

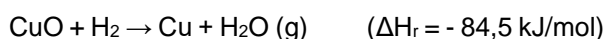
Reduction of Copper-Based Adsorbents

The following guideline applies to PuriStar® R3-11, PuriStar® R3-11G, PuriStar® R3-15 and PuriStar® R3-16.

Introduction

PuriStar® R3-11, PuriStar® R3-11G, PuriStar® R3-15 and PuriStar® R3-16 are used in a number of applications in reduced form. For application details, please refer to the respective technical datasheets.

The adsorbents as produced contain copper in its oxidic form, which needs to be transferred into reduced copper. Not necessarily all copper oxide will be reduced as certain parts of the copper oxide might not be accessible for the reducing agent. The typical reducing agent used is hydrogen (H₂). The overall reduction can be described by the following equation:



The reduction is typically carried out by passing a non-reactive (inert) gas (e.g., nitrogen) containing small amounts of hydrogen (H₂) through the bed at temperatures of 200 – 220°C (390 - 430°F), preferably at a space velocity of at least 300 hr⁻¹ (GHSV). To avoid any fluidization of the bed and to allow for any liquid water formed to drain from the bed, the reduction is typically carried out in down-flow. The procedure is described in more detail further down. Temperatures in the bed should be limited to 230°C (445°F), to avoid an irreversible deterioration of the adsorbent.

If a material is reduced, it does not need to be dried out before being brought on-stream.

Monitoring of the progress of the reduction can be done by monitoring the temperatures at the inlet,

outlet and in the bed and by either determining the consumption of H₂ (measuring the inlet and outlet concentration) or by monitoring the concentration of water in the gas coming out of the bed.

During the reduction of the respective CuO, a significant amount of water will be released (between 60 and 90% of the stoichiometric amount of water when taking into account any water still adsorbed on the material as delivered). This water can condense out of the gas coming from the bed being reduced and should be properly handled by e.g. cooling the outlet gas and having the water condense out in a properly designed separator. This is especially important, if a recycle loop is used for reduction.

Safety

To control the temperature during the reduction, hydrogen is mixed with inert gases, like nitrogen. The flow rates of both gases must be tightly controlled to avoid any temperature excursion. To cap the maximum flow of H₂, installing orifice plates, limiting the maximum feed pressure or other measures can be considered. Alternatively, also the H₂ concentration in the inert gas can be monitored and limited.

To monitor the temperature during the reduction, temperatures must at least be measured at the inlet to the respective vessel, where the bed to be reduced is located, and at the outlet of the respective vessel. It is preferable to have some more temperature measurements along the bed length. When installing these measurements, it must be assured that the measurements are really located in the bed to be reduced.

The respective temperature measurements should be used to protect the mechanical integrity of the vessel by using them also for switches which become active when excessively high temperatures are measured.

Protective switches linked to these temperature measurements should shut down any heat source used for heating the gas flow fed to the vessel as well as stopping the H₂ flow. The flow of inert gas must be maintained to assure proper cooling of the bed.

When choosing an inert carrier gas, the inert gas or components thereof must have no reaction with hydrogen, (reduced) copper or copper oxide.

Examples of stream component reactions, which could occur with H₂ in the presence of copper are at reduction temperatures are:

- (1) H₂ + Olefins → Alkane (exothermic)
- (2) H₂ + Di-Olefins → Olefin/Alkane (exothermic)
- (3) H₂ + CO → Methanol (endothermic)
- (4) H₂ + CO/CO₂ → CH₄ + Water (exothermic)

Reduction Procedure

This procedure is designed to reduce a 10 m³ bed of adsorbent in approximately two (2) days. Higher or lower gas hourly space velocities (GHSV) will result in shorter or longer reduction times.

The recommended gas flow (H₂ + N₂) should be no less than 3,000 Nm³/hr (GHSV=300 hr⁻¹) to insure good gas distribution and reaction efficiency.

The indicated temperatures are inlet temperatures to the respective vessel. In case significant temperature losses along the length of the adsorbent bed are observed (> 5 – 10°C / 10 - 20°F), the indicated temperature should be read as bed average temperature and the inlet temperature should be adjusted accordingly.

The “hot spot” referred to under point 3 refers to a local temperature increase (due to the reduction in place), which typically moves from the inlet of the vessel to the outlet of the vessel within a certain time. The time it takes for such a “hot spot” to move from one temperature measurement to another can

be used as a characteristic time for the reduction to move through the bed.

1. Preheat the bed with 3,000 Nm³/h of N₂, gradually bringing the inlet temperature up to 150°C/300°F during a three (3) hour period. The N₂ flow should be maintained at this rate throughout the reduction step.
2. Begin dosing H₂ at 1 % by volume by adding 30 Nm³/h of H₂ to the N₂. This should cause a moderate exotherm (max. 30°C). Holding the H₂ concentration at 1 vol. %, gradually bring the inlet temperature up to 180°C/355°F during a one-hour period.
3. Hold the 1 vol. % H₂ concentration and the 180°C/355°F inlet temperature for at least 8 hours for the initial stage of reduction to be completed at the conditions selected. The “hot-spot” should have traveled all the way through the bed during this time. Else continue until the “hot-spot” has passed through the bed. Cut back or stop the H₂ if necessary to keep bed temperatures below 225°C/435°F.
4. Increase the H₂ concentration to 2 % by volume (60 Nm³/h of H₂), and continue feeding the 2 vol. % mixture for 4 - 6 hours, maintaining the inlet temperature at 180°C/355°F. Cut back or stop the H₂ if necessary to keep bed temperatures below 225°C/435°F.
5. Increase the H₂ concentration to 4 % by volume (120 Nm³/h of H₂) and continue at 4 vol. % H₂ for 4 hours. During this step, slowly increase the inlet temperature to 200°C/390°F without allowing the bed temperatures to exceed 225°C/435°F.
6. Finally, increase the H₂ concentration to 6 % by volume (180 Nm³/h of H₂), increase inlet temperature to 215 – 225°C/420-435°F and hold for one hour at this temperature to complete the reduction. The production of water at the outlet should have gradually decreased to near zero at this point.

Additionally, the hydrogen levels at the outlet of the bed should be close to the inlet hydrogen levels.

7. Stop the H₂ flow and cool slowly with 3,000 Nm³/h of N₂ at a cooling rate of not more than 50°C/h/ 90°F/h, until the bed temperatures are below 50°C/120°F. The catalyst is now activated and must not be allowed to be brought into contact with air. Maintain the reduced bed under inert gas until it is put into service.

Reduction with Recycle Loop

In case the reduction is carried out with a recycle system, the following points need to be considered:

- The recycle system typically consists of the following components:
 - A cooler to cool down the gas coming from the reduction. While cooling down the gas, part of the water generated during the reduction will start to condensate.
 - A two-phase separator to separate any water or water droplets generated during the cooling step. To maximize the separation of water a properly designed demister section should be included in the gas space of the vessel.
 - A blower or compressor to recirculate the gas.
 - Proper instrumentation to monitor flows, temperatures, pressures and gas composition.
- The major part of the unreacted H₂ will be fed to the inlet of the bed to be reduced with the recycle stream. When determining the amount of H₂ to be added to the stream fed into the respective vessel, the amount of H₂ recycled must be considered to avoid a temperature increase, which is too high compared to limitations defined earlier.
- The recycle stream will contain water, which has been generated during the reduction of the

copper oxide. This water can lead to a partial inhibition of the reduction reaction as well as condensation in the pore system. Thus, the amount of water recycled should be kept as low as possible.

- Towards the end of the reduction, the amount of water should be limited to more or less 0 to avoid having any water left on the adsorbent before bringing it into operation. Less water is produced towards the end of the reduction, which should assist with keeping water levels near zero.
- The flow rate of recycle stream will be significantly higher than the feed stream flow rate. Thus, in case of a failure of the recycle stream or a too low recycle stream, the amount of heat, which can be entrained with any remaining feed stream, will be low. One alternative is to ramp up the feed stream of the inert gas to reasonable values to assure proper cooling of the bed. The other alternative, in case a rapid temperature increase is observed (see also chapter on safety), would be to depressurize the whole system (to free the system from any remaining H₂) and to ensure proper flow over the bed after depressurization to allow for cooling of the bed.

In case of any questions regarding the indicated procedure do not hesitate to contact your local BASF representative.

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BASF-10246 Rev. 06/24