mono/di-/tri+), wt %	44.5 (20.6/11.0/12.9)
Operating parameters	
LHSV, hr ⁻¹	1.27
Inlet pressure, barg	45
Temperature, °C	360

accepted that the conversion of these molecules proceeds via the prehydrogenation route under idealised conditions. However, despite the importance of the prehydrogenation route, very limited information is available on the precise molecular reaction steps. In our efforts to make more active catalysts Topsøe has, together with the University of Aarhus, Denmark, been involved in research work that has shed light on the hydrogenation step. The studies carried out have shown that the sites responsible for hydrogenation are located on top of the Co-Mo-S (Ni-Mo-S) slabs. As can be seen in Figure 2, the reaction sites are located close to the edges, and researchers have correspondingly named them 'brim sites'. The studies showed that thiophene can be hydrogenated and ring opened on the brim sites, after which sulfur extraction takes place in the Co-Mo-S sulfur vacancies also known as Type II reaction sites.

With a fundamental knowledge and understanding of the hydrogenation functionality, Topsøe researchers have developed a novel catalyst preparation procedure, which gives high-activity catalysts. With the new BRIM™ technology not only the brim site hydrogenation activity is increased, but also the number of sites for direct desulfurisation. The combination of high hydrogenation and high direct desulfurisation activity makes the BRIM™ technology very suitable for hydrotreating applications covering a wide pressure range.

The first commercial BRIM™ catalysts were TK-558 BRIM™ (CoMo) and TK-559 BRIM™ (NiMo). These catalysts were developed for FCC pretreatment and have been successfully adopted by more than a dozen refiners in the US and Europe. Very recently, TK-576 BRIM™ (CoMo), developed for diesel service, was commercialised.

FCC pretreatment catalysts

The new TK-558 BRIM™ and TK-559 BRIM™ will in many cases enable refiners to meet future specifications for ultra low sulfur gasoline without any post treatment. The economic benefit is gained from better product yield structures, cleaner FCC products and longer pretreatment cycles.

The very high hydrogenating power of the BRIM™ catalysts in FCC pretreatment service is of great importance to HDN and to the saturation of aromatic compounds, which positively affect the yield and quality of the gasoline produced in the FCCU. With tighter fuel specifications, the increased activity of the BRIM™ catalysts is thus primarily utilised to achieve better product properties. Despite the significantly higher workload of BRIM™ catalysts in FCC pretreatment service, the performance of these catalysts has shown equal or better stability than previous catalyst generations.

Traditionally, NiMo catalysts have been looked upon as having a higher HDN activity for FCC pretreatment service and CoMo catalysts as having a higher HDS activity. A high HDN activity is desirable for removal of nitrogen compounds and in particular basic nitrogen compounds from the FCC feed. These compounds would otherwise adversely affect the yield and quality of the gasoline produced in the FCCU.

Based on tests conducted at a pressure below 55 bar using typical US FCC feeds (including coker gas oils and SR VGO's) it was found that the CoMo catalyst (TK-558 BRIM™) has a volume HDS activity of up to 150% relative to the new NiMo catalyst (TK-559 BRIM™) and a volume HDN activity of up to 110% relative to the latter catalyst. As a result it is recommended that TK-558 BRIM™ is used for low to moderate pressure applications and a full load of the NiMo catalyst TK-559 BRIM™ for high pressure applications.

Commercial experience

In November 2003, Haldor Topsøe A/S decided to carry out a pilot plant test of TK-558 BRIM™ on a SR VGO Russian export crude received from refinery A in order to compare its performance with other catalyst loads at conditions very similar to actual commercial SOR conditions (Table 1). The FCC pretreater in refinery A is operating at a rather low pressure with two reactors in parallel. During the previous cycle, the reactors were loaded with TK-554+ as the primary catalyst, topped with a grading of demetallisation catalysts. For the present cycle, TK-558 BRIM™ 1/16 in. TL was selected as the bulk catalyst. Startup took place in April/May 2004, using standard sulfiding procedures for the catalyst activation. The FCC and the associated pretreater constitute a key complex for refinery A, producing 750 ppm sulfur FCC feed. Feed characteristics and SOR operating conditions are given in Table 1.

The aim of the pilot plant testing was to identify the best catalyst candidate for improvement of the operation and performance of the FCC pretreater and the FCCU, and four different catalyst samples were evaluated.

The results from the pilot plant evaluation in Table 2 clearly show the superior HDS and HDN performance of TK-558 BRIM™.

In Figure 3, a plot is shown of the average operating temperature during the present and previous cycle.

The commercial data confirm the superior performance of TK-558 BRIM™. The higher HDS activity makes it possible for the refiner to achieve target product sulfur at a lower temperature with the added benefit of a slightly higher throughput. The significantly higher HDN activity improves the operation of the FCCU, resulting in increased upgrading margins for the refinery. Despite the higher workload of the TK-558 BRIM™ catalyst in FCC pretreatment service, an unchanged or even a better stability is demonstrated compared with the previous catalyst cycle. Refinery A utilises the improved activity/stability to extend the cycle length. In addition to the lower SOR temperature, a lower pressure drop across the reactors is observed due to the larger sized catalyst pellets.

An extreme stability of the new family of catalysts produced with the BRIM™ technology is also demonstrated in the present cycle at refinery B. The refiner, which has two FCC pretreaters in series, purchased TK-558 BRIM™ from Topsøe and started up operation on this catalyst in December 2003. The unit processes Russian export crude with properties rather similar to those given in Table 1. The operating conditions of the FCC pretreater of refinery B are milder than those of refinery A. Refinery B produces FCC feed with 1700 ppm sulfur. Figure 4 and Figure 5 show the run plot summary with feed/product sulfur and the normalised average operating temperature during the first nine months of operation.

Figure 5 shows the very stable performance of the

Table 2. Summary of pilot plant test results

Catalyst system	HDS activity, RVA (%)	HDN activity, RVA (%)
TK-554+, 1/20 in. threelobe, catalyst in previous cycle	118	83
TK-558 BRIM™, 1/20 in. threelobe	125	115
TK-558 BRIM™, 1/16 in. threelobe, catalyst in present cycle	131	117
TK-557, 1/20 in. TL, CoNiMo FCC pretreatment catalyst	100	100

Table 3. Performance of TK-576 BRIM™ versus TK-574

Feed properties				
Density, kg/m ³	0.8690			
Sulfur, wt %	1.836			
Nitrogen, wtppm	195			
ASTM D-86, °C				
10/50/95 vol%	236/284/355			
Total aromatics, wt%	36			
Polyaromatics, wt%	21			
Performance				
	TK-574		TK-576 BRIM™	
Product S, wt ppm	50	10	50	10
H ₂ pressure, bar	30	30	30	30
LHSV, hr ⁻¹	Base	Base	Base	Base
WABT, °C	350	369	345	362

BRIM™ catalysts loaded in the FCC pretreater at refinery B.

The commercial data confirm that the radical BRIM™ technology provides high-activity catalysts with improved activity and high stability for many refining services. The hydrogenation activity of the catalysts has been improved, and they have a very high dispersion of active metals. These advantages are achieved without reducing catalyst strength, without changing the porosity and even with a low bulk density of the catalysts. Standard sulfiding procedures are used for activation of the catalysts.

Catalyst for ULSD

For diesel service, Topsøe has developed the CoMo catalyst, TK-576 BRIM™. Depending on the operating conditions and feedstock properties, TK-576 BRIM™ is found to be 5 - 10 °C more active than Topsøe's previously best CoMo catalyst, TK-574 (Table 3). Since it is possible to obtain very active catalysts with the BRIM™ technology for both the hydrogenation and the direct desulfurisation routes, TK-576 BRIM™ improves ULSD operation over a wide range of hydrogen pressures. At a very low pressure, direct HDS is the predominating desulfurisation route, and at medium up to high pressure, the prehydrogenation route will become more important. At the highest pressure, a NiMo catalyst is still the preferred choice, unless hydrogen availability is limited. The first two charges of TK-576 BRIM™ were started up in the US in July 2004, and in November 2004, a German ULSD hydrotreater will be loaded and started up with TK-576 BRIM™. As of September 2004, five charges of TK-576 BRIM™ have been sold, corresponding to more than 450 t of catalyst.

Conclusion

Due to new insight into the hydrogenation function of hydrotreating catalysts, Topsøe has managed to develop a radical new preparation technology called the BRIM™ technology. The key to success has been a combination of fundamental and applied research. Three new catalysts have been commercialised using the BRIM™ technology: TK-558 BRIM™ and TK-559 BRIM™ for FCC pretreatment with TK-558 BRIM™ being favoured at low to moderate pressures. TK-576 BRIM™ has been specifically developed for ULSD applications. Today, more than 2500 t of the new BRIM™ catalysts have been sold. ■



The new TK-576 BRIM™ ULSD catalyst

- **Benefits that count!**

TK-576 BRIM™ is the latest of the new generation high-activity catalysts based on Topsøe BRIM™ Technology. The unique combination of improved Type II and brim reaction sites makes TK-576 BRIM™ ideal for ULSD applications.

TK-576 BRIM™ shows benefits such as:

- 5-10°C improvement vs. current generation of HDS catalysts
- High stability in low pressure ULSD applications

A combination of the above improves the margins in ULSD hydrotreatment because, with TK-576 BRIM™, the refiner gets the flexibility to:

- Operate at a higher throughput
- Extend catalyst cycle length
- Process heavier and more difficult gas oil fractions

Contact Topsøe and learn more about the valuable assets with our new ULSD catalyst.

The Catalyst and Technology Company



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