Guarding against contaminants

Analysing spent hydroprocessing catalyst underpins the development of guard bed catalysts to counter contaminants

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A very important parameter for the cycle length of a hydroprocessing unit is the deactivation rate of the installed catalyst. The deactivation of a hydrotreating catalyst can be coke induced and contaminant induced. Coke deposition is to a large extent controlled, but also dictated, by the unit operating regime (temperature, hydrogen availability, residence time and partial pressure of hydrogen). This will normally cover most middle distillate units making ULSD or lighter products. However, in units processing heavier feedstocks like vacuum gas oil (VGO), heavy coker gas oil (HCGO), deasphalted oil (DAO), or even heavier cuts, the refinery normally faces a dual type deactivation. The coking reactions here are even more significant because the feedstock is heavy and contains lots of aromatic coke precursors in the high boiling fraction. But heavy feedstocks will often also contain a significant amount of heavy metals and other contaminants. In particular, this includes nickel, vanadium, iron, silicon, arsenic, phosphorus, calcium and sodium. These contaminants are present in processed feedstocks at ppm or even ppb levels, but the effect is significant. Following a non-reversible pathway, heavy metals will be deposited on active catalyst following different mechanisms. The outcome is that activity is lost permanently and will thus not even be regained during catalyst regeneration.

Topsoe researchers have within the past few years analysed and characterised a huge number of spent catalysts retrieved from industrial hydrotreater units operating on heavy feedstocks like VGO and HCGO. This characterisation work tries to understand how these contaminants are depos-
Contaminants to deal with
In general, the heavier the hydrocarbon cut the higher the content of contaminants. In a feed stream such as VGO, DAO and HCGO, metals contamination is therefore mainly an issue for FCC pretreaters, hydrocracker pretreaters and lube units.

Vanadium and nickel are mainly found in large, porphyrin-like structures (asphaltenes) in crude oil (see Figure 1). Generally, the metallic species of the crude are concentrated in the resid portion, but some organometallic species are present in the lower boiling ranges with a boiling point above 660°F (350°C).

Introduction of feeds containing vanadium, nickel or iron (such as atmospheric tower bottoms) into VGO hydrotreating could have severe consequences in terms of cycle length. The relatively high space velocity of these units (compared to resid hydrotreating) could result in metal migration into the active, main bed catalyst. To overcome this problem, a highly active demetallation catalyst with a high metal pick-up capacity must be installed on top of the main catalyst bed. Topsoe has commercialised specially designed VGO demet catalysts designated TK-453 and TK-455 MultiTrap.

The large molecules containing these metals require catalyst shapes with a high surface to volume ratio to remove these metals efficiently. Iron will mainly deposit on the catalyst surface, whereas nickel and vanadium will deposit inside the catalyst pore structure due to the very large average pore sizes of TK-453 and TK-455.

Arsenic is a true catalyst poison as it will chemically react with active catalytic sites, for instance transforming the catalyst’s nickel and cobalt into NiAs or CoAs. Poisoned sites will not be reactivated during regeneration, and even small amounts on the catalyst will affect catalyst activity in a critical way. Fortunately, the concentration of arsenic is in the ppb range and can be effectively dealt with by utilising Topsoe’s high capacity arsenic traps TK-49 as an extrudate, and TK-45 and TK-41 in a ring shape.

Silicon found in oil fractions originates from Si-containing anti-foam additives used in coker units, as well as from the use of chemicals introduced during oil transport and tertiary oil recovery. Silicon reacts with the surface of the catalyst and forms a silica gel, hindering access to the active catalytic sites and thereby deactivating the catalyst. Silicon penetrates into the pore system of the catalysts, and deactivation is proportional to the concentration of silicon on the catalyst.

Haldor Topsoe’s TK-400 series catalysts for naphtha and TK-453 for heavier fractions provide the highest silicon pick-up on a volume basis.

Phosphorus species are rarely found in typical crudes; however, some opportunity crudes (and, in particular, renewable feeds) often contain significant amounts of phosphorus. Furthermore, phosphorus containing anti-corrosion additives can be found in diesel and VGO fractions. Phosphorus compounds are decomposed in the hydrotreater, and the phosphates react with the alumina support (much like silicon), forming very stable aluminium phosphates. Accumulated amounts of phosphates will reduce accessibility to the active sites of hydrotreating catalysts and lower the activity accordingly. Phosphorus compounds are often found to originate from injection of corrosion inhibitors in the form of thiophosphorus compounds like thiophosphate esters, thio phosphites and tributyl phosphate.

Handling of organic phosphorus compounds in the VGO being fed to FCC pretreaters or hydrocracker pretreaters is a major challenge in some refineries. The phosphorus quickly deactivates the conventional catalyst and reduces cycle length dramatically. Topsoe has developed specific guard bed catalysts, TK-31 and TK-455 MultiTrap, to effectively protect the main catalyst. These guard catalysts, with proprietary properties and composition, will be able to prolong the cycle length of the unit.

The main source of sodium in a FCC or hydrocracker pretreat feed is normally poorly desalted crudes. This type of inorganic sodium will not easily enter the catalyst’s pore system. Sodium will therefore tend to deposit around the exterior of the catalyst, forming a solid crust between catalyst pellets, which will harm activity and cause pressure drop issues.
We should not forget to mention inorganic iron, which is a very common contaminant. Iron rust originates from corrosion of upstream equipment and may consist of everything from large flakes to the smallest particle tank rust. Large particle rust is known to be easily trapped in filters, scale catchers and high void catalytic materials. However, 5-10 micron inorganic iron particles are very hard to handle as they will pass feed filters and, without a proper graded bed system, enter the catalyst bed. Inorganic iron will also preferentially deposit in the outer surface of the catalysis, unless a very large pore demet catalyst is utilised as a guard catalyst, and will eventually lead to increasing pressure drop.

To handle inorganic iron, Haldor Topsoe introduced the macroporous particulate trap TK-25 TopTrap a number of years ago and it has proven to be a leading trap material.

The company recently launched an improved particulate trap, designated TK-26 TopTrap, with an optimised daisy shape with three axial holes to provide about 20x higher pick-up capacity as compared to TK-25 TopTrap. TK-26 TopTrap is designed with a 61% particle void fraction as well as a large internal pore volume and macro pores. Larger sized inorganic contaminants deposit in the spaces between traps; fines or smaller sized materials enter the pore system and are trapped within the structure of the particle itself (see Figure 2). The internal particle void of TK-25 TopTrap is 25%, so that the total void in this product is greater than 85%.

More exotic metals like calcium, zinc and magnesium are also observed in some units. These can all originate from different additives but are also occasionally found in porphyrin structures in crude. These contaminants are quite common in units upgrading spent lube oils to new base lube stocks and can be a challenge. They are harmful to the main bed catalyst because they tend to stick to the surface of the catalyst, thereby preventing access to the pore system. Table 1 summarises the mechanisms of contamination.

The importance of utilising specialised graded bed catalysts and guard catalysts designed to handle these many poisons with different deposition mechanism cannot be overstated. The ‘one size fits all’ approach will simply not provide the refiner with an optimised catalyst loading for proper protection of the main bed catalyst and the cycle length will be reduced. Haldor Topsoe has fine-tuned its catalyst portfolio to provide proper main bed protection by constantly adding new and improved graded bed products. This is illustrated in Figure 3, which expresses 23 graded bed products as a function of size vs catalytic activity.

Demetallisation functionality (HDM) in a gas oil hydrotreater is a function of pressure, temperature, residence time (LHSV), catalyst and feed. The catalyst system selected is a key factor in determining the cycle length. It is not only important to install the proper HDM catalysts but also a main bed catalyst that has both a high capacity and tolerance for metals. The metal capacity of a hydrotreating catalyst is mainly determined by the catalyst’s porosity. However, the rate of metal removal is a catalytic reaction and is therefore very much dependent on catalyst activity and reactor operating temperature. Based on experi-
ence, it is advisable to have reactor temperatures above 600°F (315°C) to ensure that enough demetallisation takes place. The severity of the feed is also an important factor. The actual metal pick-up for a catalyst is dependent on all of the above factors.

Haldor Topsoe’s demet catalysts show very high metals pick-ups, with as much as 40 wt% of nickel plus vanadium pick-up in FCC pre-treat service and over 20 wt% each of both silicon and phosphorus. This high level of capacity of demet catalyst will protect the main bed catalyst and allow for longer run lengths.

Our main bed catalysts, BRIM and HyBRIM, show a high level of both capacity and tolerance for metals. In FCC pre-treat services, these catalysts have shown as much as 25 wt% of nickel, vanadium and iron. Designed with an optimum combination of pore diameter, pore volume and surface area, the catalysts have also shown pick-ups as high as 20 wt% of silicon and phosphorus.

Retrieving spent catalyst samples
It is essential to have access to relevant and representative spent catalyst samples if a detailed understanding of contamination type, degree and profile is to be obtained. Because the contamination process is difficult to simulate in a realistic manner in lab-scale pilot units, almost all development work for making new, improved guard catalysts relies on retrieving industrially aged spent catalysts. One option is to sample catalyst while the industrial reactor is being unloaded. This obviously gives valuable information about the contamination profile and illuminates how well certain contaminants migrate through the different catalyst layers. The best way to get good samples is to unload the catalyst by vacuuming. However, if the catalyst is being dumped through a bottom dump chute it is not possible to identify the exact position of the catalyst that is being sampled. The catalyst unloaded by gravity through a dump tube will funnel out like grains emptying from a silo. Alternatively, we recommend using Petroval’s sampling method called Probacat, which will drill down through the bed and a set of perfect core samples of the bed is collected.

The other option is to have catalyst test baskets or canisters installed in a known location within the reactor during the entire cycle. The canister will hold several catalysts in different compartments, and each catalyst within the canister is exposed to practically the same type and amount of contaminants. In collaboration with clients, Topsoe installs 10-20 test canisters in various hydrotreating units every year, and we analyse the contents after the cycle to continuously optimise the catalyst formulation for maximum pick-up of the contaminants mentioned here.

Our research laboratories are equipped with a wide range of analytical tools for characterising spent catalysts. ICP-MS, X-ray fluorescence, X-ray diffraction and state-of-the-art microscopy are within the range of possibilities.

The first thing in the toolbox is always to characterise the spent catalyst using a precise bulk analysis method. An exact quantification of what is present in the sample is required. The most efficient method to apply for this purpose is inductive coupled plasma mass spectrometry (ICP-MS).

Scanning electron microscope (SEM) and electron microprobe analyser (EMPA) are tools used to determine the chemical composition in localised areas of solid materials. The method is ideal for a combination of structural and
chemical information. An electron beam interacts with the sample and produces electrons both for imaging and characteristic X-rays. Both the energy and the wave length of the X-rays can be detected.

**The strength of canisters and spent catalyst analyses**

Topsoe installed canisters in a hydrotreater designed to process and upgrade spent lube oils to base oils and group 2+ lubes. Spent lube oil contains large amounts of contaminants and additives, such as zinc, magnesium, calcium and, in particular, phosphorus and silicon. All of these contaminants deposit on catalysts, causing significant loss of activity. Two canisters were installed in the top of the reactor with catalysts having different properties (pore volume, pore size, surface area and active metal content). Besides the canisters, catalyst samples were also obtained from the unloading of the three reactors. Some of the unloaded catalyst samples had been in operation for one cycle and other samples had been in the reactor for two cycles.

**Analysis by ICP-MS**

The spent catalysts unloaded from the reactors were analysed using ICP-MS in order to quantify the bulk amounts of phosphorus and silicon in particular. This analysis confirmed that the catalysts indeed were heavily contaminated. The numbers also confirmed the theory that catalysts with a high pore volume and large open pores could trap most phosphorus and silicon. **Figures 4 and 5** illustrate how three different catalysts from the canister picked up different amounts of phosphorus and silicon, reflecting the difference in porosity and activity.

**Analysis by SEM and EDS**

Now it was time to apply the SEM technique to map and quantify exactly where the contaminants were present. Figures 6 to 8 show the quantitative cross-section analyses of TK-562 BRIM, TK-831 and TK-743 using the SEM/EDS technique. These catalysts were all grabbed from different locations in the reactor and represent a bulk catalyst, a graded bed catalyst and an effective HDM catalyst. Hence, the last two mentioned have the biggest pore systems and the largest pores.

A firm crust of phosphorus is seen on the surface of the main bed catalyst pellet. The phosphorus content in the crust exceeds 15 wt% and silicon is around 10 wt%. In fact, the
Crust appears to be a complex matrix of the impurities of the spent lube oil as it also contains high amounts of calcium, magnesium and zinc. The two measurements made within the catalyst pellet show a steep drop in the phosphorus content, whereas silicon is fairly constant at all points.

Looking at the TK-831 and TK-743 samples, there is a significant difference. While they also have a crust layer surrounding them, the crust is thinner and, more importantly, the phosphorus species are found in much higher concentrations within the catalyst pellet than was the case for TK-562 BRIM. The crust itself is again very rich in phosphorus, silicon and the other contaminants.
The data shows a good correlation between the catalyst’s porosity and pore size and its ability to allow phosphorus and silicon compounds to enter the catalyst pore system. This data as well as dozens of other similar canister studies has enabled Haldor Topsoe to generate optimised catalysts designed to pick up the specific poisons causing issues in each individual hydrotreating unit, resulting in a better performance and cycle length. The graded bed system needs to be designed for each unit to effectively eliminate unit constraints.

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