Feed Purification Catalysts

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The new generation of ammonia, methanol and hydrogen plants is designed for more severe conditions than old plants and the demand for catalyst activity has therefore increased. Since some elements in the hydrocarbon feed (in particular sulphur and chlorine) are serious poisons for the downstream catalysts it is crucial for optimal plant performance that the hydrocarbon feed is purified properly.

For decades, Topsøe's complete line of feed purification catalysts has proven very effective for economical removal of unwanted compounds in hydrocarbon feedstocks.

Purification Steps
The purification section may consist of the following steps:

- Hydrogenation
- Absorption
- Final Purification

Hydrogenation Step
The hydrocarbon feedstock may contain various compounds of sulphur and chlorine as well as olefins, which have to be removed to minimise problems in the downstream units.

Feed purification is commonly initiated by a hydrogenation step, where organic compounds are converted with hydrogen into inorganic hydrogen sulphide and hydrogen chloride over a hydrogenation catalyst. The hydrogenation step is necessary, as organic compounds are not as easily absorbed on downstream absorbents as inorganic compounds.

A problem, which may arise when processing various types of feedstocks, is a large variation in sulphur content in the feed. The hydrogenation catalyst, which normally is a cobalt or nickel molybdenum type, possesses the highest activity in the sulphided state. If the feed is essentially sulphur-free for longer periods, the sulphur on the catalyst will gradually be stripped off and the catalyst activity will decrease. When switching to a feed with high sulphur content, the catalyst activity may not be sufficient for converting all the organic sulphur. This problem can be solved by continually adding a small quantity of sulphur to the sulphur-free feed, ensuring that the catalyst is kept in its sulphided state, at all times.


If the feedstock contains olefins it may have to be treated in a special way. Hydrogenation of olefins is a strongly exothermic reaction. It is generally recommended to limit the operating temperature to 400°C/750°F in order to prevent possible carbon formation. If the olefin content in the feed is high, the temperature increase across the catalyst may result in a temperature higher than the allowed maximum. In such case, recycle of part of the hydrogenated gas can solve the problem.

Absorption Step

Downstream the hydrogenator all sulphur and chlorine compounds are now present as inorganic hydrogen sulphide and hydrogen chloride. The hydrogen sulphide is absorbed effectively and rapidly on zinc oxide, which today is the most widely used chemical absorbent.

If the feedstock contains chlorine, an additional chemical absorbent is installed.

Chlorine Absorption

Chlorine is a serious potential problem and may deactivate downstream catalysts and/or lead to corrosion in downstream equipment.

Chlorine compounds are mainly a problem in certain refinery off gases as well as natural gas spiked with landfill gas.

Topsøe has developed a superior chlorine absorbent with high absorption capacity at low as well as high temperatures. The absorbent should be installed upstream the zinc oxide to avoid formation of zinc chloride and normally downstream the hydrogenation catalyst, as only chlorine in form of hydrogen chloride is reacting with the absorbent.

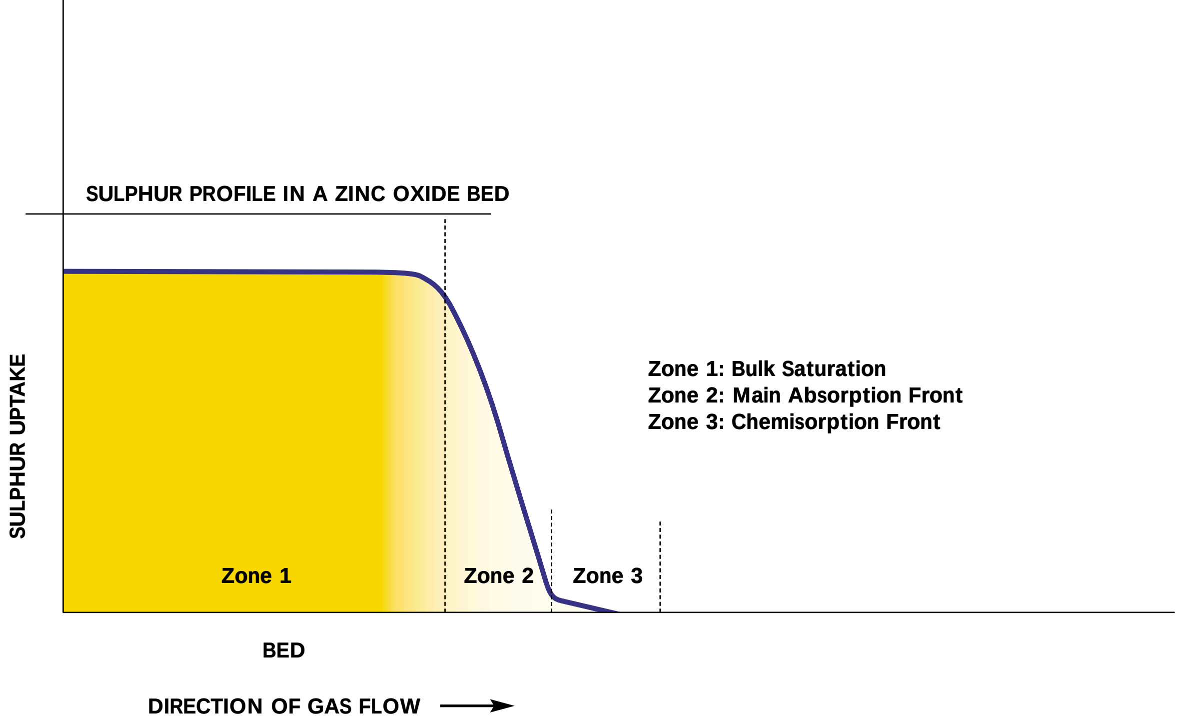
Sulphur Absorption

Zinc oxide reacts with hydrogen sulphide according to the following equation:

$$ZnO + H_2S \rightleftharpoons ZnS + H_2O$$

Based upon detailed analyses of catalysts downstream the sulphur absorption section, it is Topsøe's experience that a system of hydrogenation followed by zinc oxide absorbers can bring the sulphur concentration down to a level around 0.005 vol ppm. In order to achieve this, Topsøe has developed a series of zinc oxide absorbents, which provide a very high absorption capacity for all applications.

When a zinc oxide bed has been in operation for some time, the axial distribution of sulphur in the bed will ideally have a sulphur profile as illustrated in the graphic above.



Bulk Saturation

In top of *Zone 1*, the zinc oxide is bulk saturated and completely converted into zinc sulphide.

Solid State Diffusion

Below the saturated zinc oxide there is a layer which has not been completely saturated, and the rate of absorption will in this layer be determined by the rate of diffusion in the solid state from the surface into the interior of the material.

Gas Diffusion

Further down in the bed, the absorption rate is mainly determined by gas diffusion restriction in the pores *(Zone 2)*. The gas diffusion is a much faster process giving a sharper declining profile. This part of the bed is normally referred to as the “front”.

Chemisorption

Zinc oxide further has the ability to chemisorb hydrogen sulphide on the active surface area. Small quantities of hydrogen sulphide passing the front will consequently be removed by chemisorption *(Zone 3)*. In practice, this means that the hydrogen sulphide slip may be lower than the zinc oxide/hydrogen sulphide equilibrium. However, the chemisorption capacity is very low compared to the bulk absorption capacity of zinc oxide, so in most cases the slip of hydrogen sulphide below the equilibrium may be sustained only during a fraction of the entire lifetime of the zinc oxide charge.

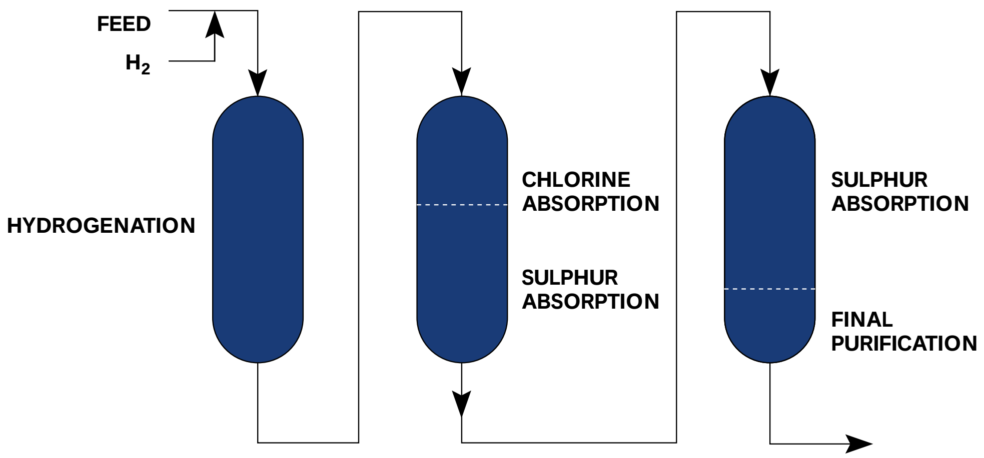
Proven by Performance

Final Purification

Some plants experience problems due to insufficient desulphurisation of the feedstock. Reasons for this may be a large variation in sulphur content in the feed, low operating temperature, high carbon dioxide or water content in the feed. In these cases the solution may be installing a special guard catalyst in the bottom of the zinc oxide reactor for final clean-up of sulphur.

For this purpose, Topsøe has developed a catalyst with a very efficient pick-up of all sulphur down to nil. The sulphur pick-up takes place by chemisorption, but at certain conditions, bulk absorption will take place as well.

SIMPLIFIED FLOW SCHEME OF A DESULPHURISATION SYSTEM



Topsøe R & D
Topsøe's worldwide services to the chemical, petrochemical and refining industries are based on a fundamental understanding of heterogeneous catalysis, including development and production of catalysts, process technologies and engineering services.

Quality catalysts
– proven by performance
Topsøe's unique integrated approach has resulted in profitable solutions providing catalysts in the areas of:

► **Feed Purification**
· Adiabatic Steam Reforming
· Steam Reforming
· CO Shift Conversion
· Methanation
· Ammonia Synthesis
· Methanol Synthesis
· Formaldehyde
· Sulphuric Acid
· Refinery Hydroprocessing
· DeNOx and DeSOx
· Combustion of VOC

Based on many years of experience, the development of Topsøe catalysts is dedicated to provide a second-to-none performance. This means that focus always is on key factors such as enhancement of high and stable activity, long operating life, high resistance to poisoning, low pressure drop, energy savings and reduced emissions.

Customised after sales service
Topsøe's after sales service relies upon an on-going exchange of information between the client and us, to provide clients with relevant and most up-to-date information. The four pillars in Topsøe's service programme are:
Frequent Contact and Discussions, On-site Supervision, Evaluation of Plant Performance and Troubleshooting.

Visit www.haldortopsoe.com for more information.

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