In August 2004, Topsøe launched a new CoMo catalyst for ULSD production, the TK-576 BRIM™. The development of this new catalyst relied on fundamental research in the area of HDS catalysis, which led to identification of the brim sites that are known to be responsible for desulfurisation via the pre-hydrogenation route. This article will look at how the BRIM™ catalyst preparation technology differs from the past generation of catalysts, and present data from the first industrial ULSD unit using TK-576 BRIM™.

**Reaction sites on hydrotreating catalysts**

It has been well known for some time that production of sulfur free diesel requires the hydrotreating catalyst to be able to remove the sterically hindered sulfur compounds, such as the alkyl-substituted dibenzothiophenes, and that these refractive sulfur compounds can be removed by using either the direct route or the pre-hydrogenation route. With the direct route, the sulfur molecule is extracted in one step, whereas the pre-hydrogenation route involves two steps; namely hydrogenation of one of the benzene rings on the alkyl-substituted S compound in the first step, then extraction of the S molecule in the second step. Not surprisingly, the reaction sites responsible for the extraction and hydrogenation reactions differ from one another in physical characteristics and, as will be shown below, the sites likewise have different locations in the catalyst.

A traditional diesel hydrotreating catalyst is composed of Co or Ni (or both) and Mo, metals that catalyse the chemical reaction. These active metals are dispersed on the support material (alumina), which is porous so that the surface area per volume becomes relatively high, typically from 150 - 250 m²/g catalyst. In the late 1970s, Topsøe researchers discovered that HDS catalyst activity correlates with the concentration of CoMoS structures, which are dispersed on the alumina catalyst support (Figure 1). To put it simply, the CoMoS structure is the ‘heart’ of the catalyst, as it is here that the extraction and hydrogenation takes place.

The location and the characteristics of the extraction sites on the CoMoS slabs are well described and understood, but until recently, this has not been the case for the hydrogenation sites. Due to the importance of hydrogenation sites in deep HDS, Topsøe researchers have been involved in fundamental research work that has provided insights into the hydrogenation function of hydrotreating catalysts.

**Sites at the heart of the catalyst**

**Extraction sites**

It has been shown that the extraction sites that account for the direct route are located at the edges of the CoMoS structures (Figure 2). 20 years ago Topsøe researchers discovered that there exists a modified CoMoS structure, which has substantially higher activity per active site, and to differentiate between the ‘old’ and the ‘new’ CoMoS structures, the researchers named them Type I and Type II.

**Hydrogenation sites**

All hydrotreating catalysts have hydrogenation activity, but the sites responsible for hydrogenation have not, until recently, been studied and characterised by scientific and industrial researchers to the same extent as the extraction sites. Together with researchers from the University of Aarhus and the Technical University of Denmark, Topsøe has been engaged in research that provided atom resolved images of the active CoMoS structures for the first time. More importantly, such studies have provided direct information on how sulfur containing molecules may interact and react with the active structures, and this insight has provided a new picture of the hydrogenation function of hydrotreating catalysts. On the top of CoMoS slabs, close to the edges, there exist special brim sites with metallic character, and it was observed that thiophene can be hydrogenated and ring-opened on the brim sites. Figures 1 and 2 show the location of the brim sites on top of the CoMoS slabs.

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new insight to the hydrogenation function of hydrotreating catalysts. With the new knowledge that was gained from this work, it is now possible to visualise how desulfurisation via the pre-hydrogenation route occurs. In the first step, one of the benzene rings on alkyl substituted dibenzothiophene is hydrogenated on the brim sites on top of the CoMoS slab. After breakage of one of the C-S bonds, the S molecule migrates to the extraction site at the edge of the CoMoS slab where the S is extracted in the second step (Figure 2).

New catalyst preparation technology

In parallel with the new basic research activities, Topsøe developed a new catalyst preparation technology that provides high activity hydroprocessing catalysts. This new BRIM™ technology not only optimises the brim sites’ hydrogenation functionality, but also increases the activity for the direct desulfurisation. The first two commercial catalysts based on this technology were Topsøe’s TK-558 BRIM™ (CoMo) and TK-559 BRIM™ (NiMo) for FCC pre-treatment service. At the time of writing, 3000 t of these new catalysts have been sold.

In 2004, a new CoMo catalyst for ULSD production was released, known as TK-576 BRIM™. This catalyst is the successor to Topsøe’s current leading CoMo catalyst, TK-574, and it shows an improvement in the catalyst performance, which in terms of WABT is typically 6 - 8 ºC. As for the FCC P/T catalyst, the features of the new ULSD catalyst is an enhancement of hydrogenation activity combined with a higher activity for the direct desulfurisation. Since the direct route is favoured in operations where the feed concentration of inhibiting nitrogen species are high (for example, if the feed contains LCO, see case study below) and if it is physically impossible to remove these inhibitors due to equilibrium constraints in the reactor environment (e.g. at very low pressure), it is important that the catalyst exhibits high activity for both the desulfurisation routes.

The actual activity difference between the new and the previous generation of catalysts depends on feedstock type, operating conditions and unit severity, but in all events the refiner has several options to improve margins with the new catalyst, such as increasing production rate, extending cycle length and processing heavier and more difficult feedstocks. The overall refinery configuration determines how the high activity is best utilised to maximise margins.

Case study: Increase LCO in the feed slate

The following example will demonstrate how TK-576 BRIM™ can create value in a FCC refinery that upgrades LCO from fuel oil to ULSD. The refinery produces diesel with less than 10 wtppm S from a blend of SRGO and LCO, in a unit with a nameplate capacity of 25 000 bpd and a reactor pressure of 35 bar. The catalyst is replaced every 2 1/2 years, and the operating strategy that the refinery has chosen is to process a feed that contains up to 20% LCO at start-of-run (SOR) until the WABT approaches 400 ºC, which is the EOR temperature. When the WABT is close to EOR, the refiner reduces the amount of LCO in order to relax the severity of the unit and eventually obtain a cycle of 2 1/2 years. Table 1 summarises the unit operation.

Table 1. Key operational data for ULSD hydrotreater co-processing LCO

<table>
<thead>
<tr>
<th>TK-574</th>
<th>TK-576 BRIM™</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feedrate, bpd</td>
<td>25 000</td>
</tr>
<tr>
<td>Reactor pressure, bar</td>
<td>35</td>
</tr>
<tr>
<td>Product S, wtppm</td>
<td>8</td>
</tr>
<tr>
<td>Cycle length, years</td>
<td>2 1/2</td>
</tr>
<tr>
<td>LCO content at SOR, %</td>
<td>20</td>
</tr>
<tr>
<td>LCO content at EOR, %</td>
<td>2</td>
</tr>
<tr>
<td>Total amount of LCO processed, million bbl</td>
<td>3.66</td>
</tr>
<tr>
<td>Improved margin over 2 1/2 years, US$ million</td>
<td>6.3</td>
</tr>
</tbody>
</table>

Figure 1. The ‘heart’ of the (CoMo) hydroprocessing catalysts: CoMoS slabs.

Figure 2. Hydrogenation of the refractive S compound takes place on the brim sites, and the extraction of the S atom takes place at the edges of the CoMoS slab.

Figure 3. Performance of the TK-576 BRIM™ vs. TK-574 at ULSD conditions.

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SOR WABT is 364 °C and the amount of LCO is 20%. However, after 15 - 16 months, the WABT is close to 390 °C, and the refiner must reduce the amount of LCO. Reducing the LCO will influence the operation in two ways. First of all, the feed blend becomes easier to treat, and therefore it is possible to reduce reactor temperature. Secondly, with less LCO in the feed slate, the catalyst deactivates at a lower rate. In the example, it is not sufficient to reduce the LCO content from 20% to 18%, and 25 months after SOR the refiner again has to relax on the amount of LCO. The WABT is now 395 °C, which is only 5 °C from EOR conditions, and still the scheduled replacement of catalyst is five months away. In order to reach the planned cycle length of 2 1/2 years, it is now necessary to adjust the amount of LCO and replace it with SRGO almost every week. As seen in Figure 3, the LCO content is reduced from 16% to only 2% in the last five months of the cycle with TK-574.

If the refiner replaces catalyst and installs TK-576 BRIM™, it is possible to operate at a WABT that is 6 °C lower at SOR conditions. The deactivation rate is the same with the two catalysts, but due to the higher activity of TK-576 BRIM™, the refiner can operate with the 20% LCO for a longer period before it is necessary to cut back in the amount of cracked feedstock. As was the case with TK-574, the refiner is forced to intensify replacement of LCO with SRGO as the WABT approaches EOR, but with the new catalyst the amount of LCO is not at any time less than 12%.

In the cycle with TK-574, the refiner can process 3.66 million bbls of LCO in 2 1/2 years, and this is increased to 4.29 million bbls with TK-576 BRIM™. What this means in added value varies from refinery to refinery, but assuming an upgrade value of US$ 10/bbl between fuel oil and ULSD, refinery margins are improved US$ 6.3 million over 2 1/2 years.

**Commercial status**

The extra value that TK-576 BRIM™ creates has spurred several refineries to use this catalyst, and seven months after its launch total sales exceed 1600 t. One of the TK-576 BRIM™ charges was sold to a Western European refinery that produces ULSD with either 50 wtppm or 10 wtppm sulfur at a total reactor inlet pressure of 27 bar. The decision to choose TK-576 BRIM™ was made after evaluation of the catalyst in a pilot plant test using the relevant feed and simulating the performance of the industrial unit, from which it was demonstrated that it was possible to improve the performance by 5 - 6 °C relative to the previous operation. Table 2 lists the design feedstock characteristics and operating conditions for the reference unit. The crude is of North Sea origin, which is low in sulfur but has a relatively high concentration of refractive sulfur compounds.

In December 2004 TK-576 BRIM™ was loaded and started up using a SRGO spiked with DMDS. The SOR performance was as expected from the pilot plant testing, and as such, the refiner is able to operate at a lower temperature than in previous cycles. Figure 4 and 5 shows feed and product sulfur and the normalised temperature for the first three months of operation. The majority of the time the unit produces diesel with less than 50 wtppm S, but diesel with less than 10 ppm S is produced approximately 15% of the time.

The refiner is satisfied with the performance of TK-576 BRIM™ and decided to buy a second charge for the other diesel hydrotreater at the refinery. The second charge has been delivered and is being started up at the time of writing.

**Conclusion**

Topsøe’s new CoMo catalyst, TK-576 BRIM™, significantly improves performance compared with previous generation CoMo catalysts. The catalyst is produced with the novel BRIM™ catalyst preparation technology. The new technology is the result of fundamental research work carried out in the field of catalysis, which has led to identification and characterisation of the active sites for hydrogenation: the brim sites.

**References**

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.