Economic benefits of presulphurisation technology in an evolving market

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The refining industry is experiencing significant changes. Today, the market is defined by uncertainty and volatility – resulting in major shifts in supply and demand, with environmental impact and energy consumption a particular focus. At the same time, refiners strive to increase yields and improve operational efficiencies, whilst aiming to minimise costs.

Catalysts are a vital part of most production processes, playing a key role in making them more efficient. For hydrotreating applications, optimised catalyst activation – where hydrotreating catalysts are prepared before use in chemical reactions – can deliver significant economic benefits.

While in situ sulphiding or full preactivation are methods which can be employed, each has limitations that can conflict with overall refinery aims; the former is inconvenient, slows down unit start-up and has potential hazards, the latter is costly and can present safety concerns.

However, presulphurisation – whereby the catalyst is partially activated – can offer a low-cost, low-risk and flexible alternative, with notable economic benefits and reduced generation of pollutants.

Existing methods of activation

Refineries need to be able to get hydrotreating units online quickly after catalyst changes – ensuring that production targets are met, operational costs are minimised, and the risk of downgrading products is reduced.

In situ sulphiding of hydroprocessing catalysts, whereby a sulphur compound is injected into the reactors after catalyst loading, is one option that can be used as part of the startup process. However, it is a complex method that contains multiple, time-consuming hold steps, including pre-wet, dry-out and temperature holds.

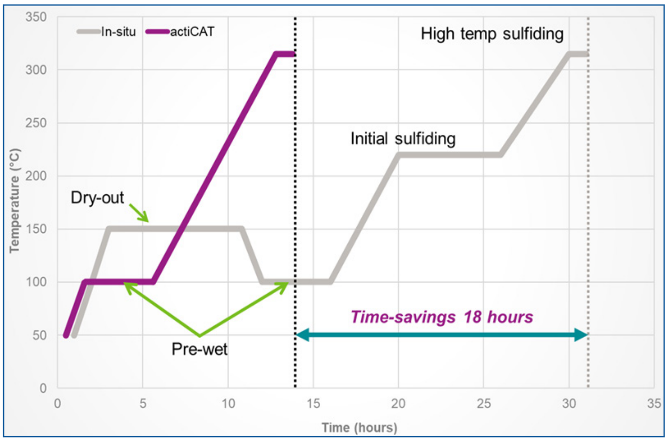

Figure 1 Time savings of presulphurisation technology, in comparison to in situ

In addition, there are the hazards associated with in situ sulphiding – including toxic sulphur additives, and the production of hydrogen sulphide (H_2S). These can cause environmental and community concerns, with operators also having to monitor for H_2S, posing a risk to team members.

Then there is full preactivation – also referred to as ex situ catalyst activation. This process sees a catalyst fully activated via conversion of metal oxides to active metal sulphides, delivered to the site in drop-in, ready-to-use form. In the current environment, where refineries are facing pressure to reduce catalyst changeout costs, full preactivation is an expensive option. Additionally, full preactivation must be loaded inert, which can pose a safety hazard.

Separately, but also important to note, precautions need to be taken with the freshly sulphided catalyst when introducing cracked feedstocks. As these feedstocks contain high levels of olefins and aromatics, it may rapidly lead to coke and gum formation – resulting in blockage of the pore structure and active sites. This, in turn, can induce catalytic underperformance and lower cycle length. With both methods above, a three-day break-in period using only straight run feed must be followed before introducing cracked feedstocks to prevent permanent activity loss. This may result in lower production or downgrading of products during the initial three-day hold.

A multi-faceted solution

A better solution presents itself in presulphurisation technology (also known as ex-situ presulphurisation) which can achieve the main task of assisting with a quick startup, while reducing production costs and minimising potential hazards.

With this method, the catalyst is sulphurised before being loaded into the reactor. The sulphur is uniformly distributed across the hydroprocessing catalyst, and chemically bound in place at greater than stoichiometric levels, ensuring that all active sites will be fully sulphided.

Partially activated before loading in the presulphurisation process, the rest of the sites are then fully converted to metal sulphides during the reactor heat, requiring a temperature of 315°C (600°F) to achieve full activation. During the reactor heat up, a range of sulphiding chemicals are generated, reacting with hydrogen over a broad temperature range. This results in a gradual, controlled activation.

Evonik's presulphurisation technology, actiCAT, can be

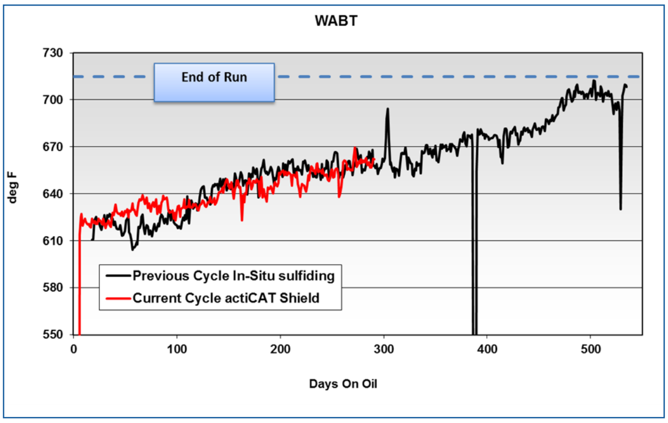

Figure 2 A North American refinery demonstrates the advantages of Evonik's actiCAT Shield

used for various hydroprocessing catalysts, with formulations for conventional hydrotreating, hydrocracking, tail gas and Pygas applications. Additionally, the company offers a specially developed cracked stock protection, actiCAT Shield. This provides a protective coating on the catalyst, preventing coking at the start of the cycle when introducing cracked feed such as light cycle oil (LCO) from fluidised catalytic cracking (FCC) units, or coker naphtha and gas oils.

'Time is money'

Where in situ sulphidation requires more complex operations due to the time required to complete the conversion of metal oxides to sulphides, presulphurisation technology like actiCAT takes a much shorter period of treating time. As seen in **Figure 1**, the amount of time saved can range from 18 hours, looking specifically at typical hydrotreater startups, to several days, for hydrocrackers and very large hydrotreaters – epitomising the well-known phrase, 'time is money'.

To add to this, when treated with actiCAT Shield, cracked feed can be introduced immediately upon startup, with the advantage of eliminating the industry standard three-day hold on straight run feed. Together, these time savings can reduce downgrading of products, keep upstream units running at higher rates and increase overall production – helping to maximise profitability.

Presulphurisation technology also outperforms alternatives with regards to safety. Unlike full preactivation, actiCAT can be loaded in air under proper precautions, eliminating inert entry concerns. It also reduces the risk of sulphur emissions and exposure to operations staff; there is no dealing with toxic additives on site with temporary pumping stations and, in addition, H_2S levels do not need to be monitored.

Furthermore, presulphurisation technology provides high levels of catalyst activity, with no risk of metals reduction during the activation process (the sulphur in the pores drives the reaction toward the desired metal sulphides), supporting increased yields and efficiency.

Case study

The application of Evonik's presulphurisation technology – specifically, actiCAT Shield – has been examined at a North American refinery jet hydrotreater. The unit produces jet fuel with nitrogen below 3ppmw, hydroprocessing a blend of 40% coker jet feed with the balance originating from the crude unit, targeting a minimum 18-month cycle.

When utilising in situ sulphiding for catalyst activation, the coker jet inventory can build during the conventional three-day break-in period where only straight run feed is processed – extending the time it spends in storage and exposing reactive olefins and diolefins to the air, which results in the formation polymers and gums. These components then promote pressure drop build up and fouling when processed in the jet hydrotreater.

In this case, actiCAT Shield was applied to the refiner's Type II NiMo catalyst, resulting in a significantly faster startup compared to the in situ sulphiding method. Not only was the sulphiding time reduced, the three-day break-in period was eliminated. This is because the technology protects against the rapid deactivation associated with processing cracked feed early in the cycle. By enabling refiners to hydrotreat cracked feed on day one of the cycle, it reduces the need to downgrade or to build inventory of difficult-to-store coker and FCC distillate and naphtha fractions.

The effectiveness of the cracked feed protection can be seen in **Figure 2**. The weighted average bed temperature (WABT) needed to achieve product specifications is identical when using actiCAT Shield and introducing coker jet within 24 hours of activation, versus the previous cycle using in situ sulphiding with a three-day hold on straight run feed.

When compared to full preactivation, actiCAT Shield boasts a significant economic advantage from the outset. In this case study, the introduction of presulphurisation technology was so successful that the refinery has since loaded multiple units with it, including FCC naphtha.

Conclusion

To keep up with the pace of industry change and the challenges this can present, refineries must continue to explore new technologies, processes and products to meet changing market demands, improve operational efficiencies and retain a profitable business.

However, in some cases it is existing technologies that offer a compelling economic case for those looking to optimise their operations. For activation of hydrotreating catalysts, presulphurisation technology remains an attractive, cost-effective and efficient option.

Evonik's actiCAT has been on the market for more than 30 years, can be used in every type of hydrotreating unit, and is applicable to most types of hydrotreating catalysts – making it a tried, tested, and trusted solution to capitalise on.

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