

PuriStar[®] R0-20

Catalyst Handling

In the following information is provided on how to handle PuriStar R0-20. The guideline covers the following points:

- 1) Loading of the catalyst
- 2) Catalyst Activation / Start-up
- 3) Regeneration of Catalyst
- 4) Unloading of the Catalyst

This document will not address questions regarding toxicological information. For this type of information please refer to the respective material safety data sheet.

The present document can only address certain aspects regarding safe handling and operation of R0-20. Further details need to be developed and reviewed before or during a process hazard analysis (PHA).

The local safety regulations must be strictly observed when handling BASF Catalyst PuriStar R0-20.

1) Loading of the Catalyst

Before loading of the catalyst, the reactor into which the material is loaded, should be thoroughly checked and cleaned. This also applies to all internals (like support grids or outlet basket) as well to the removal of any fly rust, which might have formed during manufacturing of the vessel or during water pressure tests.

The installation of the thermocouples depends on the configuration chosen. If possible, all thermocouples should be installed before loading any material into the vessel.

It should also be ensured that all parts, which need to be loaded into the vessel (e.g. the nets to be

installed between the catalyst and the layer of inert balls on top of the catalysts) are available and in a good condition.

A last point to consider is the availability of all equipment needed to load the catalyst, like hoppers, chute or filling pipe, a crane, fork lifts and experienced personnel to do the loading.

It is recommended to mark the catalyst bed height on the reactor wall. It is not necessary to screen the catalyst before loading. However, the drums in which the catalyst is supplied should be examined for any possible damage suffered in transit. The catalyst may be charged either directly from drums or by using a chute or a filling pipe. In either case free-fall heights of more than 1 meter / 3 feet should be avoided. Boards should be placed on the catalyst for protection if it is necessary to walk on the catalyst.

BASF Catalyst PuriStar R0-20 absorbs moisture from the air. Therefore the drums should be kept closed and opened only shortly before filling the catalyst into the reactor. Also care must be taken to protect the catalyst from rain.

Catalyst loading should be done steadily and without any longer interruption. Once the catalyst and the inert balls are loaded into the vessel the reactor should be closed and the vessel sealed by nitrogen.

The quickest and most proven procedure of filling a vessel evenly with a catalyst is to use a canvas sock fitted to a hopper which is supported outside the reactor opening (manhole or flange if the top has been removed). The sock is always kept full of catalyst and slowly raised in order to allow the catalyst to flow into the vessel in a controlled way.

Technical Guideline

The sock has to be guided in order to avoid catalyst discharge at the same place. By this procedure uneven packing of catalyst is avoided and even flow distribution across the catalyst bed is ensured, resulting in high effectiveness of the catalyst bed. Periodically the sock has to be shortened to prevent kinking during the filling procedure.

Because operators have to enter the vessel during or after charging the catalyst, the inert balls or the wire screens, planks should be used so that they have not to tread directly on the catalyst/inert balls. During the charging process catalyst dust will form. Therefore respiratory protection, in accordance with the information provided in the respective MSDS should be provided for anybody who has to enter the vessel during this time.

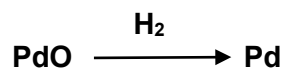
It is recommended to write a loading protocol showing the number of drums and the catalyst weight loaded into the vessel, including the catalyst's lot numbers. Additionally the bed height, the catalyst volume and the loaded density of the charged catalyst should be reported. The time needed for loading the catalyst should also be reported to allow better planning for future catalyst change-outs. The same data should be reported for the inert balls.

After filling, the reactor has to be tightly sealed until it is put in service. It is recommended to keep the reactor under a slight nitrogen pressure, e.g. 0.5 bar (7 psi) above atmosphere.

2) Catalyst Activation / Start-up

In order to give the catalysts its full activity and selectivity, a reduction of the catalyst is required before the first start up and after each regeneration in case a regeneration would be done.

By reducing the catalyst, the noble metal oxide, which is present on the freshly delivered and the regenerated catalyst, will be transformed to the respective noble metal:



The reduction is done by exposing the catalyst to hydrogen at temperatures of about 120°C / 250 °F. The hydrogen is typically diluted into an inert gas stream like nitrogen.

Due to the low content of Pd on the respective R0-20, the amount of water formed is small and is typically limited to the initial part of the reduction

Activation Procedure

After filling in the catalyst, the reactor must be blanked off from the air (oxygen) by nitrogen. The reactor should be heated up with an inert gas (like nitrogen) to 120°C / 250°F with a temperature rise of max. 50 °C / 90°F per hour.

As soon as the temperature at the outlet of the reactor reaches 120°C / 250°F, H₂ is added slowly to the inert gas stream. The observed temperature increase is marginal to only a few degrees centigrade (maximum temperature 130°C / 265°F).

After 10 - 12 hours the reduction is complete. The hydrogen addition is stopped and the reactor is cooled down with the inert gas stream to the normal operating temperature or ambient temperature depending on the next steps foreseen.

Until the reactor is required for service, it should be kept under an inert gas atmosphere of about 2 bar (30 psi).

A summary table of special operations can be found at the end of this document.

Start-Up

Start-up can be done in different ways. 1 method to start up the vessel loaded with PuriStar R0-20 is described in the following. This procedure refers to an operation with gas.

Technical Guideline

As start-up involves bringing the reduced (and thus active) catalyst in contact with a reactive feed, the following points must be observed:

- The catalyst should be brought first in contact with the reactive feed, before the reactor is heated up to the normal reaction conditions.
- An accumulation of components, which have not yet reacted, must be avoided. This can be the case, if recycle streams are used for diluting the feed stream.
- Conditions where there is no flow or only a very small flow through the catalyst bed must be avoided. Indeed as all these reactors are typically operated in adiabatic mode, the most important way to remove the heat generated during the reaction is the gas flow through the bed.

Thus a start-up procedure could look as follows:

- The bed is assumed to be under nitrogen before start-up.
- The vessel is pressurized with nitrogen to the respective operating pressure if feasible.
- A nitrogen flow is established through the bed.
- Once the nitrogen flow has been established and all temperature indications are showing similar values, the normal feed stream is mixed to the nitrogen flow.
- Depending on the design of the bed, a temperature increase can already be observed at this time. After the temperature increase has stabilized, the flow of feed gas will be increased, while the nitrogen flow will be reduced. This can be done by starting with around 25% of the normal feed flow rate and ramping up in steps of 25%.
- Once the full feed flow has been established, the temperature can be adjusted to the start-of-run temperature or to the last temperature used before in case this is a re-start after a stop of the operation.
- Once the required temperature has been achieved, it will be checked on whether the product coming from the reactor is in-spec. If the spec is not achieved, it might be necessary to increase the inlet temperature.

- If this off-spec situation continues, it is required first to check on analytics and then on the composition of the feed gas stream. The case being, the hydrogen to acetylene ratio needs to be adjusted.
- In case the specification is achieved, the inlet temperature might be reduced, as far as feasible, until the specification is just achieved.

Catalyst Shut-Down

When shutting down the unit, the aim is to achieve an overall safe state. This is achieved by first cutting the hydrogen, then the feed. The following steps are recommended:

- Bring the present feed rate (and hydrogen) down to 1/3 of the design value in 2 or 3 steps.
- Reroute the product to battery limits.
- Stop the hydrogen and block it in
- After 10 -20 minutes, stop the feed

At this time, the system can be expected to be in a safe state. In case any temperature increase is observed over the catalyst bed, it is necessary to continue gas flow (the case being by recycling) over this bed without hydrogen addition, until the temperature increase has died down.

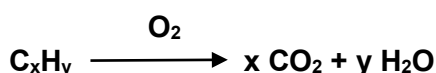
In case the system has to be opened, it is required to depressurize the vessel to battery limits and exchange the atmosphere to a safe atmosphere.

3) Regeneration

For the typical applications in which R0-20 is used, R0-20 exhibits high robustness and a long life time. During the total life time or during exceptional conditions (like when higher amounts of multiple unsaturated components come in contact with the catalyst), the R0-20 may experience more or less slow deactivation through deposition of coke on the active sites of the catalyst and by blocking part of the pore structure of the catalyst.

In cases, it is worthwhile to try to extend the life of the catalyst, a regeneration step to recover the original level of activity can be adopted. The

regeneration is done once the end of run (EOR) conditions have been achieved. Through regeneration the coke (which is a composite of different hydrocarbons) will be burnt off with air, forming carbon dioxide and water according to the following general equation:



The regeneration is carried out at temperatures between 400 to 450 °C / 750°F to 840°F. In order to control the temperature of the catalyst bed, the regeneration is carried out with a inert gas/air mixture. The inert gas is typically nitrogen. The use of steam is also possible as long as steam is only used at temperatures beyond 150°C / 300°F to avoid any condensation of water in the pore system of the catalyst.

The regeneration consists in general of the following steps, described in detail for the regeneration with nitrogen. The respective flow rates can be found in the table at the end of the document:

- Prior to regeneration, the process stream is blocked out and the reactor is separated from the rest of the plant. After blocking in, the reactor is slowly depressurized.
- “Heating”**: The reactor is heated to 150 °C / 300°F with nitrogen at a maximum rate of 40 °C / 70°F per hour.
- “Stripping”**: The flow rate of the nitrogen is then increased stepwise up to the maximum flow rate indicated and the reactor heated up to 250°C / 480°F at a maximum rate of 30°C / 50°F per hour. During this step any hydrocarbon, which can be vaporized, will be removed with the hot gas. By doing this the total amount of heat generated during the oxidation steps can be reduced.
- “Pre-oxidation”**: When the temperature has reached 250°C / 480°F, the injection of the minimum air rate is started. The temperature is kept at this level for 1 to 2 hours (depending on whether the passing of a temperature wave in the respective reactor is observed or not).

- “Heating”**: In this step the temperature is increased to 400°C / 750°F at a maximum rate of 30°C (50°F) per hour. In case a temperature increase (typically in form of a wave moving through the bed) is observed during this temperature increase, the temperature increase will be stopped until the temperature indicators have levelled down again.
- “Burning”**: Once the temperature of 400°C / 750°F has been reached and no further temperature wave is observed in the reactor, the air rate will be increased stepwise up to the maximum flow rate, without exceeding however 450 °C / 840°F in the reactor.
- “Finish Burning”**: Once no temperature rise is observed any more, the inlet temperature is increased to 430°C / 800 °F (if possible) in order to promote complete removal of carbon. Addition of air is continued until less than 500 ppm by volume of CO₂ is analyzed at the reactor outlet. The analysis for CO₂ can be done with an analyzer installed dedicatedly in the off-gas line or by taking gas samples and analyzing in the lab or with the help of length-of-stain testing tubes. The temperature shouldn't exceeding 450°C (840°F) in the reactor.
- “Cooling”**: The air is then switched off and the reactor slowly cooled down with nitrogen until the required temperature for the reduction (120 °C, 250°F) has been reached. At this point the reduction is carried out as indicated under the previous point.

A summary table of special operations can be found at the end of this document.

4) Unloading of the Catalyst

Catalyst, which needs to be unloaded, can contain hydrocarbons or other flammable components, which when brought into contact with air can start reacting and leading to a temperature increase and formation of smoke. Please note that the reduced Pd present on the catalyst will react with oxygen to form the respective oxide. However due to the small content present in the catalyst, this reaction will only lead to temperature increases of a few °C / °F.



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Technical Guideline

Thus before unloading of the catalyst, the bed is at least stripped with nitrogen at a temperature of 120°C. To further minimize any hazard during unloading, the nitrogen present in the vessel is slowly exchanged for air. In case any temperature increase would occur, the complete nitrogen blanketing is restored until all temperatures have died down. Only once no temperature increase can be detected after replacement by all nitrogen with air, can the vessel be opened. The catalyst can be discharged by using an industrial vacuum cleaner equipment and shipped safely to a metal reclaimer to recover the Palladium.

Nitrogen Procedure

- Catalyst Volume: 10 m³
- For converting the N₂ amounts indicated in Nm³/h to mass flows, please multiply the indicated values with 1,25 kg/Nm³ or 20.0 lb/cuft (once converted into cuft)
- For converting the indicated Nm³/h to scft / h please multiply with 35.8 scft / Nm³

Step	Gas components	Flow Rate	Temperature	Temperature Increase	Time at Temperature	Total Duration
		Nm ³ /h	°C	°C/hr	Hours	Days
Reduction						1
Heating	N ₂	1 000	Up to 120	Max. 50	-	
Reducing	N ₂ + H ₂	1 000 + 300	120 (max- 150)	-	10-12	
Cooling	N ₂	1 000	-	-	-	
Regeneration						2-3
Heating	N ₂	1 000	up to 150	max. 40	-	
Stripping	N ₂	1 300 – 4 000	up to 250	-	8 - 10	
Pre-Oxidation	Air + N ₂	40 + 4 000	250	-	1-2	
Heating	N ₂	40 + 4 000	up to 400	max. 30	-	
Burning	Air +N ₂	40 – 400 4 000	400-450	-	4 - 8	Air + N ₂
Cooling*	N ₂	4 000	down to 120	-	-	

* This step should normally be followed directly by the reduction of the catalyst, except when the catalyst is unloaded.

The pressure should be chosen so that the off-gases can be directed to battery limits (max. 5 bara / 70 psia)

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Americas

BASF Corporation
25 Middlesex/Essex Turnpike
Iselin, New Jersey, 08830, USA
Tel : +1-732-205-5000
Fax: +1-732-205-7725
Email: catalysts-america@basf.com

Asia Pacific

BASF (China) Company Limited
300 Jiang Xin Sha Road,
Pudong, Shanghai 200137
P.R. China
Tel: +86-21-2039 2549
Fax: +86-21-2039 4800-2549
Email: catalysts-asia@basf.com

Europe, Middle East, Africa

BASF De Meern BV Catalysts
The Netherlands
Tel: +31-30-666 9437
Email: catalysts-europe@basf.com

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