TOTSUCAT™ TECHNICAL DOCUMENT

Sulfided and stabilized hydroprocessing catalyst
Recommendations: handling under air; loading under nitrogen atmosphere

1. INTRODUCTION

This document describes the main features of the TOTSUCAT process applied at EURECAT for the activation of hydroprocessing catalysts. It applies more specifically to the TOTSUCAT versions dedicated to Light Ends or gas phase applications. The catalyst is already activated by a sulfiding treatment and then passivated by a treatment in gas phase, so called stabilization.

The following items are included :

- **Product Description**
- **Handling and Storage recommendations**
- **Reactor loading guidelines**
- **Start up guidelines**
- **Troubleshooting**

2. PRODUCT DESCRIPTION

The off-site sulfiding process called TOTSUCAT provided by the EURECAT group comprises the complete sulfiding of hydroprocessing and petrochemical catalysts using a proprietary sulfiding method. In this process, the oxides of molybdenum, tungsten, cobalt and nickel are transferred to their corresponding sulfides according to the following reactions:

$$MoO_3 + 2\,H_2S + H_2 \rightarrow MoS_2 + 3\,H_2O \quad \textbf{(1)}$$
$$WO_3 + 2\,H_2S + H_2 \rightarrow WS_2 + 3\,H_2O \quad \textbf{(2)}$$
$$9\,CoO + 8\,H_2S + H_2 \rightarrow Co_9S_8 + 9\,H_2O \quad \textbf{(3)}$$
$$3\,NiO + 2\,H_2S + H_2 \rightarrow Ni_3S_2 + 3\,H_2O \quad \textbf{(4)}$$

Catalyst treated according to the TOTSUCAT procedure is odorless, black and has a dry aspect.

The main advantage compared to the existing SULFICAT technology supplied by EURECAT is that the catalysts are delivered to the customer in a ready-to-use condition. Special attention at start-up is no longer required. Moreover, the water formation upon the activation of TOTSUCAT will be low, whereas the quantity of water formed upon start-up of SULFICAT or during *in-situ* sulfiding is roughly 10% of the total catalyst weight. In this specific Totsucat version, a quantity of 1 wt% water can be formed upon reaction of Hydrogen with the Oxygen adsorbed on the surface.

Catalysts preconditioned according to the TOTSUCAT procedure are generally sulfided to a Sulfur level between 80-100% of the theoretical stoechiometry depending on the catalyst type.

3. HANDLING and STORAGE RECOMMENDATIONS

TOTSUCAT fully off-site sulfided catalysts, as well as catalysts preconditioned according to the SULFICAT procedure, need specific care with respect to handling, storage and reactor loading.

These versions of TOTSUCAT refer to catalysts which have received an air stabilisation treatment after the sulfiding step. These materials are not pyrophoric, but are self-heating and fall (as does SULFICAT) under the UN 3190 classification with respect to transport of spontaneously combustible materials (Class 4.2). They don't react with oxygen at room temperature. However they can start to self heat under certain conditions of temperature and after prolonged exposure.
Exposure of the TOTSUCAT sulfided and stabilized catalyst to air is allowed for short periods only.

TOTSUCAT fully off-site sulfided catalysts are supplied in containers or in steel drums with liners. The catalyst should remain stored this way until the operator is ready to load the catalyst into the reactor. At the time of loading, the catalyst may be transferred from the drums into a hopper and then loaded directly into the reactor using sock-loading or dense-loading procedure. If the catalyst has to be transferred to other vessels to facilitate reactor loading, it should be done only at the actual time of loading.

It is recommended that personnel involved in handling and loading of the catalyst be properly clothed, e.g. long-sleeved shirts, gloves and safety glasses. Furthermore, self-contained breathing apparatus (SCBA) must be used by any person who must handle the catalyst in an enclosed area containing the catalyst, e.g. inside the reactor.

Refer to the Material Safety Data Sheet supplied with the totally sulfided catalyst and read the caution labels on the drums.

The minimum shelf life of TOTSUCAT sulfided and stabilised catalyst is 4 years, stored under cover in its original, hermetically closed packaging. In the unlikely event of presence of SO_2 during opening of the drums, please take the necessary precautions.

4. LOADING GUIDELINES

1. Vessel should be purged with Nitrogen to less than 3% volume Oxygen prior to loading. Self-contained breathing apparatus (SCBA) must be used by any person in the reactor.
2. Check purity and volume of Nitrogen available.
3. Vessel should be kept at a slightly positive pressure and under constant N_2 purge during the loading.
4. Continuous O_2 monitoring is desired in the vessel. If O_2 level reaches between 3 and 5% volume at these points, loading may continue for a short period (e.g. 15'), but action should be taken for decreasing O_2 content. If O_2 level reaches 5% volume at these points, loading should be halted until an acceptable value of less than 3% is reached. A good record of O_2 measurements should be kept.
5. Periodic monitoring of Sulfur dioxide (SO_2) and Hydrogen Sulfide (H_2S) is desired at the vicinity of the catalyst bed.
6. Generally, SO_2 content is below 1 ppm during loading. If SO_2 content exceeds 15 ppm and/or catalyst temperature exceeds 50°C (120°F), introduce nitrogen gas to quench the starting oxidation reaction.

7. Drums or Containers should only be opened by designated personnel. All containers should remain closed until immediately before dumping. With specially designed liners the drums may be opened but the liners should remain unopened until dumping (risk of SO_2 emissions).
8. Inert entry and confined space rules and regulation adherence required.

5. START-UP

5.1 Pressure test

For some hydroprocessing units, a leak test under Hydrogen pressure may be requested prior to oil introduction. Certain reactors are subject to hydrogen embrittlement restrictions and cannot be pressurized to normal operating pressure below a certain temperature. The leak test is performed by controlling for pressure loss at a certain reactor temperature (50-200°C). Constant hydrogen flow is thus present in this phase, which is from time to time stopped. Traces of H_2S may be released during the pressure test. During the commercial production at EURECAT of TOTSUCAT fully off-site sulfided catalyst, all traces of H_2S are completely removed from the porosity of the catalyst due to an efficient nitrogen stripping step. However, during heat-up under hydrogen pressure, some hydrogen sulfide can form by reaction with the metal sulfides. Minor quantities of H_2S were detected in an experimental set-up using a flow of 100 vol% hydrogen at temperatures higher than 100°C (at 200°C and 1 bar hydrogen pressure about 60ppm H_2S was measured in the hydrogen stream at the outlet of the reactor).

A main advantage of TOTSUCAT fully off-site sulfided catalyst is that it is stable under hydrogen pressure up to 200°C, meaning that the catalyst will not deteriorate or have any kind of reactions with thermal consequences. Catalyst is also stable under Nitrogen at any temperature and pressure.

5.2 Typical start-up guidelines

The application of TOTSUCAT catalyst does not require any specific start-up procedures, as opposed to *in-situ* sulfided catalyst. Basically, the start-up will resemble restarting a unit after a temporary shutdown. The catalyst is delivered with the metals present already in the active form and ready to work. No reactions of activation of the metal phase will thus take place *in-situ* during the start-up. Moreover, the uncertainty of incomplete activation will be eliminated. Activation of the unit can thus proceed in a smooth and very swift way without unnecessary delays. Another advantage is that the quantity of off-spec liquid product will be minimized. Possible pollution of downstream gas circuits by H_2S is also minimized.

The guidelines of a typical start-up procedure could be :

1. Pressurize with hydrogen at normal start-up conditions (temperature embrittlement restrictions may require heating).
2. Circulate gas at normal flow rate or use once through gas.
3. Heat up the catalyst at a heating rate of 25-45°C/h.
4. A slight exotherm may be seen during heat-up in gas phase, due to elimination of Oxygen adsorbed on the catalyst surface. An equivalent quantity of roughly 1wt% (compared to catalyst weight) is formed.
5. Perform pressure test (if required) as in standard procedure.
6. At 50-180°C inject Straight Run feed stock at half design rate or normal rate with or without liquid recycle.
7. Continue heating up towards Start of Run (SOR) temperature at desired heating rate.

8. Switch to normal operating conditions and normal feedstock.
9. Do not inject cracked stocks for 2 days.

6. TROUBLESHOOTING ; Risk assessment summary

The following table summarizes the issues and concerns that may occur during the various operations as well as their potential impact and mitigation.

Operations	Risk	Potential impact	Mitigation/Resolution
1: Shipping, storage, handling	• Contact of the catalyst with air either during storage or handling, in hot climate conditions or during prolonged exposure to air	• TOTSUCAT stabilized catalyst may react in air • Oxygen (O_2) adsorption may initiate temperature rise in open container or hopper. • Sulfur dioxide (SO_2) emissions are possible if contact with air • Personnel injury by toxic gases	• Personnel handling catalyst must take appropriate safety precautions. Follow handling guidelines • Keep the catalyst temperature below 50°C (122°F) to prevent oxidation • Develop action plan if SO_2>15 ppm (check refinery specs) • Make sure breathing apparatus are available and worn by catalyst handling personnel in confined spaces
2: Catalyst loading • Transfer in air is possible • Loading under Nitrogen is preferred	• Excessive contact with air during loading	• SO_2 emissions may be detected • Excessive temperature rise in the reactor • Injury to personnel and equipment	• Follow recommended loading guidelines • Load under Nitrogen with max 3% O_2 (peaks at 5% allowed for short period) • Monitor temperature, Oxygen, SO_2 and H_2S at several points • Develop action plan if SO_2>15wppm (check refinery specs) or if temperature exceeds 50°C (122°F). Fill reactor with N_2 and wait for temperature decrease.
3: Start up	• Recycle compressor loss	• No impact on quality of sulfided active phase: catalyst is already activated. • Presence of feed at high temperature without hydrogen could result in catalyst coking	• Stop the feed pump • Stop heating • Evaluate if loss of H_2 circulation could have created any coke on catalyst. • Resume operations where they have stopped.
	• Feed stock pump failure	• No impact on quality of sulfided active phase: catalyst is already activated.	• Stop heating • Resume operations where they have stopped.

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