CRITERION
CATALYSTS & TECHNOLOGIES

NAPHTHA HYDROTREATING CATALYSTS

Dealing with the more challenging streams

Criterion is a world-leading supplier of naphtha hydrotreating catalysts, the key to the effective removal of sulphur and nitrogen compounds from this valuable refinery stream. We supply about one-third by weight of all the naphtha hydrotreating catalyst purchased globally and about two-thirds of all the catalyst used by refiners operating higher-severity units.

Criterion works with customers to select the most appropriate catalysts and reactor loading strategies based on naphtha composition, the design of the individual process unit and the prevailing operating conditions and constraints. Years of research and development in this area combined with extensive commercial experience mean we have the capacity to devise catalyst solutions for even the most challenging naphtha hydrotreating applications.

PERFORMANCE AND RELIABILITY

Naphtha is catalytically reformed within many refineries to produce a high-octane gasoline blending component. Catalytic reforming is also a very important refinery process for another reason: the reformer is a significant source of the hydrogen required by various critical processes across the refinery and often in short supply. The performance and reliability of the reformer are heavily dependent on the quality of the naphtha feedstock. Sulphur and nitrogen compounds must be removed from the naphtha to protect the sensitive noble metal catalysts (usually platinum but also rhenium) used in the reforming process.

INDUSTRY BENCHMARK CATALYSTS

Criterion catalyst DN-200 was launched in the late 1990s and remains the naphtha hydrotreating catalyst of choice for many refiners. Specified by more than 100 different customers worldwide DN-200 is a Ni–Mo alumina catalyst with excellent stability, which is essential for treating more challenging naphtha streams. It offers outstanding hydrodenitrogenation (HDN) and olefin saturation activity; its hydrodesulphurisation (HDS) activity is also very close to that of equivalent Criterion Co–Mo catalysts. The optimised pore size distribution and promoter composition prolong the life of the catalyst when treating either straight-run or cracked naphthas. Good results have been obtained with DN-200, even at relatively low hydrogen partial pressures.

DN-3531 catalyst was introduced in 2006 and is an alternative to DN-200. This catalyst is also a Ni–Mo alumina, but it is based on Criterion's industry-leading ASCENT technology platform. An advanced alumina support, improved metals impregnation and greater dispersion of the active sites translate into superior activity, which can be used to raise throughput, process heavier feeds, extend cycle lengths or achieve target sulphur and nitrogen specifications at lower hydrogen partial pressures. DN-3531 is the ideal choice for tougher feeds, such as cracked and coker naphthas or naphtha derived from tar sands, which call for maximum HDN activity.

Both DN-200 and DN-3531 have excellent track records and can be supplied in the oxidic or presulphided form.

NITROGEN REMOVAL IS THE KEY

The real strength of our catalysts for this application is nitrogen removal. Getting rid of nitrogen prevents the formation of ammonium chloride in the downstream section of the catalytic reformer and protects the chloride balance in the unit. This is important because, although the noble metal provides the catalytic sites for the dehydrogenation reactions occurring in the reformer, it is the chlorinated alumina support that has the acid sites to promote isomerisation and ring closure.

DEALING WITH THE TOUGHER CHALLENGES

Throughput and cycle lengths in naphtha hydrotreaters, especially those running tougher feeds, are less likely to be limited by loss of catalyst activity than by the excessive pressure drop caused by fouling of the catalyst bed. This is the generally the result of the oxidative polymerisation of the reactive olefinic species in cracked or coker naphthas to produce gums, which ultimately convert to coke.

To defeat this problem Criterion has developed the SENTRY OptiTrap product portfolio: top bed catalysts and active and inert supports with various physical structures, void levels and flow properties. Using OptiTrap materials, we can design a top-bed grading system to filter and evenly distribute foulants rather than having them build up on the main hydrotreating catalyst, consequently blocking the flow through the reactor and increasing the pressure drop.

Hydrotreating coker naphtha often presents another specific challenge: dealing with the silicon oils that this material often contains. These originate from the polydimethylsiloxane generally added to the delayed coking process to suppress foaming. Under the conditions in most naphtha hydrotreaters, the silicon oils transform to silica gels that absorb onto the catalyst surface and restrict access to the active sites, thereby leading to premature deactivation. Whereas the average cycle length of a naphtha hydrotreater might be three or more years, coker naphtha hydrotreaters can be limited to 12 months if this issue is not addressed.

Criterion's answer to this challenge is SENTRY MaxTrap[Si], an alumina-based catalyst with moderate HDN activity and a structure designed to accommodate unusually high levels of silicon. It is typically used in stacked catalyst systems in combination with higher-activity hydrotreating catalysts.

PROOF POINTS

LIAOHE PETROCHEMICAL, CHINA

One of Liaohe Petrochemical's aims in revamping its coker naphtha hydrotreater (a twin-reactor unit) was to expand its capacity from 150,000 t/y to 200,000 t/y. The trouble was that the unit was prone to pressure drop caused by coking, which meant frequent shutdowns to skim the top off the catalyst bed. Criterion helped the operator by formulating a catalyst solution based on DN-200 as the main hydrotreating catalyst and protected from coking by a carefully designed guard bed for the upper part of the first reactor. This comprised a series of OptiTrap grading materials and catalysts of decreasing particle size and increasing activity.

The unit has performed well since its restart at increased throughput. The guard bed has proved effective in combating the pressure drop issue, and the HDN, HDS and olefin saturation levels have all met the refiner's expectations, despite maintaining a relatively low operating temperature. Liaohe Petrochemical expects to make its target cycle length for the unit.

FLEXICOKER OPERATOR, USA

A US refiner sought to extend the cycle length of its naphtha hydrotreating unit, which was running a blend of straight-run naphtha with the product of its flexicoker unit. The challenge was to deal with the silicon entering the unit with the coker naphtha stream. Criterion worked with the refiner to develop a sophisticated catalyst loading strategy aimed at maximum activity combined with strong silicon resistance. The unit was operated with a guard-bed reactor and this was loaded with OptiTrap grading materials and DN-200 for efficient olefin saturation. The twin main reactors were loaded with 45% MaxTrap[Si], 20% DN-140 (a moderately active hydrotreating catalyst with good silicon tolerance) and 35% DN-3531, the latter to provide the bulk of the required HDN and HDS activity.

Although, for other reasons, the unit was shut down following its planned 12-month cycle, the results from a hot-loop silicon sampling system installed in the unit indicated that the run could have been extended for up to five months, such was the improved state of activity of the catalyst as a result of the new loading strategy.

CONTACT US

For more information about how we can help you to enhance operational performance, meet increasingly stringent environmental regulations and increase revenues, visit us at **www.criterioncatalysts.com.**