FCC pre-treatment catalysts TK-558 BRIM™ and TK-559 BRIM™ for ULS gasoline using BRIM™ technology

Utilising new BRIM™ technology, Topsøe has developed a series of catalysts that allow the FCC refiner to make 10 ppm S gasoline.

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The latest diesel and gasoline specifications require reducing sulphur to very low concentrations. The FCC unit is the major source of gasoline in a FCC refinery; however, the sulphur content of the FCC products is also the major contributor to the fuel sulphur. In general more than 90% of the sulphur compounds in the gasoline pool originate from the FCC gasoline.

FCC feed pretreatment can improve the performance of the FCC unit and be an excellent instrument to meet the required sulphur levels in gasoline. The key is to maintain a high degree of nitrogen removal whilst extending the degree of desulphurisation. Selection of the best catalyst for a given service will depend on operating pressure, sulphur compounds present in the feed, and the nature and amounts of inhibitors to the desulphurisation reaction.

The new catalysts
Topsøe has developed new catalysts based on a unique preparation method resulting in a significantly better dispersion of the active phases giving higher HDS and HDN activities.

The first two commercial catalysts based on this new technology are TK-558 BRIM™ (CoMo catalyst) and TK-559 BRIM™ (NiMo catalyst). Both of these catalysts are characterised with a high HDS activity making them suitable for the increased demand for sulphur reduction of the FCC feedstock to meet the future gasoline sulphur specification of 10 ppm. Furthermore, the requirements for high HDN activities are maintained. Figure 1 illustrates the relative volume (RVA) HDS/HDN performance activities of the new generation catalysts compared with the previous generation catalysts in a typical FCC pretreatment service treating a VGO/CGO blend at 80 bar pressure. Since the type of FCC feed used and other process conditions influence the activities, the relative activity of each catalyst will differ among the dozen of refineries where these catalysts are currently in use.

The new catalysts will in many cases enable refiners to meet the future specifications for ultra low sulphur gasoline without any post-treatment. The economic benefit is gained through better product yield structures, cleaner FCC products and longer pre-treat cycles.
BRIM - New fundamental insight
Topsøe researchers discovered the existence of the CoMoS (or NiMoS) active sites in the late 1970’s. Much of the subsequent scientific and industrial research has focused on understanding the catalytic function of the CoMoS type structure and finding preparation procedures and methods for modifying the structures to give enhanced activity.

In the 1980’s, Topsøe researchers found that there existed at least two types of CoMoS. Type I is thought to be strongly bound to the alumina carrier, and Type II, which exhibits higher activity, is less strongly bound to the carrier. Type II can occur, for example, by stacking of the slabs in which case the upper layers will be Type II and the bottom layer may be Type I.

Recently, Topsøe has been involved in research that has provided new insight to the hydrogenation function of hydrotreating catalysts. It was shown that a new type of metallic BRIM sites located on top of the molybdenum disulphide slabs close to the edges play an important role (Fig. 2). Our research has also shown that the relative importance of the direct and hydrogenation routes depend strongly on the composition of the feed.

Topsøe has developed a radical preparation technology that, using standard sulfiding procedures, gives very high activity catalysts for many refining services. The new BRIM™ technology has several key features:

- The hydrogenation activity of the BRIM sites is enhanced
- The frequency of BRIM sites is increased by avoiding stacking of the molybdenum disulphide slabs. Although stacking can be an advantage for the occurrence of Type II structures, stacking reduces the number of BRIM sites (because BRIM sites are only available on the upper surface of the stack).
- The bonding of molybdenum disulphide to the carrier is optimised giving more Type II direct desulphurisation sites.

These advantages are achieved without reducing catalyst strength and changes in porosity or bulk density of the catalyst.

Catalyst choice
The optimal choice between NiMo (TK-559 BRIM™) and/or CoMo (TK-558 BRIM™) is dictated by the unit pressure, temperature and desired product properties. The CoMo based TK-558 BRIM™ will provide the best performance in low to moderate pressure units. TK-558 BRIM™ further exhibits an HDN activity that is unique for a CoMo based catalyst. TK-558 BRIM™ is the catalyst of choice for the refiner who wishes to produce low sulphur FCC products without changing yields of gasoline and other high quality products. In many low to moderate pressure applications, TK-558 BRIM™ even exhibits equal or better HDN activity to that of TK-559 BRIM™. Figure 3 displays performance
evaluations of the new catalysts in FCC pretreatment service treating a American West Coast VGO/CGO blend at 50 bar pressure. At these conditions the CoMo catalyst performs better than the NiMo catalyst.

In high pressure FCC PT plants and in cases where nitrogen is the main concern, the preferred choice will be the high activity HDN catalyst TK-559 BRIM™.

**Polynuclear aromatics saturation**

Aromatic compounds are not easily cracked in a FCC unit, and the limited amount of cracking achieved produces a large amount of coke. However, by saturating the PNA compounds present in typical FCC feeds and converting them into naphthenes, they are more easily cracked into valuable products. PNA saturation is negatively affected by increased FCC pretreater severity, as high reactor temperature does not favour polynuclear aromatics (PNA) saturation, and the severe operating conditions will result in higher PNA content in the feed to the FCC unit.

Running existing FCC pretreaters at higher severity (i.e high temperature) in order to meet the stringent sulphur levels in the gasoline pool will decrease the saturation of polyaromatics in the pretreater because saturation is equilibrium limited. The benefits of FCC pretreating in terms of higher conversion and increased yields of high value products will therefore decrease. Figure 4 shows the product polyaromatics at different temperatures in FCC pretreatment VGO services at low and high operating pressures.

Many FCC pretreaters are designed for use with NiMo catalysts in order to obtain the benefits of low nitrogen and polyaromatic feed to the FCC. As described above, the new CoMo catalyst system, TK-558™ prepared with the new BRIM™ technology will provide a higher degree of desulphurisation with however unchanged nitrogen and PNA content of the FCC feed, see also Figure 3.

**Identification and reactivity of sulphur compounds in VGO**

Sulphur compounds in VGO are more complex than those found in light distillates, and more structural isomers are possible.

Using gas chromatography with a sulphur specific detector, feed and products have been compared. The chromatograms show that, when the degree of desulphurisation increases, the relative concentration of 4- and 4,6-dialkyldibenzothiophenes also increases compared to the concentration of the heavier sulphur-containing compounds. Notwithstanding the presence of heavier sulphur-containing compounds in VGO’s, the least reactive compounds in both diesel and VGO are the substituted DBTs with the alkyl groups in position 4 and 4,6. The reactivity of these refractory compounds determines the reactivity of VGOs in high severity FCC pretreatment.
Conclusion
Topsøe has developed a new preparation technology. So far two new catalysts have been commercialised using this BRIM™ technology: TK-558 BRIM™ and TK-559 BRIM™ for FCC pre-treatment.

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Figure 1. Relative volume HDS/HDN activities of recent Topsøe FCC pretreatment catalysts
Figure 2. New type of metallic BRIM sites close to the edges play an important role in the hydrotreating reactions.

Figure 3. Relative volume HDS/HDN activities of Topsøe FCC pretreatment catalysts treating a West Coast VGO/CGO blend at 50 bar pressure.
Figure 4. Product polyaromatics in typical VGO FCC pretreatment service versus temperature at two different pressures.