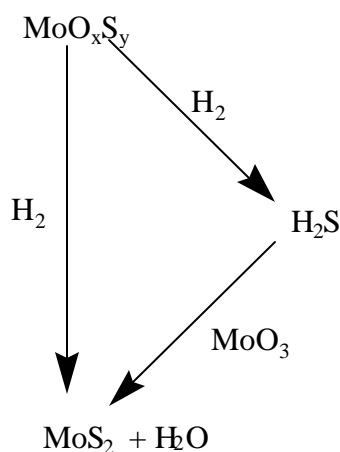


Guidelines for actiCAT® Presulfurized Catalyst

Using ex-situ presulfurized catalyst can save time on start-up and ensure high catalyst activity by minimizing the chances of metal oxide reduction. It also simplifies the start-up procedure and eliminates the handling of hazardous sulfiding chemicals, which are often odorous.

In our ex-situ presulfurizing process, known as actiCAT®, the catalytic metal oxides are converted to a range of complex metal oxysulfides. In addition, approximately one-third of the metals are completely converted to metal sulfides. When heated with hydrogen during the activation, the oxysulfides break down to form metal sulfides directly, or to form H₂S, which converts the metal oxides to metal sulfides. The following is an example of the reactions that occur during the catalyst activation:



These reactions generate heat and water and consume hydrogen. Therefore, it is important to have the reactions take place in a controlled manner over several hours. The actiCAT® catalyst helps achieve this with a variety of sulfiding compounds that react over a wide temperature range.

Enclosed are handling and start-up guidelines for actiCAT® HT presulfurized catalyst. Guidelines have been developed for both liquid-phase and gas-phase start-ups in hydrotreating units. In general, the liquid-phase procedure is preferred because the liquid provides a better heat sink for the activation exotherm and helps with the reactor heat-up. However, actiCAT® catalyst can easily be started up using either procedure or a combination of both.

In addition to conventional hydrotreating units, actiCAT® HC, actiCAT® TG, actiCAT® PG presulfurized catalysts are available for hydrocracking, Claus tail gas and pygas treating applications. If you have a hydrocracking, tail gas or pygas application, or have questions about the hydrotreating start-up guidelines, please contact our technical services group of your geographical location:

Canada: (1) 780-438-4188

US and Latin America: (1) 281-874-2600

Europe: (44) 1 489-881881

Asia Pacific: (65) 276-3627

Storage, Handling, and Loading Guidelines for actiCAT® Presulfurized Catalyst

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

1. actiCAT® presulfurized catalyst is classified as a self-heating substance and must be transported and stored in DOT, IMDG, ADR/RID and TDG approved containers.
2. Do not exposing the material to air for extended periods prior to loading. Exposure to air could cause the material to generate sulfur dioxide and heat.

Note: *Keep containers tightly sealed. During loading, open containers only as needed. Avoid storage of partially full flobins and bags by transferring material into drums. Check the integrity of containers and seals before placing material into storage*

3. Material should be stored in a cool place and kept dry. Outside storage under direct sunlight is prohibited. If stored outside, use full tarpaulins to completely cover containers. The material may generate sulfur dioxide and heat if it is wetted. Exposure to air and water may also cause discoloration and agglomeration of the material.

Note: *If the material does get wet or generate heat, the drums or flobins should be purged with nitrogen or dry ice and resealed. The material should be inspected for signs of degradation just before it is loaded into the reactor.*

Note: *Do not load oxidic (unsulfurized) CoMo or NiMo catalyst below the actiCAT® catalyst in a reactor as the oxidic layer may be sensitive to early activation and subsequent exotherms as H₂S is generated during activation.*

4. actiCAT® material can be loaded into the reactor in either an air or inert environment.* If loading in air, see "Air Loading Guidelines for actiCAT® Presulfurized Catalyst"(next page).
5. Appropriate personal protective equipment should be worn when the material is loaded. The sulfur and hydrocarbon dust from the material can be irritating to the eyes, skin, and respiratory system.
6. Once the catalyst is loaded, blanket the reactor with nitrogen and seal the reactor. Avoid having air flow through the catalyst bed. If the catalyst bed begins to self-heat, purge the reactor with nitrogen immediately.*

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

Air Loading Guidelines for actiCAT® Presulfurized Catalyst

The following are guidelines for the loading of actiCAT® presulfurized catalyst. Please refer to the Material Safety Data Sheet (MSDS) for hazards associated with this material.

1. Open air transfers between containers, i.e. from bins to drum or to bags or vice versa, are not encouraged. If material has to be transferred, do so under shelter to prevent any wind and/or rain wetting, which can cause self-heating and generation of SO₂.
2. All open flanges and manways must be closed to eliminate any source of air ingress that can sweep through the reactor bed upward (due to the chimney effect) that will result in self-heating.
3. SO₂ monitoring should be located within the airspace above the loaded catalyst, by continuous automatic analyzer.
4. Presence of SO₂ can interfere with H₂S analyzers causing false H₂S readings. H₂S can only be generated in the presence of hydrogen.
5. Monitor bed thermocouples if available during loading. Note, however, that thermocouple monitoring is not a substitute for SO₂ monitoring, as localized self-heating may evolve SO₂ without registering on a thermocouple. A rising trend in bed temperatures or SO₂ levels will necessitate reactor evacuation and sweep from bottom with nitrogen.
6. Normal exposure limits always apply, and it is understood that the contractor will wear full-face supplied air respirators.
7. The emergency nitrogen supply must be immediately available for use. Once under nitrogen atmosphere, no attempt shall be made to reintroduce an air atmosphere, as such a flow over the catalyst may restart self-heating. The remainder of the loading will be completed under inert conditions.
8. If the loading is interrupted for several hours, continue to monitor bed temperature and SO₂ above the catalyst bed. If sign of increase in either temperature or SO₂ is detected, emergency nitrogen sweep of the reactor must be commenced. The top manway must be covered to prevent airflow through the top of the reactor.
9. If loading is to be interrupted for more than 48 hours, the reactor must be blanketed with nitrogen and the rest of the loading must be done under inert atmosphere.

Guidelines for Liquid-phase Start-up of actiCAT® HT Presulfurized Catalyst

The following are guidelines for the liquid-phase start-up of actiCAT® presulfurized catalyst in hydrotreating 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 purge) so that oxygen level is below 0.5%.
2. Pressure the unit with hydrogen to the allowable pressure for cold conditions. Be sure to keep within recommended metallurgical requirements for hydrogen embrittlement.
Note: *Hydrogen should be introduced to the unit at a catalyst temperature of less than 90°C. At higher temperatures, the catalyst may react immediately with the hydrogen, causing an exotherm in the reactor. Avoid the use of pilot burners during this period. If minor exotherm develops during stagnant flow pressurization, consider using purge gas to create a flow through the catalyst bed to remove heat from the system.*
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 during the activation.
Note: *It is important to maintain gas circulation whenever there is hydrogen in the unit to remove the heat generated in the activation. **Avoid blocking in the unit with hydrogen (particularly sour H₂) since this could cause an exotherm in the reactor. Total gas flow rate through the reactor must be greater than 100 Nm³/hr/m³ of catalyst before commissioning of the furnace.** Refer to the "Responding to Mechanical Problems" section of these guidelines (page 7) to develop a contingency plan for loss of recycle compressor during start-up.*
4. Begin heating the reactor inlet to 315°C under hydrogen circulation. Heat at less than 55°C/hr and not to exceed metallurgical design rates.
Note: *The actiCAT® presulfurizing process fills the catalyst pores with sulfiding agent and hydrocarbons, so no catalyst dry-out nor prolonged wetting is required.*
5. If possible, introduce straight-run feed at ambient temperature or as soon as it can be brought in depending on constraints of the particular unit. Due to the higher viscosity of hydrocarbon at low temperatures, catalyst bed pressure drop will be increased. At this time the pilot should be lit to keep the reactor circuit warm thus reducing the liquid viscosity and delta P across the catalyst
Note: *As with any presulfiding procedure, it is important to use straight-run feed to ensure a low olefin and aromatics content. These species can 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 425°C for distillate application and less than 510°C for VGO application. **Moreover, if the feed boils in the diesel range or lighter, it will minimize pressure drop when feed is first introduced at low reactor temperatures.***
6. Route the product to slop tank and flush the reactor circuit once-thru for 30-60 minutes to remove any particulates left in low points of the line.

7. Following flushing of the reactor circuit, when possible, re-circulate the feed to minimize off-spec product storage requirements. In order to maintain good liquid distribution and minimize exotherms during activation, minimum liquid rate of at least 75% of design rate is also recommended. Adequate liquid flow ensures a proper liquid distribution in the catalyst bed and will also help with the reactor heat-up
8. Establish liquid flow through the reactor. If on liquid recycle, stabilize liquid levels in the product separators and recycle rates to the feed surge drum.

Note: *Because liquid acts as a heat sink for the activation exotherm, establish liquid flow before increasing temperature.*

Note: Some refiners believe it is important to do a formal catalyst prewet to ensure good flow distribution. This is done by introducing oil at maximum possible feed rate at a reactor temperature of about 120°C and reducing hydrogen circulation to minimum rates. This is continued for four hours. After the prewetting step is completed, hydrogen circulation is increased to normal rates.

9. When the reactor inlet reaches 120°C, begin monitoring the reactor bed thermocouples for the presence of exotherms. In most cases, the activation is so controlled and gradual that a positive ΔT will not be observed in the reactor bed.
10. When any reactor bed temperature reaches 150°C, begin monitoring the H₂S concentration in the off gas from the high-pressure separator every 30–60 minutes. H₂S levels as high as 1–2 vol% are normal (use 100–2,000 ppm and 0.2–7.0% Draeger tubes to measure H₂S). Drain separator boots of water, which is formed in the sulfiding reactions.

Note: *During the activation, the liquid product will be discolored by grayish-black color bodies. The color bodies are distillate boiling range material and will clear up within one hour at 315°C. The discolored liquid product should be recycled back to the feed surge drum or sent to a charge or slop tank.*

11. As the reactor outlet temperatures get hotter, more feed preheating will be available and furnace control must be carefully monitored such the heat-up rate does not exceed 55°C/hr or the maximum metallurgical constraint. Continue monitoring H₂S levels in the separator off gas.
12. Once reactor inlet temperature is at least 315°C with the reactor outlet temperature not exceeding 365°C, hold for one hour. Criterion recommends 345°C bed temperatures for our catalysts as the final sulfiding temperature. Lower or higher final sulfiding temperatures may be required for catalysts by other catalyst manufacturers.
13. Check the product in the stripper bottoms for sulfur, color, and H₂S. Adjust temperature as necessary before lining up to a product tank. Gradually introduce actual feed. If the actual feed contains cracked (unsaturated) stocks, reduce reactor temperature to 290°C before introducing this feed.

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

Guidelines for Gas-phase Start-up of actiCAT® HT Presulfurized Catalyst

The following are guidelines for the gas-phase start-up of actiCAT® presulfurized catalyst in hydrotreating 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 purge) so that oxygen level is below 0.5%.
2. Pressure the unit with hydrogen to the allowable pressure for cold conditions. Be sure to keep within recommended metallurgical requirements for hydrogen embrittlement.
Note: *Hydrogen should be introduced to the unit at a catalyst temperature of less than 90°C. At higher temperatures, the catalyst may react immediately with the hydrogen, causing an exotherm in the reactor. Avoid the use of pilot burners during this period. If minor exotherm develops during stagnant flow pressurization, consider using purge gas to create a flow through the catalyst bed to remove heat from the system.*
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 during the activation.
Note: *It is important to maintain gas circulation whenever there is hydrogen in the unit to remove the heat generated in the activation **Avoid blocking in the unit with hydrogen (particularly sour H₂) since this could cause an exotherm in the reactor. Total gas flow rate through the reactor must be greater than 100 Nm³/hr/m³ of catalyst before commissioning of the furnace.** Refer to the "Responding to Mechanical Problems" section of these guidelines (page 7) to develop a contingency plan for loss of recycle compressor during start-up.*
4. Begin heating the reactor inlet to 315°C under hydrogen circulation. Heat at less than 55°C/hr and not to exceed metallurgical design rates.
Note: *The actiCAT® presulfurizing process fills the catalyst pores with sulfiding agent and hydrocarbons, so no catalyst dry-out is required.*
5. When the reactor inlet reaches 120°C, begin monitor and record the reactor thermocouples for the presence of exotherms. The activation of actiCAT® presulfurized catalyst is controlled and exothermic, and typically initiates at temperatures of 120–150°C. If the reactor ΔT across a catalyst bed exceeds 30°C, hold the reactor inlet temperature constant until the exotherm is reduced to less than 30°C.
6. When any reactor bed temperature reaches about 150°C, begin monitoring the H₂S concentration in the off gas from the high pressure separator every 30–60 minutes. H₂S levels as high as 1–2 vol% are normal (use 100–2,000 ppm and 0.2–7.0% Draeger tubes to measure H₂S). Drain separator boots of water, which is formed in the sulfiding reactions.

7. As the reactor outlet temperatures get hotter, more feed preheating will be available and furnace control must be carefully monitored such the heat-up rate does not exceed 55°C/hr or the maximum metallurgical constraint. Continue monitoring H₂S levels in the separator off gas.
8. Once reactor inlet temperature is at least 315°C with the reactor outlet temperature not exceeding 365°C, hold for one hour. Criterion recommends 345°C bed temperatures for our catalysts as the final sulfiding temperature. Lower or higher final sulfiding temperatures may be required for catalysts by other catalyst manufacturers.
9. Reduce the catalyst temperature to at least 290°C prior to bringing in straight-run feed. Establish liquid levels with at least 75% of design feed rate.

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

Note: *The initial liquid product will be discolored by grayish-black color bodies. The color bodies are distillate boiling range material and will clear up within one hour at 315°C. The discolored liquid product should be sent to a charge or slop tank.*

Note: *Some refiners believe it is important to do a formal catalyst prewet to ensure good flow distribution. This is done by cooling the reactor to about 120°C, introducing oil at maximum possible feed rate, and reducing hydrogen circulation to minimum rates. This is continued for four hours. After the prewetting step is completed, hydrogen circulation is increased to normal rates. If a prewetting step is not used, at least make sure the liquid flow rate is at least 75% of design rates to ensure a proper wetting of the catalyst bed.*

10. After liquid flow has been established throughout the unit, bring the reactor to start-of-run temperature.
11. Check product in the stripper bottoms for sulfur, color, and H₂S. Adjust temperature as necessary before lining up to a product tank.

Guidelines for Responding to Mechanical Problems During actiCAT® Start-ups

The following are general recommendations for handling mechanical problems during the start-up of actiCAT® presulfurized catalyst. The guidelines should be incorporated into the refiner's standard operating procedures. We recommend that the refiner consult CRI personnel if problems arise during the start-up of actiCAT® presulfurized catalyst.

actiCAT® presulfurized catalyst is very forgiving of mechanical problems during start-up. This is because actiCAT® activates gradually over a wide temperature range and has excellent sulfur retention. However, a few situations require additional comment, and these are discussed below.

The actions taken will depend on whether or not the presulfurized catalyst has activated. In general, the most critical time during the start-up is when the catalyst has started to activate, but the reactor is not hot enough to complete the sulfiding (typically between 120°C and 260°C). In this situation, there is a high concentration of H₂S in the recycle gas, so significant amounts of sulfur could be lost if the unit is depressured.

The following actions are recommended if there is a mechanical problem either before or during the activation. The activation of actiCAT® presulfurized catalyst typically initiates between 125°C and 150°C. As the catalyst activates, H₂S is generated, heat is released, and water is formed as the metal oxides on the catalyst are converted to metal sulfides.

MECHANICAL LOSS OF RECYCLE COMPRESSOR

Before activation

Continue liquid flow (if available) and once-through makeup gas and cool the reactor beds below 65°C. When all of the catalyst is below 65°C, discontinue liquid flow to avoid washing sulfur from the catalyst. Continue once-through gas to purge liquid from the recycle system as required. Shut down once-through gas and repair recycle compressor as required.

During activation

Continue liquid flow (if available) to cool the reactor below 65°C. Minimize once-through gas to prevent the loss of H₂S from the system. If repairs can be made without purging the entire recycle gas system and H₂S levels remain high, additional sulfiding agent should not be needed when the unit is restarted. Note, actiCAT® presulfurized catalyst contains more sulfur than required to fully activate the catalyst.

If the recycle gas system has to be purged, some amounts of sulfur will be lost and an additional source of sulfur may be needed when the unit is restarted. When the unit is restarted, closely monitor H₂S in the recycle gas. If the H₂S concentration falls below 1000 ppmv, hold the inlet temperature constant and introduce sour gas, sour feed, or a spiking agent to increase the concentration above 1000 ppmv. Maintain at least 1000 ppmv H₂S as the reactor inlet is heated to 315°C. If adequate H₂S levels are not maintained during the activation, the catalyst could end up sulfur deficient. Prior to gas-phase activation, additional sulfur source should be identified and made available.

Avoid Blocking the Unit in with Hydrogen

If the unit must be blocked in with hydrogen for minor repairs, the entire catalyst bed must be cooled to below 65°C. If the activation has already started, monitor bed thermocouples to ensure that the entire bed is cooled down. If there are no bed thermocouples, monitor to ensure that the reactor outlet temperature declines for a period of time as an indication that the stagnant heat is removed from the reactor prior to blocking in the unit.

Additionally, the reactor should not be blocked in with hydrogen for more than 1 hour. If the unit losses recycle compressor before or during the activation in which long repair is required with no other mean to circulation the hydrogen, the reactor must be purged of hydrogen and blanketed with nitrogen.

LOSS OF MAKE-UP GAS FLOW

Before activation

During the start-up, hydrogen is brought in to maintain unit pressure because actiCAT® catalyst consumes hydrogen gradually while it activates. Therefore, the activation should not be initiated until make-up hydrogen is available. With the make-up compressor out of service, continue liquid flow (if available) and recycle gas and cool the reactor beds below 65°C. If the make-up compressor needs to be repaired, discontinue liquid flow to avoid washing sulfur from the catalyst. Continue recycle gas flow and minimize gas purge to keep H₂S in the system.

During activation (gas-phase start-ups)

For gas-phase start-ups, if there is adequate hydrogen in the system to complete the activation (typically, 0.1 Nm³ of hydrogen per kilogram of catalyst is needed), the sulfiding should be completed before shutting down for repairs. The catalyst vendor should be contacted to verify the minimum hydrogen partial pressure requirement during the activation.

With actiCAT®, hydrogen is mostly required at the early stage of the activation where hydrogen is consumed for the making of H₂S. Once all the H₂S is evolved, the high temperature metal sulfiding reactions take place at higher temperature where there should not be a significant amount of additional hydrogen consumption.

If the make-up hydrogen source is lost at the early stage of the activation as indicated by the continuous increase of H₂S in the system then the heat-up should be halted until the make-up hydrogen source is reestablished. Continue recycle gas flow and minimize gas purge to keep H₂S in the system.

Once the early stage of the activation is passed, most of the H₂S has already been generated and the H₂S level will begin to drop as an indication that metal sulfides are being formed. Without a significant amount of additional hydrogen consumption, system pressure can be maintained (assuming the losses from the reactor system are minimal and that purge gas valve can be shut down). Activation can be completed without additional hydrogen make-up. After the sulfiding is completed, the catalyst bed should be cooled below 150°C before shutting down for repairs.

LOSS OF MAKE-UP GAS FLOW (con't)

During activation (liquid-phase start-ups)

For liquid-phase start-ups, adequate hydrogen partial pressure is needed to prevent coking of the catalyst. Therefore, the activation should be halted if make-up hydrogen source is lost at temperatures above 175°C. If the make-up hydrogen problem can be fixed fairly quickly and the recycle gas flow is reliable and the liquid is circulating, reduce the reactor bed to below 175°C and wait for the make-up hydrogen source to be reestablished. Otherwise, reduce the reactor beds to below 65°C with recycle gas and/or liquid flow. If the liquid is once-through, discontinue liquid flow to avoid washing sulfur from the catalyst. Continue recycle gas flow and avoid gas purge to keep H₂S in the system.

If the make-up compressor needs to be taken out of service to be repaired, continue liquid flow and recycle gas to cool the reactor beds below 65°C. If the liquid is once-through, discontinue liquid flow to avoid washing sulfur from the catalyst. Continue recycle gas flow and avoid gas purge to keep H₂S in the system.

LOSS OF CHARGE PUMPS

Before activation

The loss of charge pumps is not critical. Depending on the situation, the refiner can wait for the pumps to be repaired or complete the activation under hydrogen flow only.

During activation

Complete the activation under hydrogen flow only. If liquid flow is still not available when the activation is completed, the catalyst beds should be cooled below 150°C until the repairs are completed.

If the unit needs liquid flow to heat the reactor enough to complete the sulfiding (approximately 315°C), the activation cannot be completed until the feed pumps are repaired. In this case, 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 H₂S from the system