SULFIDING SOLUTIONS

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As refiners continue to push the performance limits of their hydrotreating units, improved catalyst sulfiding techniques have become a key component for attaining maximum unit performance. Numerous sulfurization and sulfiding technologies are now available to the refiner. Every sulfiding method offers some benefits, however these must be balanced against the disadvantages and hidden costs of each process. Selecting the proper technique is a critical step that can contribute significant profits to the refinery's bottom line.

Catalyst sulfiding is a complicated process requiring careful control and steady operating conditions. Some of the sulfiding-related problems facing refiners today include:

- The expense associated with refinery downtime continues to increase.
- Different units and assorted catalyst types require distinct operating conditions for sulfiding that often cannot be achieved in the refiner's equipment.
- Fresh catalyst costs continue to rise making short cycle lengths even less desirable.
- Tighter product specifications make catalyst performance more and more critical.

Many factors must be considered in order to select the optimal sulfiding technology for a particular application and for the catalyst type being used. However, in most cases the latest sulfiding technologies offer cost savings that will far exceed the total expenditure for sulfiding.

Why Sulfide?

Most HDS and HDN hydrotreating catalysts utilize oxidic forms of molybdenum, cobalt, nickel, and/or tungsten (MO_3, CoO, NiO and/or WO_3). These metals

oxides are not catalytically active and must be converted to sulfides before they will remove impurities from the feedstock. The activation step always utilizes some form of sulfur to convert these oxides into active metal sulfides. Catalyst activation can be completed after the reactor is loaded (in-situ) or prior to loading the reactor (ex-situ).

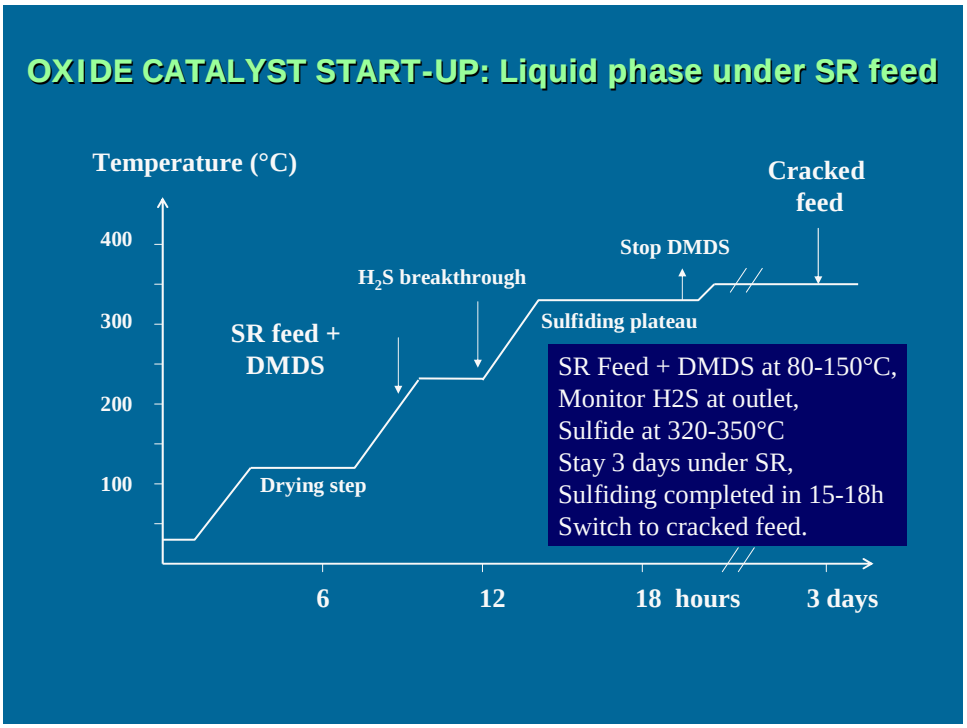
In-Situ Sulfiding

In-situ sulfiding is often the process of choice simply because units have traditionally been started this way and the cost is perceived to be lower than other techniques. In-situ sulfiding suffers from some risks, however, including exotherms during activation, poor distribution of sulfur, and equipment malfunctions during startup that can irreparably harm the catalyst. In addition, a separate sulfur injection system must be maintained and a significant amount of manpower is required at startup.

In-situ sulfiding is carried out by doping the reactor gas stream or the liquid feedstock with a sulfur-containing compound such as dimethyl disulfide (DMDS). The sulfur doped gas or feed is circulated through the bed for many hours with extended holding times at certain temperature levels. The procedure is time consuming with most startups requiring 18 hours to 2 days or more. Precious production time is lost and a quantity of off-spec product must be sent to tankage.

Further complicating matters is the handling of sulfiding chemicals since most are toxic and volatile. For example, DMDS is categorized as a flammable compound with a flash point of 16°C (61°F). It has an irritating odor and must be handled with extreme care.

Production management must closely monitor an in-situ startup and extensive laboratory analysis of the product and recycle gas is typically required. In-situ sulfiding is a very common procedure for activating hydrotreating catalysts, but seldom is it the most economical and risk averse choice.



Presulfiding

A much more convenient and cost-effective method for activating the catalyst prior to startup is ex-situ sulfiding. Ex-situ sulfiding, or presulfiding, has become a standard procedure for many refining companies and is endorsed by several catalyst manufacturers because it offers significant time savings and greatly reduces the risk of startup problems.

Presulfiding is much more than a sulfur delivery method. With true presulfiding, the catalyst is treated off-site in a high temperature processing unit at precisely controlled conditions. No additional activation steps are needed once the reactor is loaded and startup begins because the active metal sulfides are formed during the ex-situ treatment process.

Extensive R&D efforts by Eurecat have lead to the development of several sulfiding technologies designed to meet the unique requirements of both low sulfur and high sulfur applications.

Low sulfur feeds

Eurecat's standard sulfiding process, Totsucat®, is the recommended presulfiding process for most low sulfur feed applications. The name "Totsucat" derives from the phrase "totally sulfided catalyst". Totsucat treated catalysts are delivered to the customer's site in a fully active state and are ready to work immediately. The time required to complete sulfiding and the uncertainty of incomplete activation are eliminated.

Each Totsucat production run begins with a laboratory analysis of the catalyst's sulfiding requirements. This testing determines the amount of metal oxides to be sulfided and the optimum temperature required to reach the maximum sulfiding level. Experience shows that various catalyst types can have vastly different processing requirements to complete sulfiding. For example, laboratory testing with dozens of different hydrotreating catalysts has shown that the optimum sulfiding temperature can vary by as much as 150°C (302°F). Once the lab analysis is complete, a customized production plan is established for that particular catalyst type.

The advantages of Totsucat include:

- The catalyst is fully sulfided and activated at our facility and does not require any sulfiding agents or a complicated activation procedure. This allows "load-and-go" reactor startups.
- Minimal acidic water formation during startup.
- No odours.
- Catalyst performance is maximized since every available metal site is converted to the active form.
- Totsucat treated catalysts release minimal amounts of H_2S during reactor heat up under nitrogen, protecting sulfur sensitive units downstream.
- The concerns associated with handling presulfiding chemicals are avoided.

Totsucat is particularly useful for units that are difficult to sulfide due to temperature limitations, units that cannot tolerate H_2S breakthrough, units that utilize a gas phase startup, and units where the use of sulfiding chemicals is undesirable.

With Totsucat, startup time is reduced to only a few hours while bed performance and run length are optimized. The catalyst will perform at its peak efficiency since sulfiding and activation is controlled at very precise conditions. The startup process involves simply heating the reactor up to SOR temperature. The only factor limiting the rate of temperature rise is the metallurgical constraints of the reactor vessel.

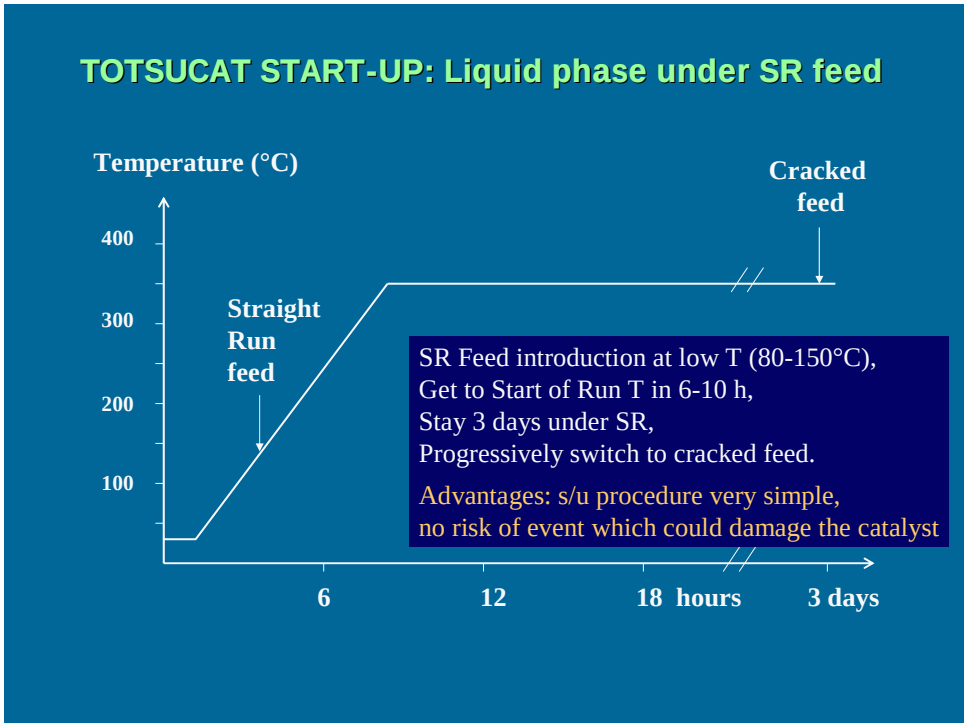
Totsucat has become the sulfiding process of choice for critical path units as well as for those requiring high catalyst performance and minimal sulfur breakthrough. This includes most hydrotreating units (naphtha hydrotreaters, lube units, tail gas units, and pygas units) as well as hydrocrackers and hydrogen plants.

High Sulfur Feeds

The latest development in presulfiding from Eurecat, called Sulficat® E, is specifically designed for large units with high sulfur feeds (S > 0.6 wt%). Sulficat E works especially well in units such as distillate hydrotreaters (DHT) and gasoil

hydrotreaters (GOHT) where long startup times and the threat of sulfiding exotherms are problematic.

Sulficat E presulfided catalysts are normally delivered in a passivated form that makes reactor loading under air possible. The catalyst reaches full activity within hours of startup and no additional sulfiding agents are required.



Sulficat E provides these advantages over presulfurization and in-situ sulfiding:

- The startup procedure is simple and straightforward.
- Complex risks associated with in-situ sulfiding are eliminated.
- No exotherms.
- Reduced acidic water generation during startup.
- No odours.
- Limited sulfur breakthrough during startup.
- If oxidic catalysts are subjected to upset conditions before completion of the active sulfide phase, catalyst damage can occur. Treating catalysts with the Sulficat E process avoids this problem.
- The Sulficat E treatment prevents the reduction of the catalytic metals prior to the formation of the active phase.

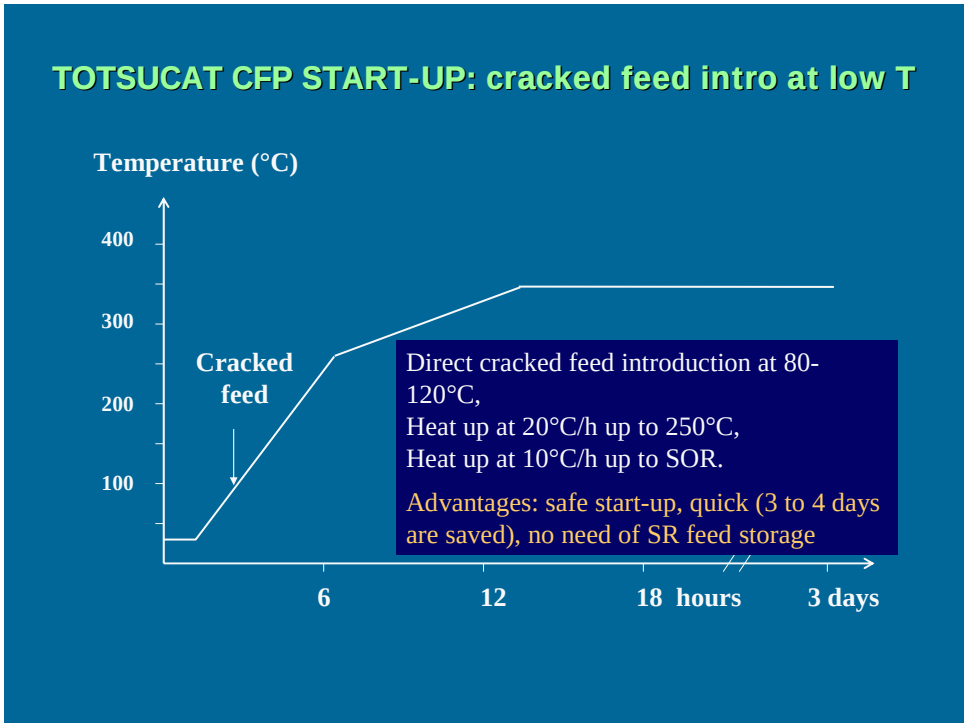
Sulficat E saves hours to days of startup time while ensuring optimal catalyst performance and extended bed life.

The Issue of Cracked Feeds

One other issue with a major impact on profitability at startup can be the three day delay typically recommended by catalyst manufacturers before cracked feeds are introduced to a hydrotreating unit. Cracked feeds contain significant quantities of olefins and poly-nuclear aromatics. Some hyper-active sites on freshly sulfided catalysts cause these compounds to form coke and gums that are readily deposited on the catalyst surface. These deposits may partly block the catalyst pores and limit access to the active sites, leading to a permanent loss of catalyst activity and a reduction in cycle length. Delaying the supply of cracked feeds to the unit allows catalyst activity to subside, thus minimizing coke and gum formation at startup.

This delay can be rather costly to the refiner due to the extra tankage required for straight run and/or cracked feeds along with the reduced production rates from the unit. To solve this problem, Eurecat has developed a unique process to allow the direct use of cracked feeds during startup of the unit. Named Totsucat CFP (CFP stands for “cracked feed protection”), this process gently moderates catalytic activity following ex-situ sulfiding of the catalyst.

Catalysts treated with Totsucat CFP are no longer ultra active at startup. Cracked and heavy feedstocks can be supplied directly to the unit at low temperatures followed by a steady heat up to SOR conditions. Coke and gum deposits will be significantly reduced since the catalyst activity has been carefully modified following activation. With CFP, catalyst life can be up to twice as long compared to a typical cracked feed startup.



Summary

Eurecat offers a variety of sulfiding solutions designed to best meet each customer's specific requirements. The choice of catalyst sulfiding technique is an important decision that merits a careful analysis. The refiner must take numerous factors into account including the cost of unit downtime, the expense of extra tankage for feed and off-spec product, and the benefits of optimized catalyst performance and flawless startups.

Eurecat provides Sulficat Presulfurization and Totsucat/Sulficat E Presulfiding services at its Houston, Texas and Gela, Italy facilities.