

JM

# Purification catalysts and absorbents



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# Introduction

**Feedstock purification is a key unit operation in any synthesis gas plant which employs steam reforming technology.** Its importance is often overlooked, however, and the consequences of not installing the correct catalysts and absorbents, or of not monitoring performance appropriately, can have dramatic and costly consequences for downstream catalysts. The key catalysts in synthesis gas plants that may be poisoned by trace components in the feed gas are pre-reforming, steam reforming, low temperature shift and methanol synthesis.

The most common catalyst poisons experienced are sulphur compounds present as hydrogen sulphide, COS, mercaptans, organic sulphides and disulphides, and thiophenes. Occasionally halogen compounds are present, usually as hydrogen chloride, but sometimes as organic chlorides. Some plants also experience feedstocks with more unusual poisons such as mercury, arsenic and other metallic species.

Very severe poisoning will lead to significant costs. For example, with severe sulphur poisoning incidents the affected steam reforming catalyst may need to be replaced. In addition to downtime, possibly measured in weeks, the catalyst cost must be added. The financial cost of such incidents varies depending on the size and type of the plant, however, for large scale plants (e.g. 100mmscfd (110,000 Nm<sup>3</sup>/h) hydrogen; 2,000mtpd (2205stpd) ammonia; 2,500mtpd (2756 stpd) methanol) each day of lost production costs in the order of US\$350,000 and typical catalyst replacement cost is in the order of US\$750,000. In comparison, the catalyst and absorbent cost in a typical purification system for plants of a similar scale is around US\$240,000. Thus, the provision and timely replacement of these materials is a comparatively small investment compared to the potential costs of poisoning the downstream catalysts.

In plants with a pre-reformer, sulphur removal is critical to successful operation of the catalyst. A serious sulphur incident usually means immediate catalyst replacement is required. In addition to downtime, the replacement catalyst cost will be significant, approaching that for a steam reformer charge depending on the pre-reformer bed volume.

Both sulphur and chlorides severely affect both low temperature shift (LTS) and methanol synthesis catalysts. These copper-based catalysts scavenge both sulphur and chlorides very effectively and are poisoned as a result. For a 2,000mtpd (2205stpd) ammonia plant, the cost in terms of lost LTS life can be of the order of US\$500,000 per year plus the incremental production loss as water gas shift efficiency decreases. The effect on methanol synthesis catalysts have similar financial consequences.

In comparison, the total cost of the catalysts and absorbents in the purification system is significantly less than the cost of the problems that can occur if the purification catalysts are not well maintained.

JM offers a range of purification products designed to give protection to downstream catalysts. Sold under our **KATALCO™** and **PURASPEC™** brands, the prolonged life of these catalysts and absorbents means that they offer exceptional payback compared to conventional products. They are also well proven, giving reliable operation over a range of operating conditions.

# Catalyst selector

**KATALCO** and **PURASPEC** purification catalysts are suitable for the full range of feeds to synthesis gas plants, whether an off gas, a natural gas, LPG or naphtha. Typical recommendations for our standard purification products are given below, however, JM will provide specific recommendations to suit particular plant conditions depending on the feedstock composition, poisons present and vessel configuration.

JM's experts have significant experience in difficult and unusual purification requirements and for these applications offer the **PURASPEC** product range for a wide range of trace impurity removal. These include HDS catalyst and ZnO absorbents for low temperature applications, as well as products to remove the less usual poisons such as mercury and arsenic compounds.

Feedstock impurity/ operating situation	KATALCO product recommendation
organic sulphur	41-6T or 61-1T
olefins saturation	61-1T, 61-2F, 61-2T
high CO <sub>x</sub> content	61-1T
low temperature HDS	61-2T, 61-2F
optional 3-in-1 design with ultrapurification	33-1
halide removal	59-series
low sulphur content (single bed)	32-4, 32-6, 33-1
moderate sulphur content (single bed)	32-4, 32-5, 32-6
high sulphur content (lead lag beds)	32-5, 32-6
sulphur spikes/ transients	32-6

Pre-sulphided HDS catalysts may be recommended in the following circumstances:









Very high sulphur feeds	fully active immediately
High olefins feeds	fully active immediately
High carbon oxide feeds	avoid methanation
Very low sulphur feeds	avoid possible over reduction
Very high hydrogen feeds	avoid possible over reduction

Pre-sulphiding can be achieved in situ by injection of a sulphiding agent with hydrogen at defined conditions. Alternatively, JM can deliver the catalyst in the pre-sulphided form.

**PURASPEC** products may be recommended for removal of the less usual poisons. The most frequently offered products are summarised.

Operating situation	PURASPEC product recommendation
mercury	1156, 6156
arsenic	1152, 5152
low temperature ZnO	2020
downstream pre-reformer	2084
long reformer catalysts cycle times	2084

# Catalyst characteristics

<p><b>KATALCO 41-6T</b></p>  <p>cobalt oxide/molybdenum oxide/alumina</p>	<p><b>KATALCO 32-4</b></p>  <p>zinc oxide</p>
<p><b>KATALCO 61-1T</b></p>  <p>nickel oxide/molybdenum oxide/alumina</p>	<p><b>KATALCO 32-5</b></p>  <p>zinc oxide</p>
<p><b>KATALCO 33-1</b></p>  <p>proprietary</p>	<p><b>KATALCO 32-6</b></p>  <p>proprietary</p>
<p><b>KATALCO 59-series</b></p>  <p>alkali/alumina</p>	<p><b>PURASPEC 2084</b></p>  <p>copper/zinc oxide/alumina</p>

## Physical properties (nominal)

Catalyst	Form	Diameter (mm)
KATALCO 41-6T	trilobe extrusions	2.5
KATALCO 61-1T	trilobe extrusions	2.5
KATALCO 33-1	spherical granules	2.8 - 4.75
KATALCO 59-series	spherical granules	2.0 - 4.75
KATALCO 32-4, KATALCO 32-5, KATALCO 32-6	spherical granules	2.0 - 4.75
PURASPEC 2084	spherical granules	2.8 - 4.75

# Advantages of choosing JM purification catalysts and absorbents

The purification section in a syngas plant is usually designed in two to four stages depending on the plant design requirements. In the hydrodesulphurisation (HDS) stage, the organic sulphur compounds are catalytically converted to liberate sulphur as hydrogen sulphide with analogous reaction of any organo-chlorine compounds. The HDS catalyst also acts as a trapping agent for many of the less usual poisons if these are present. Where necessary, an absorbent is installed next to remove hydrogen chloride by chemical reaction. The third stage is removal of hydrogen sulphide using absorbents based on zinc oxide, which reacts to form zinc sulphide. In certain plants, a fourth ultrapurification stage is used to reduce the sulphur content of the feed to extremely low levels.

## Operational benefits

All JM purification catalysts offer a number of operational benefits:

- **Flexible operating conditions**

**KATALCO** and **PURASPEC** catalysts and absorbents can be operated over a wide range of temperatures, pressures and feedstocks. For example, HDS catalysts and zinc oxide absorbents have operated continuously in systems designed to run at temperatures as low as 250°C (482°F) and pressure as high as 50bar (725psi). Our purification catalysts are proven to be effective on a wide range of feedstocks, from light natural gases, through LPG's, light naphthas to heavy naphthas containing 20% aromatics.

- **Long lives**

High activity and excellent absorption capacity mean that, with appropriate product selection, the purification catalysts lives will be maximised while extending the life of the downstream catalysts.

- **Reliable operation**

Dependable delivery of purified feed gas into the downstream process, even during upset conditions, ensures that the downstream catalysts are able to deliver high conversion and maintain long operating lives.

- **Stable pressure drop**

High strength of catalysts ensures that even if pressure drop starts to build up due to deposition of foulants on top of the bed, catalysts are strong enough to withstand the hydraulic forces applied.

## Organic sulphur removal - HDS

Effective breakdown of organic sulphur compounds in the feedstock is essential so that the H<sub>2</sub>S produced can be removed downstream. In addition, the catalyst breaks down any organo-chlorine compounds and hydrogenates olefins to a level acceptable for the steam reformer.

The **KATALCO** HDS catalysts are available in both cobalt molybdenum (CoMo), **KATALCO** 41-6T, and nickel molybdenum (NiMo), **KATALCO** 61-1T, formulations to suit the combination of reactions for particular plant situations. **KATALCO** 41-6T and **KATALCO** 61-1T are manufactured with an optimised loading of active components to give high volumetric activity and ensure high selectivity for hydrogenation. The high activity allows the catalyst to cope with increased feed rates, upsets and impurities which would otherwise lead to slippage of un-reacted organic sulphur compounds. The products also remove trace levels of arsenic compounds and, in the case of certain heavy naphtha feeds, traces of most metallic species.

The trilobe shape offers a lower pressure drop than standard extrudates. In addition, the strength and attrition resistance are improved to minimise breakage during loading and operation, so that a low pressure drop can be maintained throughout the catalyst life.

## Combined purification

Lighter feeds such as natural gas and some refinery off gases contain relatively low level of sulphur impurities and no chloride compounds. Conventionally, these feeds are purified using a two stage (HDS + H<sub>2</sub>S removal) or three stage (with ultrapurification) system. It is now possible to simplify the purification system by using a multi-functional product, **KATALCO 33-1**. This single product has HDS and H<sub>2</sub>S removal functionality and, where designed accordingly, also delivers ultrapurification performance. The multi-functionality of the product results from a bulk ZnO phase with controlled physical properties to maintain a high sulphur capacity and a sharp sulphur profile into which low level catalytically active components have been incorporated providing the HDS and ultrapurification activity. **KATALCO 33-1** is an extremely flexible product that can be deployed on its own or in combination with other purification products. It allows simplification of plant designs and removes some operating constraints which can impact conventional products.

## Chloride removal

Where chloride species are present in hydrocarbon feeds, the level is usually low. Occasionally the chlorides are present as organic compounds. After these species are converted to hydrogen chloride, they must be removed upstream of the zinc oxide absorbent. Zinc oxide reacts with chlorides to form zinc chloride and this adversely affects the porosity of the zinc oxide bed. This in turn impairs its sulphur absorption capacity and reduces the absorbent life. In addition, at normal operating temperatures, zinc chloride may migrate causing potential poisoning, corrosion and metallurgy issues downstream.

The low chloride level means that the volume of absorbent required is usually small as long as it has a good chloride capacity. Consequently, it is usually included in the same reactor(s) as the zinc oxide as a thin top layer. The low contact time necessitates a fast efficient reaction between the HCl and its absorbent to effectively remove chloride to extremely low levels needed for protection of downstream catalysts.

**KATALCO 59-series** is formulated to provide fast reaction times and to have a high capacity for chloride removal. It contains a highly reactive alkali phase. The gas phase reaction between HCl and the alkali locks up the chloride as sodium chloride. Where higher chloride levels are encountered, the high reactivity of **KATALCO 59-series** allows spikes of HCl to be removed effectively without compromising plant operation.

## Desulphurisation – zinc oxide

The performance of zinc oxide based H<sub>2</sub>S removal absorbents is strongly influenced by the formulation of the product. Usage of a very high purity zinc oxide (say 99+ wt%) of the highest possible density would place the most theoretical sulphur capacity in a reactor but would not provide the best performance in practice. This is due to the very low porosity and huge mass transfer zone of such a product, resulting in premature breakthrough of sulphur to downstream catalyst. Products must be formulated with the highest possible porosity to facilitate the reaction between the H<sub>2</sub>S and zinc oxide to maximise the rate and extent of sulphur absorption. In turn, this leads to a tight mass transfer zone and maximises sulphur absorption capacity and therefore the absorbent life for a given installed volume.

**KATALCO 32-series** absorbents combine specific zinc oxide phases with a binder using granulation technology to produce spheres with the required combination of properties to provide excellent sulphur absorption capacity in the differing designs for zinc oxide beds.

**KATALCO 32-4** is a high porosity material which has a particularly sharp sulphur profile. This ensures that conversion of the zinc oxide in the bed, and therefore sulphur pick up, is maximised before sulphur breakthrough occurs. **KATALCO 32-4** is the product of choice for plants which are designed with a single sulphur removal bed. **KATALCO 32-5** is a higher density material and provides maximum saturation pick-up. This makes it ideal material for two bed series lead/ lag system designs. The lag bed provides protection of the downstream process while the sulphur level exiting the lead bed is allowed to increase before replacement of the spent bed is required. This allows the higher saturation capacity of the **KATALCO 32-5** to be fully utilised.

## Promoted zinc oxide

**KATALCO 32-6** is a high density promoted zinc oxide. It provides maximum possible sulphur pick up whilst offering lower H<sub>2</sub>S slip than zinc oxide alone.

This premium product is designed to give the highest possible sulphur pick up in both lead-lag and single bed system designs.



## Ultrapurification

Ultrapurification or sulphur polishing absorbents are appropriate in some specific plant circumstances where the downstream catalysts are more susceptible to poisoning even by low sulphur levels. Analysis indicates that the total sulphur level exiting the zinc oxide absorbent is typically a few tens of ppb comprising of H<sub>2</sub>S, COS and traces of organo-sulphur species. The precise levels and mix vary as a function of the feedstock composition, operating conditions and effectiveness of the purification products installed. This low level of sulphur may still have a negative impact, for example, if the plant has a pre-reformer or a highly stressed top fired reformer since these are both particularly sensitive to sulphur poisoning. Thus, to maximise the life of these catalysts, JM recommends the use of an ultrapurification catalyst, **PURASPEC 2084**, as a final stage in the purification system. This reacts with and removes most of the trace sulphur compounds typically to levels below 10ppbv.

## PURASPEC for unusual purification requirements

In addition to our standard products, JM offers a number of **PURASPEC** catalysts and absorbents for difficult or unusual purification duties.

## Arsenic

Arsenic as arsine or organo-arsine can be found occasionally in natural gas and LPG cuts. Although the HDS catalyst will remove these, the arsenic compounds act as a poison. An alternative approach is to treat the hydrocarbon upstream using a dedicated arsenic guard bed. For gas phase, we recommend **PURASPEC 1152** whereas, for liquid phase LPG, it is **PURASPEC 5152**.

## Mercury

Mercury and organo-mercury compounds are being reported more frequently in various hydrocarbon sources in part due to improved analytical methods and in part due to increased processing of mercury containing sources. Mercury has been found in the ammonia synthesis section of certain plants implying that it passes through the entire flowsheet. Thus, if mercury is identified in the feed, upstream treatment should be considered. For gas phase, we recommend **PURASPEC 1156** whereas, for liquid phase naphtha, it is **PURASPEC 6156**. These products are able to remove mercury to low ppb levels.

## Low temperature operation

For various reasons, in certain flowsheets it is necessary to run the purification section cooler than usual. In these cases, special HDS catalyst and zinc oxide absorbents are preferred which are optimised for the lower temperature. Where the HDS reactor must operate at an inlet temperature below 300°C (572°F), we recommend **KATALCO 61-2F**. This has a higher active metal level to initiate the reaction at a cooler temperature. For H<sub>2</sub>S removal below 250°C (482°F), **PURASPEC 2020** is preferred to **KATALCO 32-series**.

# Additional capability with KATALCO Performance

## Trouble-shooting - sulphur analysis

It is often helpful to determine the type of poisons present in a feedstock to assist in designing the optimum purification system. JM can offer users of its products detailed sulphur analysis services through our state-of-the-art equipment for the characterisation of sulphur compounds. The equipment utilises a chromatograph with a chemiluminescence detector that allows for measurement and speciation of sulphur containing compounds at levels of between 10 and 20ppbv. In comparison, the sulphur slip from zinc oxide is typically 50ppbv and from ultrapurification is 10ppbv.



## Monitoring consumption of ZnO

Proper monitoring to ensure optimum utilisation of a zinc oxide charge is a challenging task. JM recommends supplementing sample analysis with the **TRACERCO MAXIMIZER™** zinc oxide bed scanning technique. This is a proven, highly effective method for determining zinc oxide usage and prediction of remnant bed life. It uses an external scanning device and so there is no need for a plant shutdown. Results are available almost instantly.



This measurement uses a radioactive neutron source and a neutron detector to measure neutron back-scattering and to detect density differentials in the material inside the vessel. As zinc sulphide is more dense than zinc oxide, there is greater neutron absorption through zinc sulphide than zinc oxide. This difference is measured and therefore accurately determines the position of the interface.

This service is available through the JM **TRACERCO** business.

### **Sulphur sampling system design**

Sulphur sampling and testing is a highly complex area. JM has a detailed knowledge of the process and mechanical design of the sampling system and also an extensive understanding of the analysis methodologies. Using this, JM can review sampling and testing systems to identify improvement opportunities. This will ensure that any sulphur that does slip from the desulphurisation will be detected before the impact on the downstream equipment and catalysts is significant.

### **Carbon prediction in feed pre-heat coil**

One problem that some operators have faced in the past has been a gradual build up in the pressure drop across the hydrodesulphurisation bed which is greater than expected. On inspection of the inlet distributor and catalyst bed, significant amounts of carbon were found to have been deposited. The root cause was that although the bulk gas temperature leaving the feed pre-heat coils is not high enough to cause hydrocarbon cracking, the internal metal skin temperature of the coil can be much hotter. In some cases, this temperature is sufficiently high that hydrocarbons, particularly longer chained species, will crack and the carbon is deposited on the catalyst bed.

JM can provide detailed modelling of the feed pre-heat coil to determine whether this will be an issue or not. Using the HYSYS flowsheet package available from our partner, Aspen Technology, a model can be constructed that defines the heat and mass balances around the pre-heat coil. From this heat and mass balance, a more detailed model of the coil itself is produced using the Aspen Fired Heater. This allows for determination of the internal skin temperature of the coil. Using JM's in-house carbon cracking models, it is possible to determine the cracking temperature of the feed and therefore whether there is a potential problem in the feed pre-heat coil.

Such modelling is useful in troubleshooting pressure drop problems over a hydrodesulphurization vessel and also in determining whether changes in operating conditions will change the temperature regime such that hydrocarbon cracking may be an issue.

# Case studies

## Case study - PURASPEC ultrapurification improves reformer catalyst life

A Western European HyCO plant has operated for a number of years with a two year turn-around cycle. Historically at each turn-around, the operator replaced the steam reforming catalyst in order to have confidence that the plant would operate reliably and efficiently enough in the next two year cycle. The steam reformer feedstock is a methane rich natural gas and the steam reforming conditions are relatively severe since this is a HyCO plant.

**PURASPEC 2084** was installed in the purification section to reduce the level of trace sulphur slipping to the steam reformer. Over the two year cycle following the installation of the **PURASPEC 2084**, the operator observed a much slower rate of activity decline in the steam reforming catalyst. The plant operating conditions for this cycle were the same as for previous cycles, and it was concluded that the improved performance was a result of the use of the ultrapurification absorbent. The operator therefore had the confidence that the installed steam reformer catalyst would last for a second two year operating cycle.

The benefit to the operator was the saving in terms of steam reformer catalyst purchase and replacement costs and an improved efficiency of operation during the initial two year operating cycle. This saved the plant US\$ 400,000 in catalyst replacement costs.

## Case study - Correct sampling for poisons eliminates plant operating problems

Sampling and testing for sulphur is not a simple task and there are many issues that have to be addressed. One plant suffered severe hot banding leading to regular steam outs and a loss of tube life. Sampling of the feedstock at the exit of the desulphurisation system detected no sulphur and this was therefore ruled out as the cause of the problem. A lengthy investigation was conducted to identify the root cause of the problem but no other potential causes of the hot banding were found.

The desulphurization system was then re-investigated. The first issue highlighted was that the sample lines were relatively long and the metal utilised for the sample lines would absorb sulphur. The sample lines were therefore redesigned, reducing the length significantly and using a metallurgy that would not absorb sulphur. The sample bombs were also replaced with a superior metallurgy. Subsequent analysis of the feed gas established that significant levels of sulphur were passing through the desulphurisation system to the steam reformer.

The installed catalysts and absorbents were then replaced with **KATALCO** products and the steam reformer was steamed a final time to remove the sulphur from the catalyst. As a result of this the tube appearance has now improved and the tube wall temperatures have returned to the normal value.

## Case study - KATALCO PERFORMANCE verifies plant modifications to deliver performance

Through **KATALCO PERFORMANCE JM** delivers a range of services that ensures improved performance of your plant. An example of how this has benefited one of our customers is outlined below.

As part of a project to eliminate an operational problem, the plant were proposing to change the outlet temperature from the feed pre-heat coil upstream of the hydrodesulphurisation bed. The plant operator was concerned that such a change could lead to operating problems within the coil and potentially lead to hydrocarbon cracking.

JM was requested to review the proposed modification in order to determine if there would be any problems. Our process engineers used Aspen Technology's FIHR simulation package to model the performance of the existing coil. The initial FIHR model used rationalised plant data in order to calibrate the model and ensure that it was accurate. The FIHR model was then used to predict the performance of the coil with the modifications included. The predicted internal metal skin temperatures were used in JM's in-house programs to determine if hydrocarbon cracking would occur.

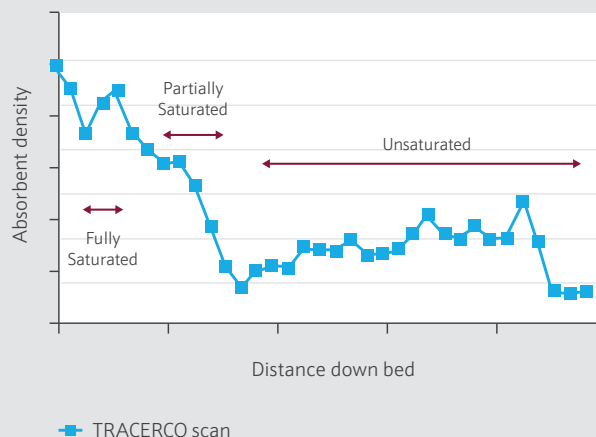
This showed that performance of the coil would be acceptable and that hydrocarbon cracking would not be an issue.

The plant has now been modified and, after a significant period of operation, has not seen any pressure drop increase over the hydrodesulphurisation bed, confirming that the model prediction of no carbon formation was correct.

## Case study - TRACERCO ZnO scan reduces turnaround costs

A Western European ammonia producer intended to replace its zinc oxide bed during a planned shutdown as it had been installed for some time. The operator however had no idea how much of the absorbent had been used. Prior to the shutdown, a **TRACERCO MAXIMIZER™** scan was performed on the zinc oxide vessel. The scan determined that the boundary between reacted and unreacted zinc oxide appeared to be approximately 40% down the bed, indicating that at least 50% of the bed was unreacted ZnO.

### Sulphur absorbent profile results of scanning zinc oxide vessel



Following the scan the vessel was discharged with samples of the absorbent taken at intervals down the bed depth. The samples were analysed in the bed and confirmed that from 50% onwards, the bed was unreacted ZnO. The operator only changed out 50% of the absorbent, which saved them US\$190,000 in turn-around costs.

# Understanding feedstock purification

Although active and selective, many catalysts used in modern syngas plants are susceptible to trace poisons that are present in the hydrocarbon feedstock. To maximise the catalyst life, effective feedstock purification is essential.

The two poisons usually encountered in syngas plant operations are sulphur compounds and, less commonly, chloride containing species. Sulphur is encountered as a combination of H<sub>2</sub>S and organo-sulphur species (such as mercaptans, sulphides, thiophenes etc.). Chloride, if present, can be encountered as hydrogen chloride or sometimes as organo-chlorides. In addition, any olefins should be removed as these can present problems with carbon formation in the steam reforming section.

Feedstock purification is usually achieved in a multi-step process employing a combination of catalysts and absorbents. The process begins with a catalytic hydrogenolysis step to convert organo-S and organo-Cl species into H<sub>2</sub>S and HCl respectively. Dedicated downstream absorbents remove the H<sub>2</sub>S and HCl produced.

Hydrogenolysis is the cleavage of C-S (or C-Cl) bonds by the action of hydrogen, known also as hydrodesulphurisation (HDS). It is carried out over a cobalt-molybdenum (CoMo) or nickel-molybdenum (NiMo) catalyst (e.g. **KATALCO** 41-6T or **KATALCO** 61-1T) operating preferably at 350-400°C and at a pressure of 25-40bara. Typical reactions are shown below [Equations 1-5]. Long service lives are common, sometimes in excess of ten years. The reaction requires hydrogen, typically 2 mol% with natural gas feedstocks and this is usually provided by a recycle of product syngas. The hydrogen concentration may need to be increased if there are also hydrogen consuming side reactions.



The reaction kinetics are first order for most poison species with a slightly positive order for hydrogen. The equilibrium constants are very large and positive, which

allows full conversion to be achieved (> 99.99%), and the reaction is relatively exothermic. For example, the  $\Delta H_{298}$  for EtSH (ethyl mercaptan) is -70.2kJ/mol and of thiophene is -280.3kJ/mol. For organic sulphides and disulphides, the  $\Delta H$  lies between these values. In reality, however, the hydrocarbon feed very rarely contains as much as 100ppmv organic sulphur and usually much less so the temperature rise is very small and is not detected.

HDS catalysts are most active when the CoMo or NiMo phases are sulphided. In most syngas plants, the catalyst is installed in the oxide form and the catalyst reaches an adequate degree of sulphidation by reaction with the sulphur compounds in the feed gas. Discharged samples generally contain from 1-4wt% sulphur depending on the level of sulphur in the feed. Plants using a typical natural gas feed with low ppmv sulphur levels are at the lower end of this range. Full conversion of the CoMo or NiMo HDS catalyst in a typical syngas plant would result in sulphur levels in discharged catalyst to be close to 7 wt% sulphur. Thus, in syngas plants a partly sulphided catalyst with the active metals in the form of a mixed oxysulphide provides sufficient activity.

Side reactions occur over HDS catalysts in normal operation which must be factored into its operation. These are reverse water gas shift and carbonyl sulphide (COS) formation/hydrolysis with CO<sub>2</sub> containing feeds, olefin and oxygen hydrogenation where these are present in the feed and a low background level of carbon formation due to cracking reactions. [Equations 6 - 9]



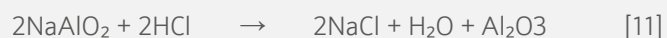
The reverse water gas shift, COS formation/hydrolysis and also COS hydrogenation reactions [Equation 10] reach equilibrium over HDS converters and can lead to increased COS at the bed exit especially if the feed contains either higher levels of CO<sub>2</sub> and total sulphur. Although there is almost full conversion of most organic sulphur species,

COS can be a problem. Additional control measures may therefore be needed to protect downstream catalysts from COS. These measures include injection of a small amount of steam (usually <<1 mol%) to move the equilibrium position, possibly combined with specialised downstream COS removal products.

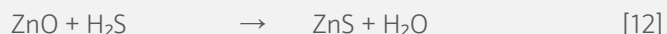
Although olefins or oxygen are unusual in natural gas, the hydrogenation reactions are strongly exothermic. To accommodate the associated temperature rise and remain within operating temperature limits, it may be necessary to install a recycle around the HDS converter to dilute the inlet olefin level with the hydrogenated effluent or use a lower inlet temperature with a more active HDS catalyst.

Undesirable side reactions such as methanation, hydrocracking and carbon formation can occur but these are very rare and generally associated with less usual feeds (high CO<sub>x</sub> and H<sub>2</sub>; LPG/naphtha feeds with high H<sub>2</sub>; heavier feeds respectively) and operation at transient or abnormal operating conditions (e.g. low flow; very low S; excess temperature). Where methanation or hydrocracking is a concern, pre-sulphiding the HDS catalyst decreases the likelihood of side reaction.

If chlorides are present, the next step in the purification process is HCl removal. This is typically carried out using an alkali promoted alumina-based absorbent. An example is **KATALCO** 59-3 which uses sodium hydroxycarbonate phases to react with HCl. [Equation 11] The sodium chloride formed by the reaction is locked into the structure of the absorbent. For a high chloride capacity, the absorbent must combine an optimised porosity, density and alkali level. The reaction between HCl and alkali is kinetically and thermodynamically favoured. This ensures removal to very low levels (< 5 ppbv) even with shallow absorbent beds operating at high space velocity.



Following chloride removal, H<sub>2</sub>S is removed by reaction with a zinc oxide (ZnO) based absorbent. [Equation 12]



The performance of a ZnO based absorbent in this duty is normally a balance between porosity and surface area versus the corresponding density. A higher density absorbent such as **KATALCO** 32-5 or 32-6 provides higher theoretical capacity in terms of sulphur removal per unit volume (e.g. kg S/m<sup>3</sup>) as there is more ZnO in the converter but the associated lower porosity leads to reduced rates of H<sub>2</sub>S removal and a broad reaction zone within the bed. In contrast, lower density, higher porosity products offer improved kinetics, generating a narrow reaction front at the expense of ultimate capacity.

Thus, to maximise utilisation of the available capacity, product design must keep the porosity as high as possible for a given density. This is important as the sulphiding process results in a lattice expansion because the molar volume of ZnS is greater than ZnO. Therefore, the porosity of the fresh material must be sufficient to allow for this expansion of the solid phase without causing excessive pore blocking. It is this process which dictates that the achieved sulphur pick up is less than the theoretical (i.e. complete conversion of all ZnO). Also, products without sufficient porosity suffer from poor conversion of ZnO and utilisation of the available S capacity due to this pore blocking mechanism.

JM's approach to maintain maximum porosity for a given density uses a binder in conjunction with the ZnO phases and forms the products using granulation technology. The characteristics and capabilities ZnO based product range is summarised in Table 1. Other suppliers take different approaches, some using much higher zinc oxide levels without binder and most others preferring extrusion to granulation; this will affect final product performance.

Product	PURASPEC 2020	KATALCO 32-4	KATALCO 32-5	KATALCO 32-6
Size	2.8 – 4.75	2.8 – 4.75	2.8 – 4.75	2.8 – 4.75
Typical loaded density (kg/l)	0.84	1.14	1.35	1.53
Zinc oxide (wt%)	> 87	93	92	proprietary
Relative S pick up (kg S/m <sup>3</sup> )	1	1.36	1.61	1.93

Table 1: **KATALCO** and **PURASPEC** sulphur absorbent characteristics

The reaction between ZnO and H<sub>2</sub>S generates H<sub>2</sub>O. Thus, high levels of water in the feed can impact the equilibrium position of the reaction resulting in increased levels of H<sub>2</sub>S slip. For feedstocks containing significant levels of CO<sub>2</sub>, reverse water gas shift over the HDS catalyst is usually the largest source of H<sub>2</sub>O in the feed to the ZnO beds. Equilibrium constants for the ZnS hydrolysis reaction, along with some indicative potential H<sub>2</sub>S slip levels, over a range of conditions are provided in Table 2. This shows that a substantial amount of H<sub>2</sub>O is needed to substantially impact on the H<sub>2</sub>S slip.

Temp. (°C)	K <sub>eq</sub> <sup>a</sup>	Water level (vol%)			
		0.17	0.33	1.70	3.30
250	3.27 x 10 <sup>7</sup>	0.05	0.1	0.5	1.0
300	6.99 x 10 <sup>6</sup>	0.3	0.5	2.4	4.7
370	1.21 x 10 <sup>6</sup>	1.4	2.7	14	27
400	6.37 x 10 <sup>5</sup>	2.7	5.2	27	52

Table 2: Impact of water on H<sub>2</sub>S (ppbv) levels in equilibrium with ZnO/ZnS<sup>a</sup> based on sphalerite

Most syngas plants operate split bed systems with combinations of dedicated HDS catalysts and ZnO based H<sub>2</sub>S absorbents. However, products are available which combine both functions in a single material, for example **KATALCO 33-1**. This has been designed to offer optimised HDS activity in combination with high saturation sulphur capacity and a narrow H<sub>2</sub>S absorption front.

In addition to ease of loading and CAPEX/OPEX advantages, **KATALCO 33-1** also provides additional benefits over a traditional two-stage sulphur removal process. An example is enhanced protection against COS slip. This is because the H<sub>2</sub>S formed by reaction over the HDS function of **KATALCO 33-1** is immediately captured by the H<sub>2</sub>S absorption function of the product. This prevents subsequent reaction of H<sub>2</sub>S with CO<sub>2</sub> so that COS is not generated.

A well run purification system operating with a combination of dedicated HDS catalyst (CoMo or NiMo) with ZnO-based H<sub>2</sub>S absorbents typically lowers sulphur levels in the feed to somewhere in the region of 10-50ppbv. This provides an adequate level of protection for downstream catalysts in many applications. However, in cases where the flowsheet contains a particularly sensitive catalyst such as a pre-reformer, further protection is usually required.

Products such as **PURASPEC 2084** are used for this sulphur polishing or ultrapurification duty to lower the sulphur level below 10ppbv. This is sufficient to provide adequate life for the most sensitive of downstream catalysts. The ultrapurification product is usually utilised as a relatively thin layer installed at the bottom of the H<sub>2</sub>S removal bed.

**PURASPEC 2084** captures any H<sub>2</sub>S/COS/organo-S slip from the upstream beds via a surface adsorption (chemisorption) mechanism on the active sites. **PURASPEC 2084** will also provide added protection for feeds containing high water levels. The species produced are much less readily hydrolysed to H<sub>2</sub>S than is the case for ZnS (see Table 2).

An alternative approach to provide ultrapurification levels of protection is possible in flowsheets using **KATALCO 33-1**. In addition to providing both HDS and H<sub>2</sub>S removal functions in a single product, **KATALCO 33-1** can be designed to additionally provide ultrapurification by extending the contact time in the bed. A particular advantage of using **KATALCO 33-1** in this way is that it does not require reduction in-situ prior to being brought on line.



Feedstock purification is a vital part of the syngas plant in that it protects the downstream investment made in the catalysts often regarded as the core parts of the process; in particular the steam reforming and water gas shift sections. The HDS catalyst must deal with numerous side reactions. The downstream products which remove  $H_2S$  and  $HCl$  are much more than "just absorbents". The  $H_2S$  removal products are often simply referred to as zinc oxide but the products require careful design and a range of products to deliver the best effects. Ultrapurification is available to deliver even better protection and multi-function products are available to simplify the purification part of the process.





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