Guidelines for XpresS ex-situ Pre-activated Catalyst

Using ex-situ pre-activated catalyst can save time on start-up and ensure high catalyst activity by uniformly converting the catalyst's active metals to the active metal sulfide state. It also simplifies the start-up procedure and eliminates the handling of hazardous sulfiding chemicals, which are often odorous.

In TRICAT's ex-situ pre-activation process, known as XpresS, the metal sulfides created by TRICAT in our plant are stabilized against further reaction in air to permit safe handling and loading.

Enclosed are handling and start-up guidelines for XpresS pre-activated catalyst. Guidelines have been developed for start-ups in hydroprocessing units.

Storage, Handling, and Loading Guidelines for XpresS Pre-activated Catalyst

The following are guidelines for the storage, handling, and loading of XpresS pre-activated catalyst. Please refer to the Material Safety Data Sheet (MSDS) for hazards associated with this material.

1. XpresS pre-activated catalyst is classified as a self-heating substance (UN3190) and must be transported and stored in DOT or IMDG approved containers.

2. Avoid exposing the material to air (especially air flow) for extended periods. Long-term exposure to air could cause the material to generate sulfur dioxide and heat.

Important note: *Keep containers sealed. During loading, open containers only as needed. Avoid storage of partially full flow bins by transferring material into drums. Check the integrity of containers and seals before placing material into storage. In case a drum has been left open for a period, remove air from the drum with nitrogen purge before sealing the drum.*

3. Material should be stored in a cool place and kept dry. Outside storage is not recommended. If stored outside, use full tarpaulins (or other plastic covers) to completely cover containers.

Important note: *The catalyst will normally not self heat unless air flows through the catalyst beds, i.e. a chimney effect. Avoid any other opening than the one used to introduce the catalyst in the reactor. Be especially careful with bottom of the reactor opening and side manhole (in case of multi-bed reactors).* ***ALL OPENINGS OTHER THAN THE ONE USED FOR LOADING SHOULD BE CAREFULLY LOCKED AND SEALED BEFORE LOADING*** **XpresS** ***TREATED CATALYST TO AVOID AIR CIRCULATION THROUGH THE CATALYST BED.***

4. XpresS material can be loaded into the reactor in either an air or inert environment. Reactor should be clean and dry. If loading in air, avoid having air flow through the reactor bed and continuously monitor the reactor bed thermocouples during the loading.

*In case there is a delay during or after the loading, monitor bed temperatures every hour for 12 hours after the loading is stopped. If the material begins to react, purge the reactor with nitrogen immediately.**

5. Personal protective equipment should be worn when the material is loaded. TRICAT recommends fresh air supply for all personnel entering a reactor vessel during or after catalyst loading. The dust from the treated (or untreated) catalyst can be irritating to the eyes, skin, and respiratory system.

6. If the catalyst loading is interrupted, monitor the reactor bed thermocouples for signs of reaction. If the delay extends more than 1 hour put the reactor on nitrogen sweep for the remainder of the delay. During the delay, the top manhole should be closed.

7. Once the catalyst is loaded, seal the reactor. Avoid having air flow through the catalyst bed. If the catalyst bed begins to self-heat, purge the reactor with nitrogen.*

**** Note:** Appropriate measures should be taken to protect personnel when a reactor is being purged or has been purged with nitrogen.*

Guidelines for Start-up of XpresS Pre-activated Catalyst

The following are guidelines for the start-up of XpresS pre-activated catalyst in hydroprocessing units. They should be used in conjunction with the standard start-up procedure set forth by the refiner's operating guidelines.

1. Air free the reactor circuit (usually done with nitrogen evacuation or purge). Reactor circuit should be placed under slight positive nitrogen pressure and oxygen content should be reduced to <0.5 vol%.

2. Pressure the unit with hydrogen. Be sure to keep within recommended metallurgical requirements for hydrogen embrittlement.

3. Establish hydrogen circulation and line out gas flow at the maximum rate possible at the allowable pressure. This will help with the reactor heat-up and provide a better heat sink for the initial exotherm. Hydrogen should be introduced to the unit at a catalyst temperature of less than 60°C. The catalyst may react immediately with the hydrogen, causing an exotherm of up to 60-100°C in the reactor. This exotherm will commence before the catalyst reaches 100°C. It is not necessary to start the H_2S scrubber. Any H_2S released during this stage (typically <100 ppmv) may be recirculated.

4. Begin heating the reactor inlet under hydrogen circulation. Heat at design rates. Check the high-pressure separator for water and drain as required. In most circumstances water release should be negligible.

5. Heat-up can be carried out with or without feed (liquid or gas phase), as follows:

   A. **Gas phase heat-up**: Continue gas circulation and heat-up until the normal feed cut in temperature is reached. No additional exotherms should be observed through the heat up. Feed cut in temperatures of as high as 300ºC have been experienced.

   B. **Liquid phase heat-up**: Introduce straight-run feed at ambient temperature or as soon as it can be circulated at adequate rates (at least 75% of design rates). Liquid flow will help with the reactor heat-up. Liquid is normally introduced at temperatures below 120°C to maintain good liquid distribution. If on liquid recycle, stabilize liquid levels in the product separators and recycle rates to the feed surge drum. Hydrotreated feeds may be used to avoid feed recycling.

Notes: *As with any start-up procedure, it is important to use straight-run (or other saturated) feed to ensure a low olefin content. Olefins react readily and may increase reactor exotherms and coke deposits on the catalyst. For best results, use oil with a final boiling point of less than 480°C.*

Some refiners believe it is important to do a formal catalyst pre-wet to ensure good flow distribution. Pre-wetting is accomplished by introducing oil at maximum possible feed rate at a reactor temperature of about 120°C with hydrogen circulation reduced to minimum rates. This condition is maintained for four hours. After the prewetting step is completed, hydrogen circulation is increased to normal rates.

Since the catalyst is truly pre-activated, no agent will come off to discolor the product and no high temperature holds are required to finish the sulfiding.

6. Heat the reactor inlet at design rates or less than 50°C/hr to 315°C or design start-of-run temperature for hydrotreater, whichever is less or design start of run temperature for hydrocrackers.

7. Check the products qualities. Adjust temperature as necessary before lining up to a product tank.

Note: *To obtain the best performance, fresh catalyst manufacturers normally recommend that the catalyst be conditioned with straight-run feed for 72 hours. Thereafter, the amount of cracked stocks in the feed should be increased gradually to normal levels.*

TRICAT

Guidelines for Responding to Mechanical Problems During XpresS Start-ups

The following are general recommendations for handling mechanical problems during the start-up of XpresS pre-activated catalyst. In case of equipment loss, action should be taken in accordance with unit licensor recommendations. We recommend that the refiner consult Tricat personnel if problems arise during the start-up of XpresS pre-activated catalyst.

XpresS pre-activated catalyst is very forgiving of mechanical problems during start-up. However, a few situations require additional comment, and these are discussed below.

LOSS OF RECYCLE COMPRESSOR

Continue liquid flow (if available) to cool the reactor below 150°C. Minimize once-through gas to prevent the loss of H_2S from the system.

LOSS OF MAKE-UP GAS FLOW

For liquid-phase start-ups, adequate hydrogen partial pressure is needed to prevent coking of the catalyst. Therefore, the start-up should be halted if make-up hydrogen is lost. Continue liquid flow and recycle gas and cool the reactor beds below 90°C. If the make-up compressor needs to be repaired, discontinue liquid flow. Continue recycle gas flow and minimize gas purge to keep H_2S in the system.

LOSS OF CHARGE PUMPS

The catalyst beds should be cooled below 150°C under hydrogen flow until the repairs are made. Once-through gas should be minimized to prevent the loss of H_2S from the system.

US HEADQUARTERS: 260 Schilling Circle, Hunt Valley, Maryland 21031, Tel. (410) 785-7900, Fax (410) 785-7901
GERMAN MANUFACTURING PLANT: Tricatstrasse (im Chemiepark Bitterfeld) D06749 Bitterfeld, GERMANY Tel:+49-3493-75910 Fax:+49-3493-75999