

JM ProcessWise Webinar

Purification of feedstocks for ammonia, hydrogen and methanol production

January 2021

Questions and Answers

Please note that a number of similar and repeated questions have been combined.

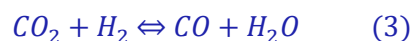
Q1. What are the advantages of using CoMo or NiMo HDS catalysts?

A1. CoMo and NiMo show the same level of performance for the HDS reactions, so from that criteria neither is better. Where they differ in the response to high levels of carbon oxides in the feed - NiMo has a lower tendency to promote methanation reactions in these regimes than CoMo, so it would be recommended for plants with high levels of CO₂ in the feed or recycle, as well as feeds containing high levels of olefins.

The conditions leading to methanation are most likely to occur during a plant upset, such as the loss of feedstock but continual operation of the purge stream, means only H₂/CO_x present and low flow giving long contact time. Many new methanol plants will have trip system configured to avoid this from occurring.

Q2. Can you comment on the activity of the CoMo catalyst to catalyse the COS reaction from CO₂ and H₂S?

A2. The formation of COS across the HDS catalyst is influenced by the presence of CO₂ and CO in the feed, due to the interlinked reactions of COS hydrogenation (1), COS formation (2) and reverse water gas shift (3).



These reactions typically reach equilibrium over both HDS catalysts, with the exit COS levels determined by the equilibrium position at the HDS exit conditions. Net COS formation can occur in feeds with high levels of CO₂ and can be compounded by high sulfur levels.

High levels of COS slip can be reduced by injected superheated steam upstream of the HDS reactor or by increasing the H₂ concentration in the feed.

If appropriate for the feed composition, it may be an advantage to use a multifunctional product, such as **KATALCO** 33-1 with both HDS activity and H₂S

absorption capability, as this helps manage COS removal and maximising the overall level of sulphur removal.

Q3. What is the typical maximum level of CO₂ to avoid difficulties in the pre-treatment section?

A3. High levels of CO₂ can cause methanation to occur over the HDS catalyst. In operating conditions where this is likely to occur, Johnson Matthey would recommend the use of **KATALCO** 61-T (NiMo based catalyst) as this product does not promote methanation when sulfided. Other feed conditions that can result in the recommendation of a NiMo catalyst are high CO levels, and moderate CO_x levels in the presence of high H₂ levels. For further information, it is recommended to contact JM with further details on plant operating conditions.

Q4. In case feed is having low content sulfur (<1 ppmv); what is the maximum allowed hydrogen concentration (in mol%) in feed for the HDS section?

A4. The maximum H₂ levels are dependent on catalyst type (e.g. standard HDS catalyst or **KATALCO** 33-1), the feed composition and the sulfur content. As an example, if you are operating a standard HDS catalyst with a natural gas feed, recommended H₂ levels are typically between 2-5%, with the actual figure depending on your specific operating conditions.

Q5. In case of absence of hydrogen during plant start-up, what is the effect of sulfur in LTS catalyst, and what is the solution?

A5. The maximum time recommended time without H₂ in the feed is dependent on the sulfur level in the feed and the type of feedstock being used. Assuming these guidelines are followed, the effect of sulfur poisoning on the LTS will be minimal. During H₂ free operation, the ZnO bed will offer some protection, as it can catalyse the breakdown reactions of simple organic sulfides absorbing the H₂S formed. However, this mode of operation is more likely to result in carbon laydown on the ZnO catalyst and is why H₂ free operation should be minimised.

There will be some poisoning of the LTS bed during this period but this will be minimal and only affect the top portion of the LTS catalyst bed. Operating without H₂ for an extended period of time will damage both the ZnO purification section, and result in higher levels of poisoning of the LTS and reforming section.

For recommendations tailored to your plant conditions, please contact JM for further information.

Q6. Is it normal to have an HDS section even if the natural gas feedstock only has low H₂S levels?

A6. An HDS catalyst may not be required if the feed contains on H₂S and no organic sulfur or chloride is present, although it is often difficult to accurately

estimate the sulfur content within the feed. The sulfur content in feedstocks can vary significantly over time, and as a result operating without an HDS significantly increases the risk of sulfur poisoning downstream catalysts. In these situations, combined purification product **KATALCO** 33-1 may be the preferred option, as this combines HDS activity with sulfur removal.

Q7. Can the ZnO bed be regenerated?

A7. The reaction by which the H₂S is removed is the conversion of ZnO to ZnS. Once the available ZnO is consumed, the absorbent must be renewed. Regeneration may be theoretically possible by heating in air at very high temperature, however, this process would collapse the structure such that the resultant ZnO rich material would not have the required physical properties to deliver a high H₂S pick up. Regeneration of the bed is therefore not practical, and the ZnO material should be replaced once it has reached end of life.

Q8. What is the minimum possibly allowed temperature for ZnO catalyst (desulfurization bed) for smooth operation?

A8. The standard ZnO products, **KATALCO** 32-4, 32-5 and 32-6, typically operating in the temperature range 350 – 400°C, although operation down to 300°C is possible for these products.

ZnO with a very well developed pore structure can offer higher activity, with JM having ZnO's that can operate down to 250°C without a significant impact on operation, however sulfur capacity and pick up are reduced at lower temperatures.

Q9. What impact with using an ultra-purification section have on the lifetime of the pre-reformer, reformer and LTS catalyst?

A9. Using an ultra-purification catalyst, or combined purification product **KATALCO** 33-1, will reduce sulfur slip beyond that of traditional ZnO beds to levels at or below 10 ppbv. As a result, lower levels of sulfur will pass downstream to poison the reforming and LTS catalysts. This will result in an extension of the operating life of these catalysts; the exact lifetime extension will vary depending on operating conditions and current levels of sulfur slip.

Q10. What is the maximum typical sulfur removal capacity by ultra-purification products?

A10. The maximum sulfur pick up for ultra-purification is a function of space velocity over the catalyst and is significantly lower than the pick-up within the bulk ZnO bed upstream, which can exceed 500 kg S/m³ fresh absorbent. For ultra-purification products, the maximum pick-up can be over 80% lower. However, there are no recorded incidents of the purification system being changed out due to the

UP product reaching maximum capacity, typically the HDS or ZnO bed will limit the lifespan of the purification section.

Q11. What is the procedure for reducing PURASPEC 2084?

A11. For full guidance on in-situ reduction of PURASPEC 2084 or any JM product it is recommended to contact JM with further details on plant operating conditions.

Q12. How can ultra-purification be used in a lead-lag system?

A12. JM's recommendation for operating with a lead-lag system is to install a layer of ultra-purification product in both vessels containing the H₂S absorbent, to allow the beds to provide continuous protection while one of the spent bed is renewed at any given time.

Alternatively, a separate dedicated ultra-purification vessel, downstream the lead/lag absorbent vessels can be considered.

Q13. Can ultra-purification products work at lower temperature (e.g. 250°C)?

A13. Typical operating temperature for ultra-purification catalyst is the same as standard purification system (typically 300-400°C). The ultra-purification catalyst can be operated at 250°C in specific applications, only when the rest of the purification system has been designed appropriately for low temperature operation.

Q14. What are the potential causes of high pressure drop across the bed?

A14. Sudden increase in pressure drop is not expected in normal operating conditions, and is likely caused by one or more of the following situations:

- External fouling of the catalyst - this has occasionally happened if there have been problems with the feed supply, perhaps due to pipe scale or other debris reaching the top of the purification bed or hydrocarbon cracking in the feed pre-heat coil/naphtha vaporiser forming carbon which is carried forward. In these cases, it is the first bed in the purification system which is affected.
- Carbon formation - if the purification system has operated at an excessive temperature, thermal cracking of the hydrocarbon feed may cause sufficient carbon formation and deposition to give a pressure drop increase. Also, carbon build up can occur at normal operating temperature in plants using heavier feeds (e.g. naphtha) and feeds containing olefins (e.g. some refinery off gases, LPGs and naphthas).
- Inadequate protection system - it is normally recommend to use inert hold-down material such as ceramic balls, which are larger and heavier than the particles of purification catalysts/absorbents, to prevent the possibility that high gas velocities in the reactor headspace disturb the smaller purification

materials. If the hold-down layer is omitted or the pieces are not heavy enough, it is possible that the catalyst/absorbent will be moved around resulting in attrition which generates smaller particles, dust and fines which compact in the top of the bed to give a pressure drop problem.

Q15. Under what operation conditions/sulfur levels would **KATALCO** 33-1 not be suitable?

A15. **KATALCO** 33-1 is suitable for feeds containing less than 30 ppm total sulfur, with further criteria on organic sulfur level and type. In addition to these criteria, the product is recommended only for use in natural gas and refinery off gas feeds that meet set criteria including a maximum gas molecular weight, olefin levels and H₂ level. If **KATALCO** 33-1 is of interest, please contact JM with further details of your feedstock to check if the product would be suitable for use in your plant.

Q16. Where in the process is mercury found if it is present in the feedstock but not removed?

A.16 If a dedicated mercury removal absorbent is not used, and mercury is present in the feedstock, the metal will pass downstream and can be very invasive following many paths in both vapour and liquid phases. Mercury will attack aluminium and copper alloys and contaminate any steels. In some instances, mercury, suspected to have entered the plant in the initial feedstock, has built up in cooler sections of the ammonia synthesis loop (e.g. ammonia separator) and has been found to have settled in downstream ammonia storage tanks.

Q17. What problems can be encountered if the operating temperature exceeds the recommended temperatures?

A17. Different problems are associated with high temperature operation across the purification system.

- Mercury removal: Maximum mercury removal occurs when operating between 0-95°C, with mercury removal rates lowering above this temperature.
- HDS: Operating above recommended temperatures can result in cracking reactions, leading to carbon deposition on the catalyst. This is more pronounced with LPG, propane and butane feedstocks, which are recommended to operate at a lower temperature than systems using NG feedstock.
- HCl removal: Operating at high temperatures, above those recommended, can result in sintering of the catalyst pellets, reducing pick-up capacity.
- H₂S removal and ultra-purification: Operating over the normally recommended operating temperature can lead to a reduction of absorbent surface area which will negatively impact performance.

Q18. Why is sulfur poisoning more of a problem for the LTS when the SMR catalyst is upstream?

A18. Due to higher temperatures in the steam-methane reformer, under normal operating conditions only low equilibrium levels of sulfur will deposit on the reforming catalyst. Most of the sulfur will slip through to the LTS, which is more prone due poisoning due to higher reactivity of sulfur with copper, and a favoured equilibrium position at lower operating temperatures. However, both can be poisoned by over 0.1 ppm sulfur so high sulfur slip will affect both.

Q19. Does sulfur poisoning affect the HTS catalyst?

A19. High temperature shift catalysts are copper promoted, and as such there is some impact on the HTS catalyst performance when it comes into contact with sulfur. However, the impact is relatively mild and mainly reduces the catalyst's resistance to over-reduction.

Q20. What are the best practises for monitoring sulfur breakthrough?

A20. Monitoring sulfur slip through the purification system can allow for estimates of residual bed life and to check that sulfur levels are below levels that will cause significant damage to downstream catalysts and equipment. Organic-sulfur slip exit the HDS and H_2S slip exit the ZnO bed should be monitored.

H_2S slip can be measured relatively well using gas detector tubes. For ZnO beds that sees very high level of sulfur and has less than 6 months design life, we recommend daily measurement of H_2S . For other beds, daily or weekly monitoring is recommended depending on the feed variability.

Organic sulfur compounds are more difficult to measure accurately using gas detector tubes. Some gas detector tube manufacturers claim that organic sulfur compounds can be measured. However, the presence of hydrogen sulfide confuses the results, so a comparison with a hydrogen sulfide analysis tube is required alongside.

Although gas detector tubes are practical in the field, accuracy can only be obtained by taking samples for gas chromatography measurement in the labs, especially for liquid feeds.

Q21. Are there any concerns over trace amounts of ammonia or nickel in the feedstock?

Organometallic compounds can be present in feedstocks, typically as a carbonyl, demetallization the process of removing traces of metal occurs across the HDS catalyst, the metal compounds breakdown and are hydrogenated to release the metal, which is absorbed onto the catalyst. Metals tend to accumulate at the top of the catalyst.

Both NiMo and CoMo catalysts are slightly deactivated by ammonia, which may be present in recycle gas from an ammonia plant. The deactivation is reversible and the catalyst quickly recovers, the general limit for safe operation is the presence of ammonia <500ppm.

Q22. What problems that can occur if there are halides in the incoming feed? What are the limits?

A22. The key halide that can cause poisoning downstream is chloride. Chlorides can be found in some natural gas feeds that have been stored in natural cavities, and can also be found in feedstocks sourced from fracking. Chloride is a severe poison to the LTS catalyst, and levels of 5ppb can cause deactivation of the catalyst. Other halides are unlikely to be present in the feed, however hydrogen fluoride can occasionally be found in some feeds. Both hydrogen halides can be removed using a dedicated chloride removal system, however in the case where only very low levels of chloride are present, the ZnO bed has capacity for chloride capture.

Q23. How can COS formation be prevented, or COS be removed, especially in feeds with high CO₂ levels? Has CS₂ ever been observed in the purification section?

A23. COS can be found in, and formed, in feeds with high CO₂ levels (see Q2 for further details). CS₂ formation is also possible in feeds with high levels of CO₂. Ultra-purification products are able to remove these organic sulfides that slip through the bulk removal ZnO bed, and these products should be considered for feeds where CS₂ and COS slip is a concern.

Q24. Are there any solutions for air flow purification (especially plants near seas/oceans) and steam purification?

A24. Purification of the air stream to ammonia plants has been considered over the years, since the air stream is a route by which low levels (ppb) of poisons such as S and Cl can be introduced. However, considering the possible benefits verses additional costs of CAPEX (purification beds) and OPEX (extra pressure drop and absorbent), such systems have not been adopted on the process air. Demineralization or reverse osmosis is common, for removal of ⁻Cl ions from Boiler Feed Water, however in plant cooling water systems often use ⁻Cl as a biocide, so leakage can introduce ⁻Cl.

Advances in LTS catalyst technology have helped with the higher active surface area a modern LTS catalysts can last longer, fulfilling acceptable CO shift performance and absorbing more S & Cl before a changeout is required, however Cl in particular remains a concern it is very mobile and can be washed into the bed if the bed becomes wetted

Here a new purification solution **PURASPEC** 2272 can help, this is low pressure drop shaped alkali-doped alumina used in place of the HTS support balls.

PURASPEC 2272 helps trap -Cl poison that may have come with the air or be in the steam. The bottom of the HTS location is the best site for an -Cl guard upstream of the LTS as here there is the largest dewpoint margin meaning risk of -Cl leaching is much lower compared to leaving Cl to be trapped in the LTS.