Clean catalysts

Lars Skyum and Per Zeuthen, Haldor Topsøe, Denmark, present new catalyst solutions for hydrotreating operations in ULSD, FCC pretreatment and hydrocracking pretreatment.

The market for ultra clean fuels continuously calls for improved hydrotreating catalysts. In order to fulfil this need, Topsøe has developed a new catalyst preparation technology, offering highly active hydroprocessing catalysts. This new proprietary BRIM™ technology not only optimises the brim site hydrogenation functionality, but also increases the Type II activity sites for direct desulfurisation. The first two commercial catalysts based on the BRIM™ technology were Topsøe's TK-558 BRIM™ (CoMo) and TK-559 BRIM™ (NiMo) for FCC pretreatment service. This was followed by a new CoMo catalyst in 2004, TK-576 BRIM™, for ultra low sulfur diesel (ULSD) production.

Topsøe's R&D team has recently applied the BRIM™ technology to develop new members of the family of BRIM™ catalysts, TK-575 BRIM™ , a NiMo catalyst optimised for the high pressure ULSD market, and TK-605 BRIM™, a NiMo catalyst optimised for the high performance hydrocracker pretreatment market. With the launch of these two new catalysts, Topsøe can now offer BRIM™ CoMo and NiMo solutions to hydrotreaters operating in all critical services: ULSD, FCC pretreatment and hydrocracking pretreatment.

New catalyst preparation technology

Fundamental research in the area of catalysis carried out by Topsøe, together with researchers from the University of Aarhus (Denmark) and the Technical University of Denmark, has shed light on the atomic scale structures of the CoMoS and NiMoS phases. This insight has provided a new picture of the hydrogenation function of hydrotreating catalysts, and shown that on top of the CoMoS (NiMoS) slabs there exist special brim sites that are responsible for the hydrogenation reactions. New research has revealed that the NiMoS slabs can exist in two different shapes. As can be seen in Figure 1, the NiMo catalysts form the same hexagons as the CoMo catalysts. However, when NiMo catalysts contain very small clusters (NiMoS), these may be formed as dodecagons, where Ni is substituted at two different types of site.

With the knowledge from the fundamental research Topsøe has developed the BRIM™ catalyst preparation technology. The use of Topsøe's BRIM™ technology in its manufacturing process enables the company to control the types of reaction sites that are desirable for a specific service. At one extreme it is preferable to use a catalyst with mainly Type II activity sites for the direct desulfurisation routes, and at the other extreme to use catalyst containing mainly brim sites, i.e. with a high hydrogenation activity. In other words, BRIM™ technology enables Topsøe to optimise and tailor make the BRIM™ catalyst to obtain the best possible performance and value combination for our clients.

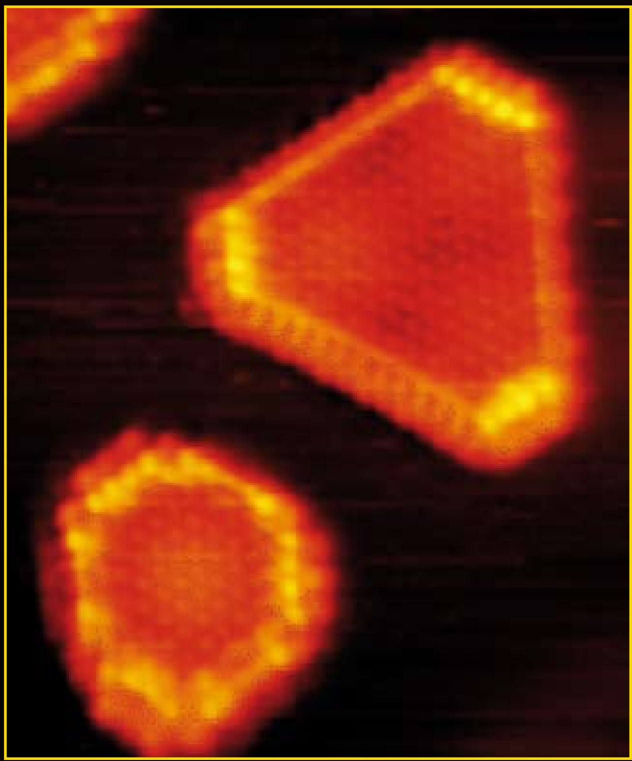

Figure 1. STM picture showing the morphology of active NiMoS structure.

New NiMo catalyst for ULSD production

Production of practically sulfur free diesel in high pressure (45+ bar (650+ psi) hydrogen pressure) diesel hydrotreaters is favoured by a catalyst with high hydrogenation activity. For this reason, a NiMo catalyst is the preferred choice for this service. Topsøe's new NiMo TK-575 BRIM™ catalyst further enhances the hydrogenation activity needed in high pressure ULSD services. On a feed mixture of straight run gasoil (SRGO) and light cycle oil (LCO), the new catalyst exhibits a 5 - 7 ˚C (9 - 13 ˚F) better HDS activity in ULSD service compared to Topsøe's well proven TK-573 ULSD catalyst. This is illustrated in Figure 2, which shows a comparison of the two catalysts at two desulfurisation levels (Table 1). The temperature difference between the two catalysts depends on the feedstock type, operating conditions and unit severity.

In addition to high activity, the BRIM™ catalysts exhibit high stability (as will be demonstrated by a commercial example later in this article). Pilot plant studies are often limited to two/three months of operation, which is too short

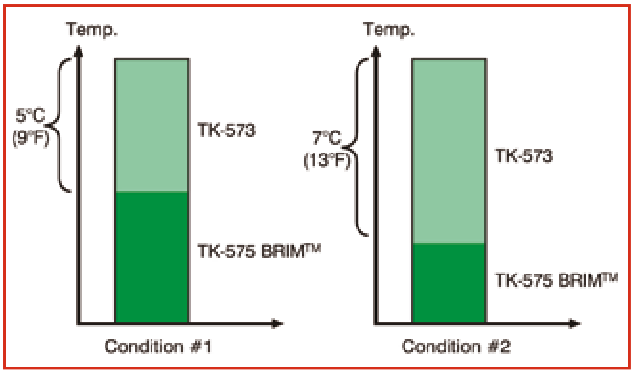

Figure 2. Performace of TK-575 BRIM™ versus TK-573 on SRGO/LCO blend.

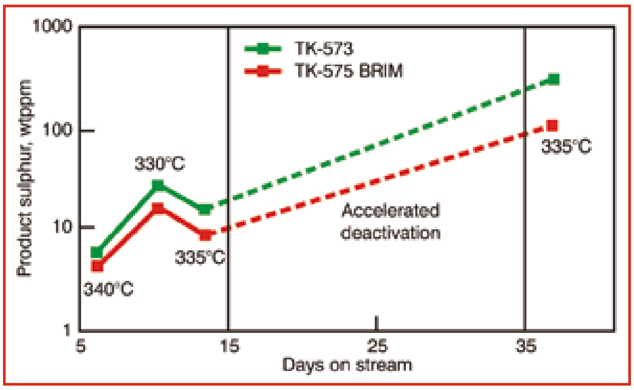

Figure 3. Accelerated deactivation of TK-575 BRIM™ and TK-573.

Table 1. Performance of TK-575 BRIM™ vs. TK-573 on SRGO/LCO blend	
Operating conditions 1	
LHSV (hr^{-1})	1.5
H_2 pressure (bar/psi)	60/870
H_2/oil ratio (Nm^3/m^3/SCFB)	500/2970
Product S (wtppm)	10
Operating conditions 2	
LHSV (hr^{-1})	2.0
H_2 pressure (bar/psi)	60/870
H_2/oil ratio (Nm^3/m^3/SCFB)	335/1990
Product S (wtppm)	10

Table 2. Performance of TK-605 BRIM™ vs. TK-565 on Californian blend in test no. 1		
Operating conditions		
LHSV (hr^{-1})	1.0	
Reactor inlet pressure (bar/psi)	110/1595	
Feed properties		
Feed type	VGO + CGO	
SG/˚API	0.936/19.7	
Sulfur content (wt%)	2.03	
Nitrogen content (wt ppm)	4276	
Basic nitrogen (wt ppm)	1417	
Distillation 10,50, FBP, (˚C/˚F)	336, 418, 533/637, 784, 991	
Total aromatics (mono/di/tri) (wt%)	37.2 (13.5/5.7/18.1)	
Product properties	**TK-565**	**TK-605 BRIM™**
SG/˚API	0.889/27.7	0.887/28.0
Nitrogen (wt ppm)	267	117
Sulfur (wt ppm)	87	50

a period in order to measure the catalyst stability. As an alternative to a very long pilot plant test, one can measure the activity of new catalyst versus the activity of a known and proven catalyst after having exposed the catalysts to accelerated deactivation, and in this way get a comparison of the stabilities. Figure 3 shows the results from such an accelerated deactivation pilot plant study in which TK-575 BRIM™ is compared to the predecessor TK-573 at 45 bar (650 psi) hydrogen pressure. Initially, the temperature was adjusted to get product sulfur levels in the 10 - 50 wtppm range. In the second step, which lasted three weeks, the catalysts were exposed to accelerated deactivation using a heavy feed, high temperature and low H_2 availability. In the third and final step, the operation was changed back to the initial conditions. As Figure 2 shows, the catalysts have indeed deactivated, but it is also clearly seen that TK-575 BRIM™ has maintained a high desulfurisation activity relative to TK-573.

New NiMo catalyst for hydrocracking pretreatment service

The pretreatment stage in a hydrocracker is a fixed bed catalytic process implemented with the primary objective of reducing organic nitrogen, particularly the basic nitrogen compounds from the feedstock. Nitrogen compounds have a significant negative impact on the activity of hydrocracking catalysts, and consequently on the performance of the hydrocracker.

The growing interest in processing heavy oils with a high nitrogen content has created a need for pretreatment catalysts for both high pressure hydrocrackers and mild hydrocrackers with higher hydrodenitrogenation (HDN) activity. TK-605 BRIM™ meets this need.

TK-605 BRIM™ is optimised for removal of refractive organic nitrogen compounds such as carbazoles, and shows a significant improvement compared to the previous generation hydrocracking pretreatment catalyst from Topsøe, TK-565. To illustrate the activity gain with TK-605 BRIM™ versus the old generation, Tables 2 and 3 present the results from two pilot plant tests. In test no. 1, the feed is a vacuum gasoil/coker gasoil blend of Californian origin, with a relatively high nitrogen content. The test conditions are typical for hydrocracking preatreatment: a LHSV of 1.0 hr^{-1} and a partial hydrogen pressure of 110 bar (1600 psi). As Table 2 shows, both sulfur and nitrogen removal is significantly improved with TK-605 BRIM™ compared to TK-565. In test no. 2, the two catalysts were tested on a Mideast vacuum gasoil containing less aromatics and nitrogen than the feed in the first test. Also on this feed, which is more reactive and easier to hydrotreat, TK-605 BRIM™ demonstrates much better performance than the previous generation catalyst.

The two tests demonstrate that the new TK-605 BRIM™ shows a superior HDN performance with typically 20 - 30% higher activity equivalent to 5 ˚C (9 ˚F) than that of the previous generation catalyst TK-565.

Commercial experience

Topsøe's BRIM™ catalysts are recognised as top tier catalysts for ULSD and FCC pretreatment service and have been sold to more than 60 high severity hydrotreating units over the past couple of years. Performance data from the many commercial applications have proven the superior activity of the BRIM™ catalysts compared to conventional Type II site catalysts. The superior hydrotreating activity along with an excellent stability allows the refiner to process higher feed rates, poorer quality feeds and to obtain better quality products with longer operating cycles. The following example

Table 3. Performance of TK-605 BRIM™ vs. TK-565 on Mideast VGO in test no. 2		
Operating conditions		
LHSV (hr^{-1})	1.5	
Reactor inlet pressure (bar/psi)	90/1305	
Feed properties		
Feed type	VGO	
SG/˚API	0.926/21.3	
Sulfur content (wt%)	2.95	
Nitrogen content (wt ppm)	841	
Basic nitrogen (wt ppm)	283	
Distillation 10,50, FBP, (˚C/˚F)	369, 443, 538/696, 829, 1000	
Total aromatics (mono/di/tri) (wt%)	39.8 (14.6/11.1/14.1)	
Product properties	**TK-565**	**TK-605 BRIM™**
SG/˚API	0.886/28.2	0.882/28.9
Nitrogen (wt ppm)	88	38
Sulfur (wt ppm)	717	487

Table 4. Operating conditions and feedstock properties at European refinery making ULSD with TK-576 BRIM™	
Operating conditions	
LHSV (hr^{-1})	1.9 (50 ppm S)/1.3 (10 ppm S)
Reactor inlet pressure (bar/psi)	37/536
Treat gas H_2 purity (vol%)	76
Feed properties	
Feed type	70% HGO + 30% MGO
SG/˚API	0.857/33.6
Sulfur content (wt%)	0.19
Nitrogen content (wtppm)	200

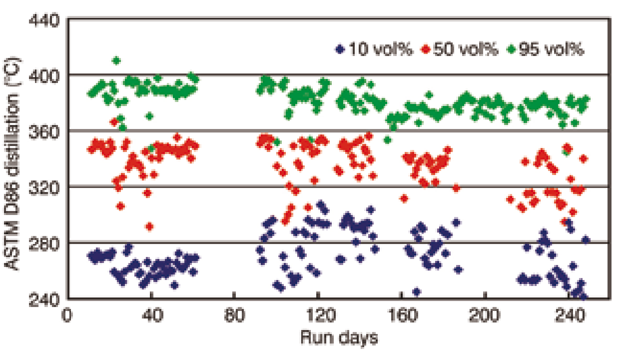

Figure 4. ULSD production with TK-576 BRIM™: ASTM D86 feed distillation data.

demonstrates its performance in a European ULSD hydrotreater that operates at very severe conditions.

A European refinery has two ULSD hydrotreaters: HDT no. 1 is a relatively large hydrotreater producing close to 80 000 bpd ULSD, and this has been operating with TK-576 BRIM™ since the end of 2004. This is a high activity CoMo catalyst specially developed for low to medium pressure ULSD production. The hydrogen pressure inlet to HDT no. 1 is 27 bar (390 psi), and the hydrogen to oil ratio is only 55 Nm^3/m^3 (325 SCFB). Due to the low availability of hydrogen, the feedstock is primarily diesel in the light to medium distillation range. During Spring 2005 TK-576 BRIM™ was selected for the second ULSD hydrotreater. HDT no. 2 has a capacity of 15 000 bpd, and as the hydrogen pressure is higher in HDT no. 2, distillates in the medium to heavy range are processed in this unit. The products from the two hydrotreaters are blended and sold as ULSD with either 50 or 10 wtppm sulfur.

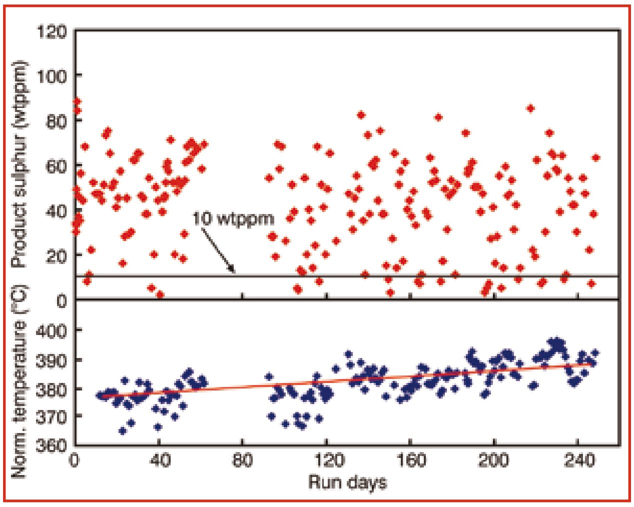

Figure 5. ULSD production with TK-576 BRIM™: product sulfur and normalised WABT.

Table 4 lists the key operational parameters as well as the average values of the feed properties to HDT no. 2 from SOR to the present. For the majority of the time the unit produces diesel with 50 wtppm S, but approximately 15% of the time diesel containing less than 10 wtppm S is produced at reduced throughput. During the first six months of the cycle, HDT no. 1 was operated in summer mode and in this period the feed density was typically 860 kg/m^3 (33.0˚API), for some periods even above 870 kg/m^3 (31.1˚API). To meet the cold flow properties, the feed is slightly lighter during winter operation, approximately 855 kg/m^3 (34.0˚API). The feed distillation curve (ASTM D-86) in Figure 4 shows that the 95% cut typically was 385 ˚C (725 ˚F) in summer mode, but relaxed to 380 ˚C (716˚F) in the winter season. It is known that the most refractive sulfur compounds (the sterically hindered substituted dibenzothiophenes) are concentrated in the heavy end of diesel feed, and even the winter feed is therefore considered to be a very difficult feed for an ULSD hydrotreater, not least when taking the low reactor pressure into account. Figure 5 shows the product sulfur versus catalyst life. This is on average less than 45 wtppm, but as it is blended with the product from the other ULSD hydrotreater, it has been up to 70 - 90 wtppm on a few days. The normalised weighted average bed temperature (WABT) for the unit is shown in Figure 5. Due to the high fraction of HGO in the feed blend and the low reactor pressure, the WABT is high from start of run. Refiners operating ULSD hydrotreaters on a severe feed at a relatively low pressure often plan for shutdown and catalyst replacement at the time when the WABT reaches 380 - 390 ˚C (716 - 734 ˚F) as there is a risk that the catalyst will deactivate rapidly at these conditions. Nevertheless, Figure 5 shows that the observed deactivation is modest, demonstrating that TK-576 BRIM™ shows excellent stability in this tough operation.

Conclusion

Using the proprietary BRIM™ technology, Topsøe has developed and commercialised two new NiMo catalysts for ULSD and hydrocracker pretreatment: TK-575 BRIM™ and TK-605 BRIM™ with superior hydrotreating performance. In ULSD applications TK-575 BRIM™ shows 5 - 7 ˚C (9 - 13 ˚F) activity improvement compared to TK-573, and TK-605 BRIM™ has 5 ˚C (9 ˚F) higher activity than that of its previous generation hydrocracking pretreatment catalyst. BRIM™ catalysts have been sold to more than 60 hydrotreaters and have demonstrated high activity as well as excellent stability. ■

The Brand New TK-575 BRIM™ NiMo Catalyst for ULSD Service

- A NiMo catalyst optimized for medium to high pressure ULSD units
- Designed using Topsøe's proprietary BRIM™ technology
- Improved HDS activity with maximum hydrogenation activity due to the BRIM™ sites
- Optimized ratio of Type II activity sites and BRIM™ activity site for demanding ULSD service
- High activity and excellent stability allowing the refiner to process higher feedrates, worse quality feeds and obtain better quality products and longer operating cycles

The Catalyst and Technology Company

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