



Our World of Cats: Panthera leo. The most distinctive feature of the male lion is its mane. A male lion can reach 2–3 meters in body length and is surpassed in size only by the larger species of tiger. The lion is unusual amongst the 'big cats' in that it lives in organised social groups called prides.

Topsøe Refinery Catalysts



TK-576 BRIM™ – ULSD Catalyst





The market demand for Ultra Low Sulphur Diesel (ULSD) with a sulphur content of less than 50 down to less than 10 wtppm sulphur is increasing due to environmental legislation that is being introduced all over the world, with Europe and USA as the pioneers. Besides reduction of sulphur, diesel characteristics such as aromatics, specific gravity and final boiling point must be reduced to meet the new specifications, but in most diesel hydroprocessing units it is the sulphur limit that determines the capability to produce ULSD. For units which are limited in hydrodesulphurisation activity operating at low to medium reactor pressure, the most suitable HDS catalyst is a CoMo type.

TK-576 BRIM™ – ULSD Catalyst

To meet the increased demand for high activity CoMo catalysts, Topsøe has developed TK-576 BRIM™ that has a higher desulphurisation activity than any other commercially available CoMo catalyst. TK-576 BRIM™ is based on a new catalyst technology that enhances the number and activity of brim active sites.

In the late 1970's, Topsøe researchers discovered that the activity of HDS catalysts correlates with the concentration of CoMoS active sites. Much of the subsequent

scientific and industrial research on hydrotreating catalysts 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 exists two types of reaction sites on the sides of the CoMoS slabs. Type I is thought to be CoMoS that is strongly bound to the alumina carrier, and Type II, which exhibits higher activity, is CoMoS that is less strongly

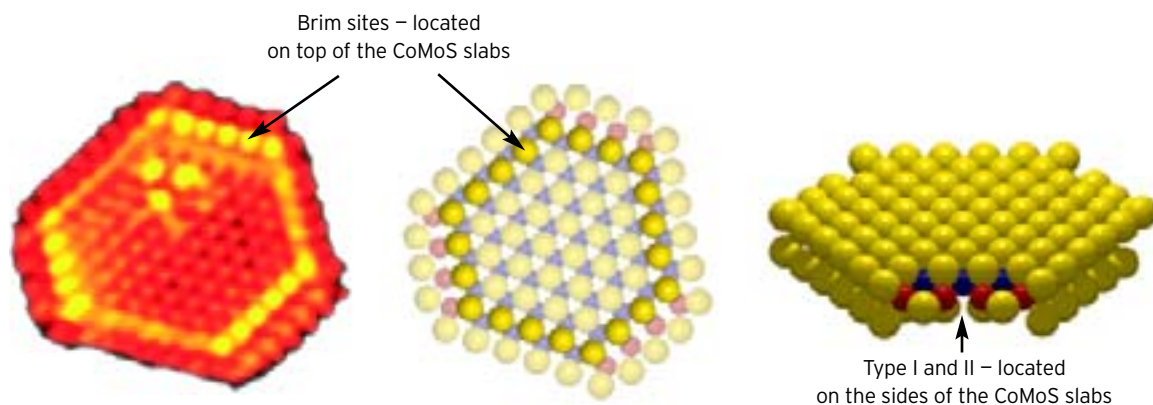


Figure 1. CoMoS model

By use of Scanning Tunneling Microscopy (STM) it is possible - in atomic scale - to study the functionality of the active sites on a hydrotreating catalyst during the hydrotreating reactions. A new type of metallic brim sites close to the edges on the CoMoS slabs plays an important role in the hydrotreating reactions. The reaction sites for the direct desulphurisation are found on the sides of the CoMoS slabs. Topsøe researchers showed in the mid 80's that there existed two direct desulphurisation sites and to differentiate between these they named the sites Type I and Type II.

bound to the carrier. State-of-the art catalysts developed in past years have relied on the high activity of Type II reaction sites in particular (Figure 1).

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 site located on top of the molybdenum disulphide slabs and close to the edges, plays an important role (Figure 1). The researchers named these sites: Brim sites. Brim sites are thought to be responsible for desulphurisation via the hydrogenation route, which is important for conversion of the most refractive sulphur compounds.

Topsøe has developed a radically new preparation technology that, using established sulphiding procedures, provides very high activity catalysts for many refining services. This technology we call BRIM™ technology and it has several key features:

- * The hydrogenation activity of the brim sites is enhanced
- * The frequency of brim sites is increased

- * Bonding of molybdenum disulphide to the carrier is optimised giving more Type II direct desulphurisation sites.

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

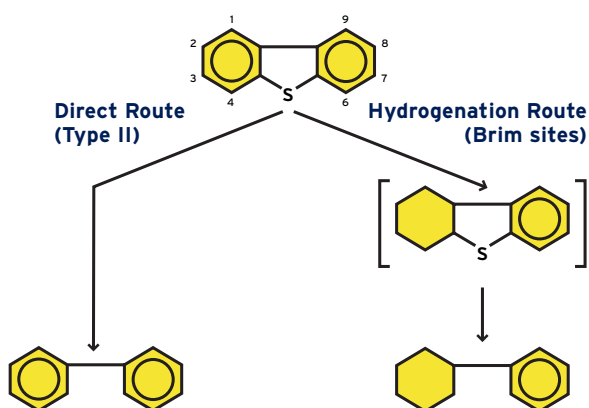
The first two catalysts introduced to the market using the new BRIM™ preparation technology were TK-558 BRIM™ (CoMo) and TK-559 BRIM™ (NiMo). These catalysts were commercialised in late 2002 for use in FCC pretreatment service, and they have been successfully adopted by the industry with the delivery of more than a dozen applications for FCC pretreatment.

TK-576 BRIM™ – Topsøe's New ULSD CoMo Catalyst

The most refractive sulphur species in diesel are alkyldibenzothiophenes with alkyl groups adjacent to the sulphur atoms. The reason for the low reactivity of

Figure 2. Boost the hydrogenation activity with BRIM™ Technology

Reaction pathways for HDS of dibenzothiophenes (DBTs). For DBT-molecules with alkyl substituents in position 4 and/or 6, both routes are important, but for all other sulphur-containing molecules in the diesel boiling range, only the direct route is important for HDS. Whether or not the fast pre-hydrogenation route can be used is determined by equilibrium constraints, and in general the pre-hydrogenation route is favoured by a high hydrogen pressure. The reaction sites for the direct desulphurisation are Type II, and for the hydrogenation brim sites are used. In diesel units operating at low to medium pressure the refractive DBTs will be desulphurised using both reaction pathways, and it is thus important that the catalyst has a high activity for either routes. TK-576 BRIM™ is developed to meet this demand.



Catalysts for All Applications



Topsøe hydroprocessing catalysts have been developed in-house and are manufactured in Topsøe plants.

these species is that the presence of the alkyl groups hinders the access of the molecule to the active sites (the sulphur vacancies). This phenomenon is known as steric hindrance. However, as seen in Figure 2, desulphurisation can also occur via the hydrogenation route. Normally, this route is slower than the direct route, but becomes more significant for the sterically-hindered alkyldibenzothiophenes.

In diesel hydrotreaters that are operated at a low to medium pressure, the desulphurisation of the refractive sulphur compounds will follow both routes and it is therefore desirable to promote the activities for either route. Some promoters, such as phosphorus, enhance the hydrogenation activity of a catalyst but unfortunately at the same time inhibit and therefore reduce the activity for the direct desulphurisation. In the development of TK-576 BRIM™ the above problem was

addressed, and we succeeded in developing a catalyst preparation technology that increases the concentration of brim sites while at the same time strengthening the direct desulphurisation sites.

Table 1 shows a comparison of TK-576 BRIM™ with Topsøe's current leading CoMo catalyst, TK-574 on a diesel feed consisting of 75% straight-run gas oil (SRGO) and 25% FCC light cycle oil (LCO). The two catalysts are compared at two desulphurisation levels to obtain a diesel product containing 50 and 10 wtppm sulphur, respectively. The difference in the required temperature to produce ULSD with the two catalysts is in this test 5–7°C. Other tests have shown that TK-576 BRIM™ is up to 10°C more active than TK-574. The actual difference depends on the feedstock type, operating conditions and unit severity.

In an existing diesel hydrotreater with a fixed catalyst

Feed properties

Density, kg/m ³	0.8690
Sulphur, wt%	1.836
Nitrogen, wtppm	195
ASTM D-86, °C	
10/50/90vol%	236/284/355
Total Aromatics, wt%	36
Polyaromatics, wt%	21

Performance

	TK-574		TK-576 BRIM™	
	50	10	50	10
Product S, wtppm	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

Table 1. Performance of TK-576 BRIM™ vs. TK-574 at ULSD conditions

Pilot plant test results showing the difference between TK-574 and TK-576 BRIM™ on a feed mixture of 25% LCO and 75% SRGO.



volume, the high activity of TK-576 BRIM™ can be utilised by for instance increasing the amount of cracked feedstock or extending the cycle length, changes which lead to improved margins during diesel production (Tables 2 and 3).

Stability and Regenerability of TK-576 BRIM™

Figure 3 illustrates the stability of TK-576 BRIM™ at ULSD conditions in very low pressure operation. After initial stabilisation, TK-576 BRIM™ was operated in ULSD mode (Step 1). In the 2nd step, which lasted 1 month, the catalyst was exposed to more severe operation at a high temperature resulting in near zero product sulphur levels (< 1 wtppm). In the 3rd and final step, the operation was changed back to initial conditions used in step 1. As seen in Figure 3 the observed activity loss with TK-576 BRIM™ was negligible despite the rough treatment during the

period with accelerated deactivation.

Studies have also been made on TK-576 BRIM™ to check the regenerability using known and proven regeneration procedures. The studies showed that the activity of regenerated TK-576 BRIM™ is 75% compared to fresh TK-576 BRIM™. This means that the refiner using conventional regeneration procedures gets a regenerated catalyst that has similar activity to that of fresh TK-574.

Topsøe – Leading Supplier for ULSD Production

For more than 10 years Topsøe has designed and delivered catalysts for hydroprocessing units producing diesel with less than 10 wtppm S. Throughout this period Topsøe has offered licensed technology for aromatics saturation that combines deep desulphurisation/denitri-

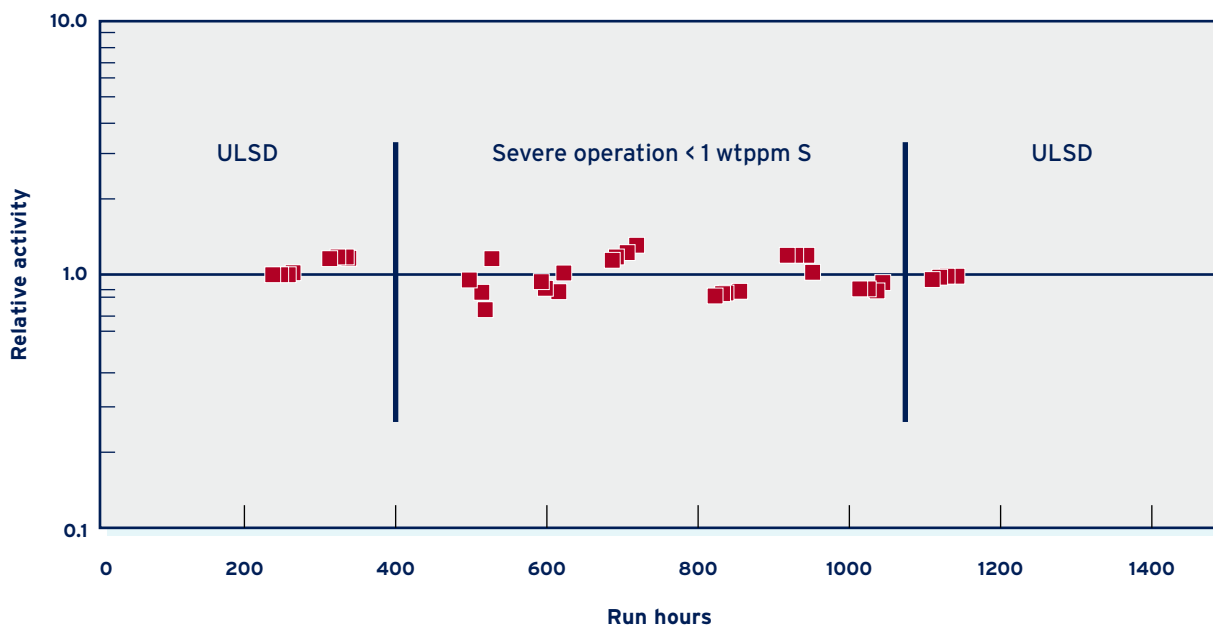


Figure 3. Stability of TK-576 BRIM™

Pilot plant test showing the stability of TK-576 BRIM™ at ULSD conditions at a hydrogen pressure below 20 bar.



fication in a first stage with dearomatisation in a second stage. The second stage uses a noble metal catalyst which requires a feedstock which is essentially sulphur and nitrogen free. So in the first stage (the pretreat step), the S and N must be reduced to typically below 5 wtppm. The knowledge we have gained from the design of these units has led to the development of new reactor internals, and today more than 200 distributor trays from Topsøe are designed for hydrotreaters worldwide. The experience has furthermore helped understanding the reactions and the kinetics that apply for ULSD production, including the effect of inhibitors for the desulphurisation routes.

TK-catalysts have been well accepted by German refineries, where a tax incentive makes it attractive to produce diesel with less than 10 wtppm S. As of August 2004, 1,100 tonnes of Topsøe ULSD catalysts will be or are already installed in Germany. In the United Kingdom, who together with Germany has taken the lead in

Europe to produce ULSD, Topsøe has sold more than 1,000 tonnes of ULSD catalysts. In total, Topsøe has a 40% share of the ULSD catalyst market in these two countries.

In addition to extensive sales of hydroprocessing catalysts for ULSD production, Topsøe has revamped and designed many new grassroots diesel hydrotreaters. As of August 2004, 39 diesel hydrotreaters used for production of diesel with less than 50 wtppm S have been built or are projected using Topsøe diesel technology. Of these, more than 75% are for production of diesel with less than 10 wtppm S.

Importance of Distribution

Efficient distribution of the reactants is a prerequisite to achieve ultra low sulphur levels. Poor liquid distribution will contribute to channeling through the catalyst bed

	TK-574	TK-576 BRIM™
Product S, wtppm	10	10
H ₂ pressure, bar	30	30
Feed rate, BPSD	25,000	26,500
LHSV, hr ⁻¹	Base	Base + 6%
SOR WABT, °C	358	355
Cycle length, years	2	2
LCO content, vol%	25.0	29.2
Improved margins per year (330 run days), million USD	-	5.0

Table 2. Addition of 6% LCO to a ULSD hydrotreater.

Case study which shows how a refiner, making 25,000 BPSD ULSD by replacing TK-574 with TK-576 BRIM™ can process an additional 6% LCO. The cycle length is the same for the two catalysts. If it is assumed that the LCO is upgraded from fuel oil to ULSD, and if it is assumed that the upgrade value is USD 10 per barrel, then the refiner will increase margins by USD 5.0 million per year.



resulting in inefficient utilisation of the catalyst, development of hot spots and catalytic deactivation due to coke formation.

In the proposal phase for a catalyst for ULSD service, Topsøe engineers evaluate the performance of the existing distributor tray installed in the diesel hydrotreater using computer models that have been developed from cold-flow modelling studies.

The result of this simulation will show whether the internals are appropriate for production of ULSD. If new internals are required, these can be delivered together with the catalyst.

Even with a well designed distributor tray and a high activity catalyst it is not possible to produce ULSD if the tray is installed incorrectly and/or if the tray is damaged. In order to ensure optimal performance of the distributor tray, Topsøe service engineers are trained to conduct inspection of distributor trays, and they can advise

the refiner about cleaning, sealing, repairing, etc. prior to the activation of the catalyst.

Topsøe Solutions for Optimised ULSD Production

Fundamental research by Topsøe has led to the understanding of the hydrogenation sites of a hydrotreating catalyst – the brim sites. Based on this knowledge a new preparation technology – the BRIM™ Technology – has been developed, and as a result of this Topsøe has commercialised TK-576 BRIM™. With TK-576 BRIM™ in your diesel hydrotreater it is possible to achieve a desulphurisation performance unmatched by other CoMo catalysts.

With more than 10 years of industrial experience in ULSD service, Topsøe's leading expertise within catalyst and technology will be used to ensure that your hydrotreater needs for ULSD would be met.

	TK-574	TK-576 BRIM™
Product S, wtppm	10	10
H ₂ pressure, bar	30	30
Feed rate, BPSD	25,000	25,000
LCO content, vol%	25.0	25.0
LHSV, hr ⁻¹	Base	Base
SOR WABT, °C	358	351
Cycle length, years	2	2 ½

Table 3. Extension of the catalyst cycle in ULSD hydrotreater.

In this study the refiner has chosen to extend the catalyst cycle by replacement of TK-574 with TK-576 BRIM™. While it is possible to operate in cycles of 2 years with TK-574, the refiner can now extend the cycle to 2 ½ years.

Meet Your Objectives

Refinery Services

Topsøe's worldwide services to the refining industry are based on a fundamental understanding of heterogeneous catalysis, including catalysts, process technologies and engineering services.

Topsøe's unique integrated approach has resulted in profitable solutions in the areas of:

- * FCC Pretreatment
- * Hydrocracker Pretreatment
- * Hydrocracking
- * Deep HDS of Diesel
- * Diesel Dearomatisation
- * Resid Hydroprocessing
- * Kero/Naphtha Hydroprocessing
- * Pressure Drop Control
- * Reactor Design
- * Reactor Flow Distribution
- * Hydrogen Production
- * Sulphur Management
- * Spent Acid Regeneration
- * Alkylation
- * Flue/Waste Gas Treatment

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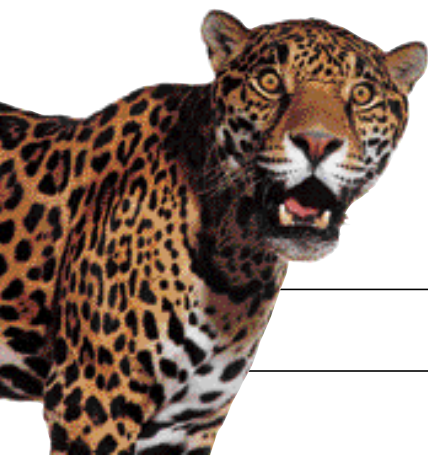
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The information and recommendations have been prepared by Topsøe specialists having a thorough knowledge of the catalysts. However, any operation instructions should be considered to be of a general nature and we cannot assume any liability for upsets or damage of the customer's plants or personnel. Nothing herein is to be construed as recommending any practice or any product in violation of any patent, law or regulation.



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