



DEACTIVATION BEHAVIOUR

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explores the loss of activity
in fluid catalytic cracking pretreating.

When selecting hydroprocessing catalysts for fluidised catalytic cracking (FCC) pretreaters, the main focus is on the catalyst's start of run (SOR) activity, i.e. the ability to desulfurise and denitrogenate the FCC feed at the beginning of the cycle. Obviously, this is a very important parameter, and a lot of research and development work is put into optimising the SOR activity of new catalysts. However, something which is actually more important than initial activity, and that does not receive the same amount of attention, is the deactivation behaviour of a certain catalyst, i.e. the parameters causing catalyst deactivation and the different catalysts' ability to defy the loss of activity in fluid catalytic cracking pretreating.

The importance of the deactivation rate can be illuminated by the small example in Table 1, where the difference in activity is compared with the difference in deactivation rate.

As can be seen in Table 1, the gain by choosing a high activity catalyst is three months, whereas the gain by operating a catalyst with low deactivation is seven months.

Loss in catalytic activity in vacuum gas oil (VGO) services is caused either by carbon lay down on the catalyst surface (coking) or by contamination with poisons on the catalyst surface and in the catalyst pores.

The parameters recognised to influence the permanent loss in catalytic activity are the partial pressure of hydrogen, the hydrogen availability, the reactor operating temperature and certain feedstock characteristics. These characteristics comprise content of coke precursors (various nitrogen and polyaromatic species) but also contaminants acting as catalyst poisons (Ni, V, Fe, As etc.).

Since these deactivation parameters are mainly unit specific and dictated by design and refinery requirements, they can be optimised, but it is difficult to change them significantly. Therefore, it is a major task for the catalyst developers to come

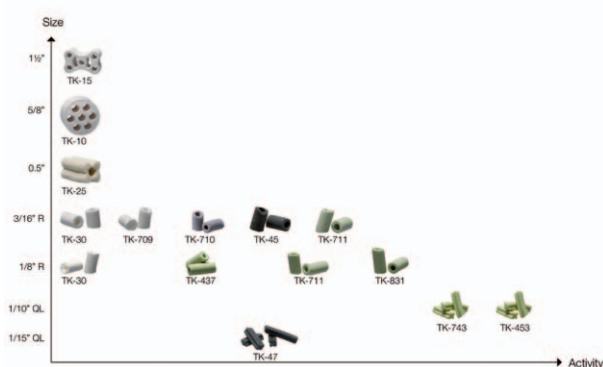


Figure 1. Topsøe offers a variety of products to alleviate pressure drop problems, ranging from large inert topping material to small rings with high catalytic activity. High void products are shown in this figure. Catalytic activity of the products increases along the X axis as shown.

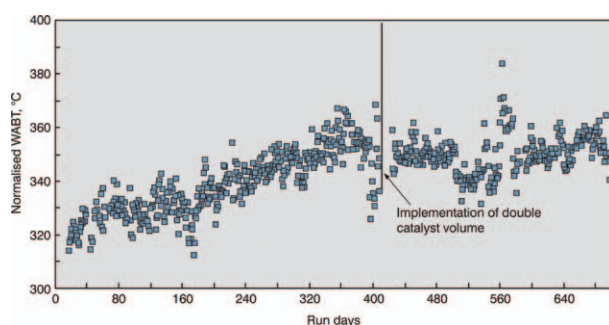


Figure 2. Deactivation profile in low pressure Russian FCC pretreater, treating high metal VGO feed.

Table 1. Illustration of impact of stability and activity on cycle length		
	High stability catalyst Deactivation 1.5 °C/month	Low stability catalyst Deactivation 2.0 °C/month
Low activity catalyst SOR temperature 360 °C EOR temperature 400 °C	27 month cycle	20 months cycle
High activity catalyst (+20%) SOR temperature 355 °C EOR temperature 400 °C	30 months cycle	23 months cycle

up with catalyst formulations and tailor made guard bed solutions that will help to prolong the cycle length of the unit.

Another parameter which is known to cause reduction in cycle length is the fast and accelerating increase in reactor pressure drop, which is caused by fouling, plugging and formation of solid reaction products in the upper part of the reactor vessel. For installation upstream the main treating catalyst, a variety of different grading and guard catalysts are available, all with the purpose of preventing pressure drop problems and protecting the high active catalyst from severe fouling and poisoning. These products come in different shapes, sizes and activities, and using them in combination provides the very important size and activity grading. In Figure 1, the catalysts TK-45 and TK-47 are very effective arsenic guards; TK-743 has a huge capacity for nickel, vanadium and iron, whereas TK-453 can trap VGO silicon species as well as heavy metals.

But even from the best guard catalyst in the world, a small slip of contaminants entering the main treating catalyst during the cycle will always exist. This is realised from the fact that the residence time of the oil across such guard layers is far from sufficient to allow full uptake of the most common poisons such as nickel, vanadium and arsenic. The thermodynamics of the uptake reactions require more time in order to yield full removal. With this knowledge in mind, the design of the BRIM™ VGO catalysts' porosity and skeletal structure has been optimised in such a way that even after exposure to significant amounts of contaminants, these catalysts are able to maintain their primary functions (HDS, HDN and aromatic saturation) to a much higher extent than conventional catalysts.

One of the unique features of the Topsøe BRIM VGO catalysts is exactly their open and robust pore structure, giving a very high poison tolerance and low affinity for coking reactions. This has resulted in a generation of catalysts that deactivates significantly slower than older conventional catalysts, thereby providing longer cycles than previously possible. Here, the author presents industrial examples of the deactivation behaviour of BRIM VGO catalysts in very different operating regimes such as severe contamination, low pressure coking, low pressure combined with high temperature coking etc.

The BRIM VGO catalyst portfolio for FCC pretreating currently includes the products listed in Table 2.

Industrial deactivation

Metals tolerance

The first example of deactivation is from a unit operated at low temperature (310 – 330 °C) and also low pressure. In this unit, the catalyst is not deactivated due to coke lay down but mainly due to heavy metal contamination. Figure 2 shows the catalyst deactivation, expressed as normalised reactor temperature, in this Russian FCC pretreater operated at only 47 barg H₂ partial pressure. The catalyst is treating a VGO feed with 18 wt ppm Ni+V.

The average deactivation is 4 °C/month. This is obviously a fast rate, but it is regarded as low when considering the type of feed being processed. The catalyst is continuously being exposed to a feedstock containing extremely high levels of nickel and vanadium.

From sample analyses of spent BRIM VGO catalyst from other units, it has been demonstrated that the catalyst is able to withstand a contamination level of more than 8 - 10

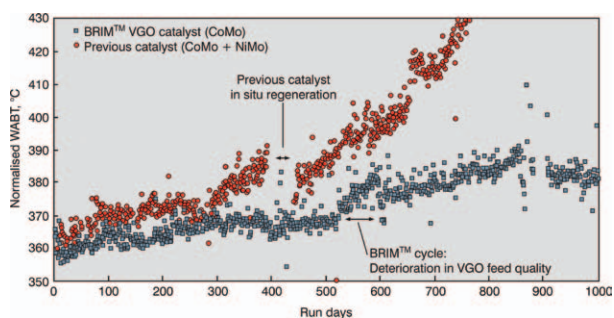


Figure 3. Deactivation profile caused by coking in low pressure European FCC pretreater.

wt% Ni+V, while still providing activity for removing sulfur and nitrogen. A conventional hydrodesulfurisation (HDS) catalyst with a traditional pore system would not be able to maintain its HDS function while being subjected to such level of contaminants.

Low partial pressure of H₂

Figure 3 shows the catalyst deactivation, expressed as normalised reactor temperature, in a European FCC pretreater operated at 45 barg H₂ partial pressure. The plot is an illustrative example of how a critical low H₂ partial pressure is handled by a BRIM CoMo VGO catalyst and by a more traditional CoMo/NiMo stacked bed solution. The deactivation seen here is a classic example of catalyst coking.

The cycle with the BRIM catalyst actually lasted more than three years, which was a record for this unit, and the operating stability was remarkable.

When looking into the data more closely, it can be seen that in periods with lower than average PH₂ (< 40 barg), the deactivation rate was clearly higher for both catalysts, whereas the deactivation slope flattened when the refiner was able to increase PH₂ to above 45 barg. The BRIM catalyst was simply more capable of handling both regimes and never experienced accelerated coking as the other catalyst did.

High partial pressure of H₂

Figure 4 illustrates the catalyst deactivation, expressed as normalised reactor temperature, in a European FCC pretreater operated at 83 barg H₂ partial pressure, which is considered semi high for this application type. In this case, a BRIM VGO catalyst of the CoMo type is working in a high severity unit, operated at a somewhat higher pressure than seen in Figures 2 and 3. The average reactor temperature for the cycle has been >385 °C, which implies that accelerated coking normally is at risk.

Instead of accelerated deactivation, which is very difficult to deal with, the BRIM catalyst has shown a steady and predictable behaviour with a deactivation rate of 1 °C/month.

The overall performance of the BRIM catalyst has outperformed the previous experiences with NiMo catalysts in the same unit.

Low partial pressure combined with high temperature

From a FCC pretreat catalyst point of view, one of the worst scenarios is one with low H₂ partial pressure and a high temperature. This is likely to give a very fast deactivation, since the coking reactions are favoured in all possible ways.

In Figure 5 the catalyst deactivation, expressed as normalised reactor temperature, is shown for a European FCC pretreater operated at 43 barg H₂ partial pressure and 380 - 405 °C for the

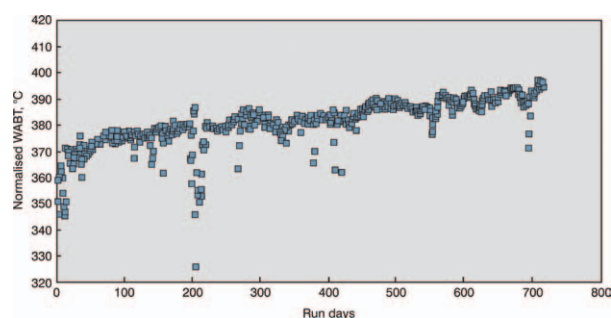


Figure 4. Typical deactivation profile for semi high pressure European FCC pretreater.

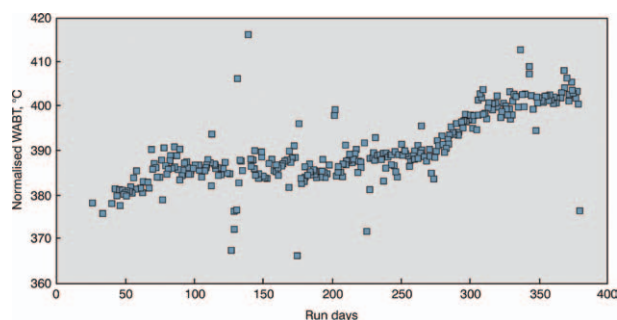


Figure 5. Deactivation profile in low pressure European FCC pretreater operated in MHC mode.

Table 2. The latest generation of Topsøe BRIM VGO catalysts for FCC pretreating

TK-560 BRIM	Cobalt/molybdenum based with very high HDS/HDN activity
TK-561 BRIM	Nickel/molybdenum based with high HDS and very high HDN activity
TK-562 BRIM	Cobalt/molybdenum based with the highest HDS/HDN activity

entire cycle. This unit (low pressure) is operated in mild hydrocracking mode (MHC) to achieve as much VGO conversion into gas oil as possible. The average deactivation rate in the MHC mode has been kept at 2 °C/month with a BRIM VGO catalyst based on cobalt and molybdenum. This performance is significantly better (more VGO conversion) and more stable than with the previous catalyst which was based on cobalt, molybdenum and phosphorus.

Conclusion

Hydroprocessing catalyst deactivation is caused by carbon lay down (coking) and/or by contamination of the catalyst with contaminants/poisons such as Ni, V, Fe, As etc. Compared to conventional catalysts, the family of BRIM VGO catalysts is designed to withstand the typical deactivation in a highly improved manner due to the nature of the catalysts' structure. The catalyst coking rate is observed to be much lower when utilising the BRIM technology, and their tolerance towards metal contamination and resistance to coking are clearly exceptionally high. In different operating regimes, the BRIM VGO catalysts have shown very high operating stability, while dealing with low pressure, high temperature and feedstock contaminants. **IE**



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