

JM

# Low temperature shift catalysts



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# Introduction

The low temperature shift (LTS) reaction is vital to the economic operation of today's ammonia plants, and features in many hydrogen plant flowsheets. It generates the last 5% of hydrogen and, through low CO slip, minimises the hydrogen consumed in the downstream methanation stage. In ammonia plants this minimises the synthesis loop purge, which is twice as important in plants without purge gas hydrogen recovery units.

The most important factors to consider when selecting a low temperature shift catalyst will vary from plant to plant, and depend on a variety of factors including the plant design, age and operating conditions. Some operators will be concerned about efficiency and reliability whilst others will be looking to increase throughput or have strict environmental criteria that must be met.

Johnson Matthey (JM) offers a world-leading family of low temperature shift catalysts, the **KATALCO™** 83-series. **KATALCO** 83-series catalysts offer outstanding catalyst lives, resistance to plant upsets and low methanol by-product formation. These are delivered through world-leading poisons resistance and activity, and low methanol by-product options, which features extend catalyst life or enable short loads to fit planned turnaround cycles, maximise hydrogen production and address environmental concerns. The result is that **KATALCO** 83-series catalysts are the number one catalyst of choice in more than 175 of the world's ammonia and hydrogen plants.

JM also offers a range of other services and diagnostic skills aimed at ensuring that our customers get the best possible performance from their assets. Examples of this include:

- **KATALCO PERFORMANCE STREAMLINE system**  
Used in conjunction with **KATALCO** 83-series catalysts this system can significantly reduce the pressure drop through the low temperature shift converter.
- **Radial reactive technology**  
Pressure drop savings of up to 50% can be achieved by installing Johnson Matthey's radial reactor technology and **KATALCO** catalysts.
- **Advanced reactor thermometry**  
Together with Daily Thermetrics, we offer catalyst users the most advanced temperature tracking technology currently available.



# KATALCO catalyst selector

JM manufactures a range of catalysts for use in low temperature shift converters, allowing you the optimal choice for loading low temperature shift and guard reactors, where present.

## **KATALCO 83-3**

This is a proven high activity low temperature shift catalyst, which has demonstrated its ability to deliver long life, durability to upset conditions and excellent resistance to poisons. The self-guarding properties allow the effective capture of both sulphur and chloride such that the installation of a dedicated layer of guard catalyst is not required.

## **KATALCO 83-3M**

This is a smaller size variant that offers superior activity and poisons retention where a small increase in pressure drop can be tolerated. This increase can be partially compensated for since a smaller catalyst inventory is usually needed for a given expected life.

## **KATALCO 83-3X**

This catalyst contains an optimised combination of alkali metal promoters to suppress methanol formation. Methanol levels are reduced by more than 90% compared to **KATALCO 83-3**, making it the lowest by-product make of a low temperature shift catalyst.

The promoters also boost poisons pick-up, resulting in the highest poison capacity and greatest protection of any commercially available low temperature shift catalyst.

## **KATALCO 83-3MX**


This smaller size catalyst offers the same relative benefits of **KATALCO 83-3X** compared to the non-promoted catalysts, as noted above. In particular, **KATALCO 83-3MX** has the best poison resistance in the **KATALCO 83-3** range. Where poison levels are higher than normal, installation of a layer of MX catalyst on top of the main bed or in a separate guard bed will extend catalyst life.

Johnson Matthey will make detailed recommendations on the optimal type and volume of catalyst based upon your individual operating conditions and requirements. The excellent performance of the **KATALCO 83-3** series often exceeds the original plant design basis and means a lower catalyst volume is required to achieve a target number of turnaround cycles.

# Catalyst characteristics


## KATALCO 83-series

**KATALCO 83-3**




low temperature shift catalyst

**KATALCO 83-3X**




low temperature shift catalyst

**KATALCO 83-3M**



low temperature shift catalyst

**KATALCO 83-3MX**



low temperature shift catalyst

### Composition

**KATALCO 83-3 & 83-3M:**

Copper oxide/zinc oxide/alumina

**KATALCO 83-3X & 83-3MX:**

As above, promoted by alkali metals

### Physical properties (typical)

Catalyst	83-3	83-3M	83-3X	83-3MX
Form	pellets	pellets	pellets	pellets
Diameter (mm)	5.2	3.1	5.2	3.1
Length (mm)	3.0	3.2	3.0	3.2
Typical loaded density (kg/m <sup>3</sup> / lb/ft <sup>3</sup> )	1360 / 85	1360 / 85	1360 / 85	1360 / 85

# Advantages of choosing KATALCO low temperature shift catalyst

The KATALCO 83-series of low temperature shift catalysts offers a reliable and sustainable option for this duty. Only one catalyst is required in the low temperature shift bed as the formulation provides self-guarding capability and maximises sulphur retention.

At the same time it demonstrates a high activity whilst maintaining high strength to ensure physical robustness. The product is also available in a range of sizes to allow optimisation of pressure drop and catalyst activity.

## Reliability

### Minimum CO slip

The position of the thermodynamic equilibrium for the water gas shift reaction favours maximum CO conversion at low temperature. The excellent activity of the KATALCO 83-series catalysts accelerates the rate of reaction such that in many plants, the water gas shift reaction achieves equilibrium when operated with an inlet at temperature as low as 190°C (375°F) and remains at or close to equilibrium when operated with an inlet throughout the catalyst life. Catalyst activity is high enough that in most situations, the minimum allowable operating temperature is determined by the dew point of the gas.

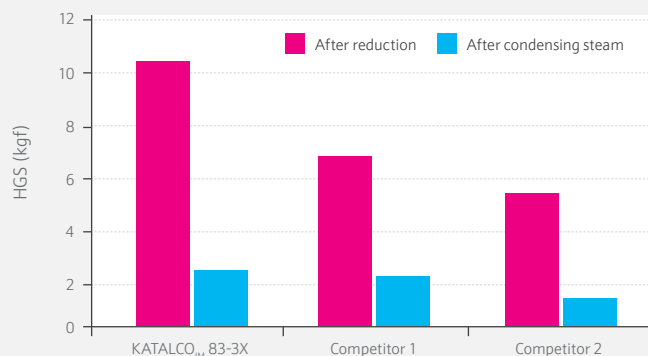
### Low, stable pressure drop

Catalyst strength in service is equally as important as fresh pellet strength. The KATALCO 3-series is formulated to give high strength following reduction as shown opposite. The enhanced robustness allows full advantage to be taken of the high activity by operating at the lowest possible temperature. The high strength minimises the rate of pressure drop rise over time on-line, which results from hydraulic effects as the catalyst weakens from thermal sintering, and helps resist breakage following condensation incidents.

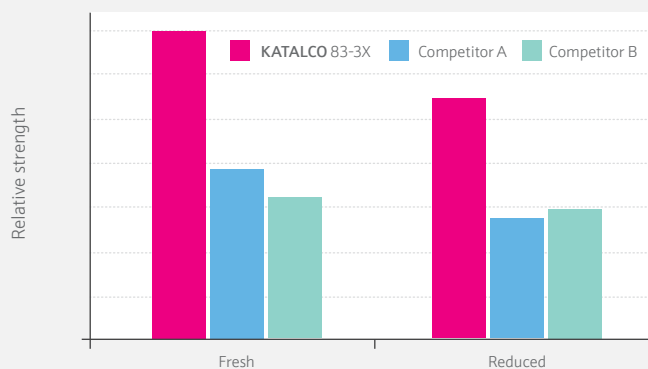
## Robustness to operational upsets

The stable activity and high strength of KATALCO 83-3 and 83-3X ensure that the catalyst operates according to our expectations; however, the catalyst must also be resistant to operational upsets.

In the case of low temperature shift converters, the most common operational upsets are condensation on the catalyst or wetting from an upstream water quench system. KATALCO 83-series catalysts are extremely robust to withstand these upset conditions. The diagram below shows the relative strength of KATALCO 83-3X and other commercially available low methanol products after a simulated condensation incident.



Relative strength after simulated condensing incident



Relative strengths of fresh and reduced catalysts

## Fast start-up

**KATALCO** 83-series catalysts require reduction before they can be brought on-line. To avoid overheating, this process must be carefully controlled to an inlet temperature of about 180°C (356°F) and the hydrogen addition rate must be limited. A lower reduction strike temperature allows earlier introduction of hydrogen and shortens reduction time. For **KATALCO** 83-series, reduction commences at temperatures as low as 150°C (302°F), and research tests confirm this to be as much as 25°C (45°F) lower than competitive catalysts.

Experience in commercial plants confirms the catalyst can be safely and rapidly reduced with a minimum of inconvenience and maximum reliability. The unique structure of **KATALCO** 83-series catalysts means that there is no limit on the CO<sub>2</sub> concentration during catalyst reduction. JM offers on-site support for LTS catalyst reductions, and our experienced engineer will provide analysis equipment, ensuring a quick and safe start-up.

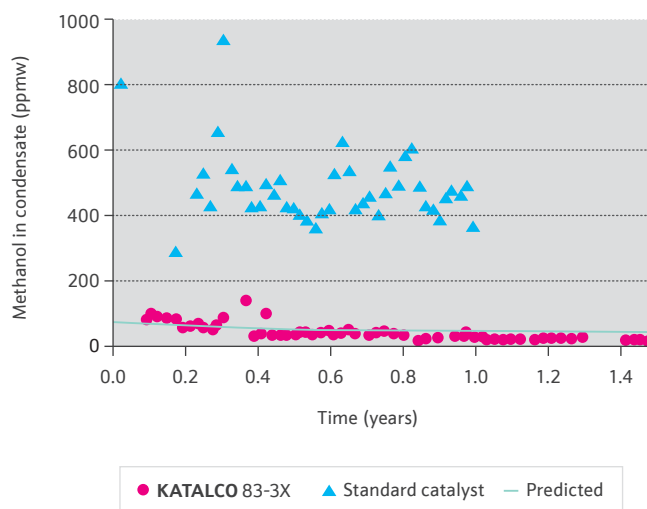
## Sustainability

### Minimum by-products

Low temperature shift catalysts form methanol as a by-product. Methanol emissions can be an environmental issue, in some cases exceeding consent limits under environmental legislation. Problems occur in the treatment of process condensate and in wet CO<sub>2</sub> removal flowsheets. Methanol also represents a process inefficiency since every molecule of methanol consumes 2 H<sub>2</sub> and 1 CO molecules. For example, 1.0 tonne of methanol equates to a loss of about 180 kg H<sub>2</sub> and 1.05 tonnes of ammonia or about 100,000 SCFD and 5 tonnes/day for a large hydrogen and ammonia plant, respectively, with conventional LTS catalyst.

**KATALCO** 83-3X incorporates carefully optimised levels of alkali promoters and retains excellent high activity for shift conversion with much reduced activity for methanol synthesis. Commercial experience with **KATALCO** 83-3X has shown it to have reduced methanol formation by more than 90% while still achieving a high activity for the CO shift reaction. This is illustrated in the figure below, which shows the actual performance of **KATALCO** 83-3X in a plant requiring low methanol by-products from its LTS converter.

In support of plant operators, JM has developed a kinetic model that accurately predicts methanol formation rates. This is used to advise on the optimal operating conditions to minimise methanol formation.



Plant performance of **KATALCO** 83-3X

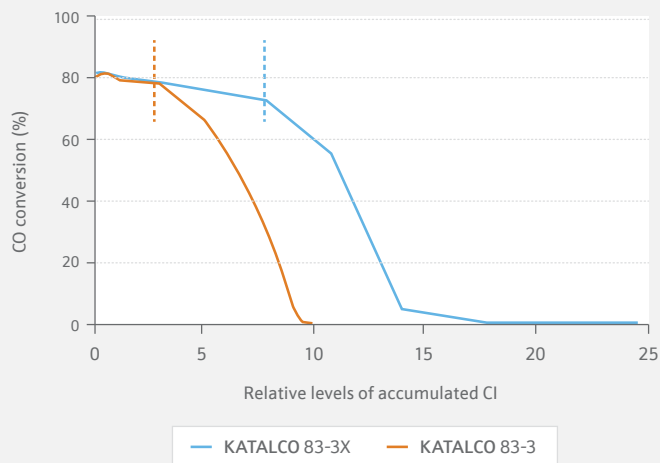
### Long life and economic performance

The life of most charges of LTS catalyst is determined by the capacity of the catalyst to absorb trace poisons that are inevitably present in the process gas. In most ammonia and hydrogen plants, the key poisons are sulphur and chloride. The LTS catalyst must be designed to tolerate these poisons to prolong the active life of the catalyst. **KATALCO** 83-3 and **KATALCO** 83-3X have unparalleled self-guarding for both sulphur and chloride poisons in which the active shift catalyst itself provides its own protection.

Some ammonia and hydrogen plants feature LTS guard reactors. These relatively small vessels contain a sacrificial catalyst that retains the poisons to protect the main catalyst bed downstream. By timely renewal of the guard reactor catalyst, the life of the main bed can be extended to ten or more years. For optimal protection, the guard catalyst should provide the maximum poisons capacity and a sharp absorption profile. Johnson Matthey will normally recommend **KATALCO** 83-3X for this application due to its superior poisons pick up.



Due to the method of incorporating the alkali promoters, **KATALCO 83-3X** gives better poison retention than **KATALCO 83-3**. This is illustrated in the diagram below, which shows the effect of cumulative levels of chloride poisons on shift conversion activity.



**Effect of chloride poisoning on CO conversion for KATALCO catalyst range**

When LTS catalyst becomes fully deactivated and requires changing, the sulphur concentration in the catalyst is approximately 1% near the top of the vessel and 0.1% near the bottom. However, for **KATALCO 83-3** the sulphur concentrations have been significantly above this level as indicated in the table here:

**Excellent sulphur retention of KATALCO<sub>JM</sub> 83-3**

Plant location	% Sulphur (w/w) Top sample	% Sulphur (w/w) Middle sample
USA	2.1	0.14
Europe	4.4	0.16
Australia	2.9	0.09

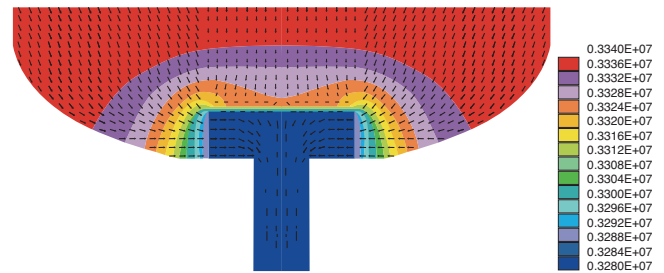
The mini versions **KATALCO 83-3M** and **KATALCO 83-3MX** have greater poison retention than the standard sizes and are proven to give the longest plant runs ever in service.

# Additional capability with KATALCO Performance

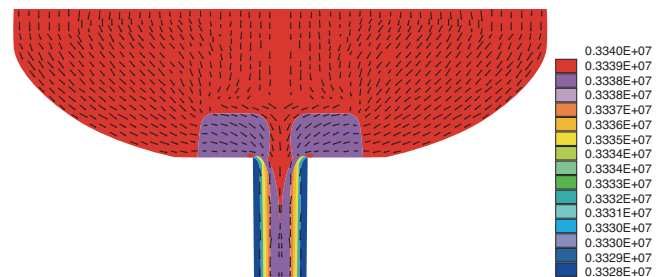
## STREAMLINE

Many operators, particularly in ammonia plants, want to minimise pressure drop. The value of pressure drop saved is typically US\$10,000/psi or US\$150,000/bar per year. Operators have reported pressure drop across the bottom of a shift converter as high as 0.6bar (9psi). The **STREAMLINE** low pressure drop system was developed by JM in the late 1990s and resulted from a thorough study of all the pressure drop contributors in a shift converter. This study indicated that the majority of the pressure drop is due to the support material, outlet collector and exit nozzle. **STREAMLINE** involves a specially designed support system in place of the standard alumina support balls, without any mechanical modifications to the vessel. The pressure drop across the annulus in a typical Kellogg ammonia plant shift reactor is almost 0.5bar (7.5psi), whereas the pressure drop across the same vessel is 0.01bar (0.15psi) with **STREAMLINE** installed.

By installing **KATALCO** catalyst and the **STREAMLINE** system, a significantly lower pipe-to-pipe pressure drop can result across the shift vessels, and has been proven in operation in more than a dozen plants.



Pressure drop across a standard Kellogg shift reactor



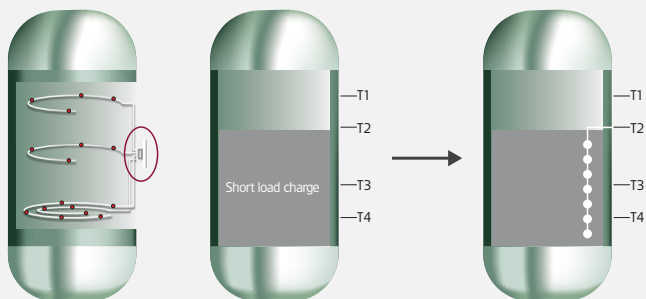
Pressure drop across a standard Kellogg shift reactor with STREAMLINE

## Advanced reactor thermometry

Accurate temperature measurement within a catalyst bed can be crucial for understanding the performance of the catalyst, diagnosing operational upsets and determining remaining life. Johnson Matthey has formed a partnership with Daily Thermetrics to offer catalyst users the most advanced temperature tracking technology currently available – the CatTracker™.

Each CatTracker probe consists of a minerally insulated cable that can sense temperatures at various pre-determined locations along its length. They are available as either four or nine point thermocouples. These multiple temperature sensing points are independent and isolated from one another, while at the same time ungrounded from the sheath.

A single CatTracker can be used to provide temperature measurements in both the radial and axial planes.



CatTracker installation options

## Radial reactor technology

Increased focus on efficiency can result in every part of an ammonia or hydrogen plant being scrutinised for pressure drop savings without compromising on performance. JM's radial reactor technology and catalyst offers a lower pressure drop than traditional axial reactors through internals that can be retrofitted into the existing reactor shell. Pressure drop savings of up to 50% can be achieved due to the smaller gas flow path over the catalyst.

A radial bed requires radial temperature profile measurements at intervals along the bed length to provide monitoring of:

- Uniform reaction and thus gas distribution throughout the bed
- Detection of any potential process problems
- The progression of any poisoning of the catalyst bed

JM achieves this using CatTracker technology.



Inside a JM radial flow reactor

# Case studies

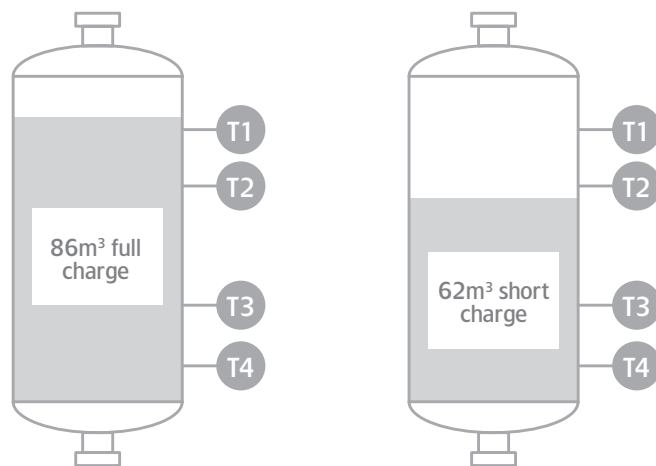
## Case study 1 - Impact of short loading on catalyst bed design and monitoring

Hydrogen and ammonia plants should always be designed to include sufficient catalyst volume to operate satisfactorily with average levels of poisons present in feedstocks. Improvements in catalysts over the past 50 years have resulted in reduced catalyst volumes in older plants, often whilst also increasing the plant rate. An example of this is illustrated by the following case study from a large ammonia plant.

In this case study plant rates have progressively been increased from the original design of 1,200MTPD to around 1,400MTPD. Over the same time period, installed catalyst volumes have decreased and the lifetime of the installed catalyst volumes has also increased, as illustrated in the table below.

Volume (m <sup>3</sup> )	Catalyst type	Installed	Life (years)
86	KATALCO 52-1	05/1988	3
86	KATALCO 53-1	06/1991	6
65	KATALCO 52-1	08/1997	4
62	KATALCO 83-3X	12/2001	5
62	KATALCO 83-3X	07/2006	6
62	KATALCO 83-3X	07/2012	-

By accurately understanding the deactivation characteristics it is possible to predict how long the catalyst charge will last for and optimise the volume of catalyst charged at the next turnaround to match the planned turnaround frequency. One of the key pieces of information in determining the residual life is the movement of the reaction profile. However, what is apparent in this plant is that the thermocouple locations chosen at the time of the original plant design for a full load of catalyst with a relatively fast moving reaction profile are not ideal to assess a modern catalysts performance. The figure shows the relative locations of the four thermocouples fitted to the vessel with respect to bed heights for the full charge of 86m<sup>3</sup> and the current reduced load of 62m<sup>3</sup>. Other than the gas temperature inlet and exit the LTS converter there are only two thermocouples in the bed this makes assessment of the catalyst performance a challenge.



Thermocouple locations versus full load and short load catalyst bed heights

JM's experienced engineers have however used their detailed knowledge of the plant operation and its typical LTS poisoning rates together with proprietary modelling tools to accurately estimate the expected life of the catalyst.

## Case study 2 - STREAMLINE gives excellent pressure drop reduction

An ammonia plant in Asia, built in the late 1960s, had been updated to approximately 130% of its nameplate capacity. Consequently the pressure drop through the front end of the plant had increased and, due to a process air compressor limitation, rates could not be increased further. JM worked with the customer to reduce the pressure drop through the shifts section of the plant.

JM recommended and supplied:

- The bed commissioning.
- CFD modelling of a new outlet collector
- Detailed mechanical design including full installation inspection, specification, manufacture and supply of the new outlet collectors
- **STREAMLINE** support media
- HTS and LTS catalysts
- Technical supervision of installation.

After installation of the new collectors, **STREAMLINE** and **KATALCO** catalysts, the pressure drop through the front end of the plant was reduced by 1.5bar (22psi) as shown in the table below.

Pressure drop	Before installation	After installation	Actual saving
HTS	0.90bar (13psi)	0.34bar (5psi)	0.55bar (8psi)
LTS	1.38bar (20psi)	0.41bar (6psi)	0.97bar (14psi)

Relieving the air compressor limit allowed an additional 8% increase in plant production.

### Case study 3 - **KATALCO 83-3** recovers from wetting

Several years ago a 74MMSCFD hydrogen plant with **KATALCO 83-3** installed condensed water onto their LTS bed during a short period of reduced rate operation. By following the drying out procedures recommended by Johnson Matthey, the plant was able to continue to operate using the same LTS catalyst charges with no impact on plant performance.

Two months after the completion of a successful scheduled turnaround, this plant found that two of their reformer tubes were leaking at the outlet pig tails, and it would be necessary to nip these tubes. In order to complete this process, it was necessary to reduce the plant rate to 50% of design rate; an operating condition that required bypassing of the LTS beds for the duration of the reduced rate. On completion of the pig tail nipping, the process operator noticed a positive pressure reading in the isolated LTS beds, suggesting that the inlet valves were passing. The operators checked for the presence of condensate in the LTS beds; a quantity of condensate was then drained from both beds.

JM was able to give the plant operator detailed guidance on how to deal with this situation. Two main concerns had to be addressed:

- **Migration of poisons (chlorides) through the bed**  
As the catalysts were very new (on-line for approximately two months) this was not considered to be a significant concern as only small levels of poisons would be present at this point in the catalyst life.
- **Drying out the bed**  
As mentioned previously in this paper, if a drying out procedure is performed too rapidly, the water that is within the pores will undergo an explosive expansion to steam stressing the microstructure of the LTS pellet which compromises its integrity.

JM provided the process operator with a detailed methodology for bringing the bed back on-line successfully, including steps to:

- Remove any reactants from the LTS beds
- Warm up the catalyst without causing damage to the LTS catalyst pellet integrity
- Commission the bed

On following this advice, the process operator was able to bring the LTS catalyst charge back on-line successfully. At the time of writing, it is two years since this incident occurred. The plant continues to meet predicted performance projections and is expected to remain in service until its scheduled replacement several years from now.



# Understanding low temperature shift section

The water gas shift (WGS) reaction follows the reforming section of the plant. The reaction serves two purposes, firstly to maximise the extraction of H<sub>2</sub> from the reformed gas and secondly to convert CO to CO<sub>2</sub> to aid removal downstream. The WGS reaction is shown in Equation 1.



The reaction is moderately exothermic, therefore high CO conversion is favoured by low temperature. In conventional ammonia plants based on steam reforming technology, the thermodynamic limitation is addressed by use of a series of adiabatic converters where the off gas from the reformer section is converted in two stages with the second stage being at a significantly lower temperature in order to shift the equilibrium towards the favoured hydrogen product.

The graph in Figure 1 shows the position of the equilibrium line for a typical ammonia plant. The equilibrium constant for the reaction  $K_p$  is as follows:

$$K_p = \frac{p_{\text{H}_2} p_{\text{CO}_2}}{p_{\text{H}_2\text{O}} p_{\text{CO}}}$$

$$K_p = \exp(Z(0.63508 - 0.29353 Z) + 4.1778) + 0.31688$$

where  $Z = (1000/T) - 1$  with  $T$  being the absolute temperature (Kelvin).

This means that the position of the equilibrium is not just dependent on the temperature, but also on the initial steam to dry gas ratio at the inlet of the shift reactor.

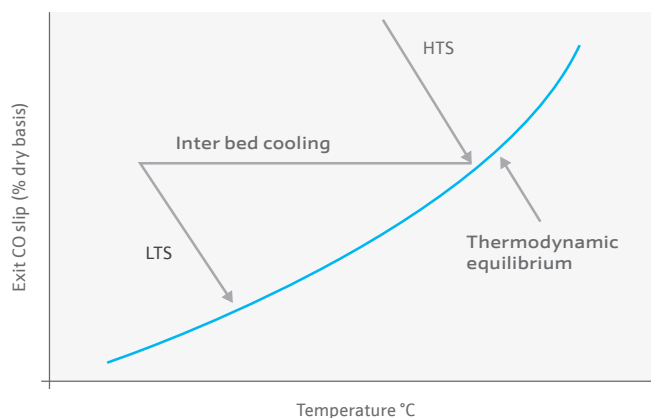


Figure 1: Variation of the exit CO content in a typical Ammonia plant

The reaction in the first stage is known as high temperature shift (HTS) and employs an iron oxide based catalyst. As the reaction proceeds the bed temperature increases until the equilibrium limit is reached. Upon exit of the HTS bed the gas passes through a heat exchanger that enables cooling to below 200°C (392°F) before entering the low temperature shift (LTS) bed. The copper based LTS catalyst is active at these lower temperatures thereby enabling the reaction to proceed to a CO content of approximately 0.1–0.3%.

The pressure of the system does not affect the equilibrium position. The pressure will, however, impact on the kinetics due to pore diffusion limitations and partial pressure effects of the reactants. Higher pressures will improve overall CO conversion in kinetically limited regimes.

The LTS reaction, due to the lower operating temperatures, typically employs a Cu based catalyst. Modern LTS catalysts, such as the **KATALCO** 83-series, utilise a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> formulation that is multi functional and delivers improved selectivity and resistance to common poisons, in addition to stable activity.

LTS catalysts are typically supplied in the oxidic form and therefore they must be reduced to metallic copper, the active species, before use. The reduction reaction is highly exothermic and to maximise the catalyst activity it is of paramount importance that the reduction is controlled carefully to minimise the temperature to which the catalyst is exposed.

between poisons resistance, stability, selectivity and activity. Typically it is manufactured to achieve a high dispersion of Cu crystallites within the ZnO/Al<sub>2</sub>O<sub>3</sub> structure. The ZnO/Al<sub>2</sub>O<sub>3</sub> refractory crystallites add strength to the catalyst and act like a barrier while providing a stable support maintaining the high dispersion of the active Cu sites and therefore inhibit the Cu crystallites from sintering. This feature dates back to the development of the **KATALCO 83** series in the 1960s, and is illustrated in Figure 2. The design of the catalyst structure can influence the stability of the catalyst, particularly during reduction in high CO<sub>2</sub> conditions or during wetting incidents.

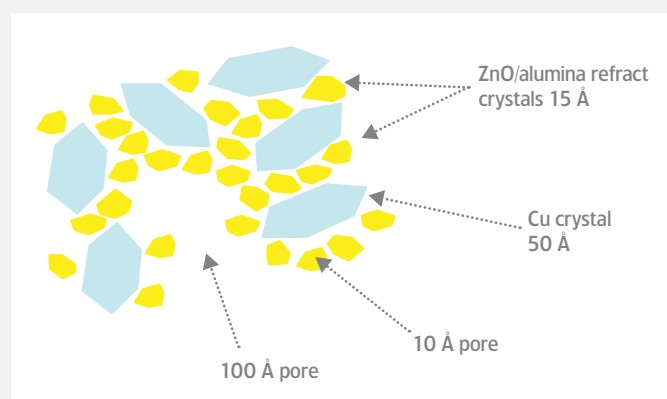


Figure 2: Diagram illustrating a good LTS catalyst structure

LTS catalysts are inherently less pore diffusion limited than those employed in the high temperature shift reaction due to the lower operating temperature. However, little doubt exists that LTS catalysts typically operate in pore diffusion regimes, although the extent of this limitation in industrial catalysts is the subject of continuing debate.

When formulated and manufactured correctly the resultant Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst is robust and will continue to function well for many years under typical LTS operating conditions. The major causes of LTS catalyst deactivation, and therefore replacement, are thermal sintering of the copper crystallites and poisoning by sulphur and chlorine compounds.

## By-product formation

The main by-product associated with the LTS reaction is methanol. Unlike the water gas shift reaction, where catalyst activity depends on the structure of the copper crystals present on the catalyst surface, methanol formation depends only on the total copper surface area of the catalyst. The copper surface area in LTS catalysts sinters rapidly at the start of life as a consequence of the operating temperature and the presence of steam. Since methanol formation in an LTS reactor is kinetically limited, such changes in copper area have a direct impact on the levels of methanol formed over the catalyst. As a result, methanol by-product formation, which is highest at the start of catalyst life, falls rapidly within the first six months of operation as the copper surface area of the catalyst falls by sintering.

For customers with particular sensitivity to methanol, multi-promoted catalysts such as **KATALCO 83-3X**, significantly lower the methanol formation by the judicious incorporation of promoters. This improvement has been made without impacting the activity of the catalyst. The promoters which suppress methanol, in **KATALCO 83-3X** are also effective at retaining trace poisons and so the life of the catalyst is extended compared with traditional LTS catalysts.

## Catalyst deactivation

Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts readily sinter and lose copper surface area, and therefore catalytic activity, when continually operated above 300°C (572°C) due to the inherent low melting point of Cu metal and therefore the low temperatures at which surface and bulk mobility of Cu occurs (Tammann and Huttig temperatures). One of the major roles of the ZnO/Al<sub>2</sub>O<sub>3</sub> crystallites is to retard such growth of copper crystallites and function as a textural promoter.

The second major cause of deactivation of these catalysts is poisoning by compounds present in the reactant gas stream. The Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst operates at a temperature sufficiently low wherein thermodynamics favours strong adsorption of poisons.

Sulphur species first adsorb onto the copper component of the catalyst, preventing any reaction from occurring on these sites. Once adsorbed, the sulphur species reacts with the free zinc oxide on the catalyst surface, forming a surface zinc sulphide species. Subsequent reaction leads to the formation of bulk zinc sulphide species, the most thermodynamically stable form, which may be observed in discharged LTS catalyst samples. These four stages of poisoning are in equilibrium and therefore even though the final stage is the most stable, there will be sulphur present in the other stages and hence there will be a loss of activity due to sulphur absorption on the copper crystallites. Therefore an effective LTS catalyst needs intimate mixture of Cu, ZnO and a high free ZnO (+ alumina) surface area.

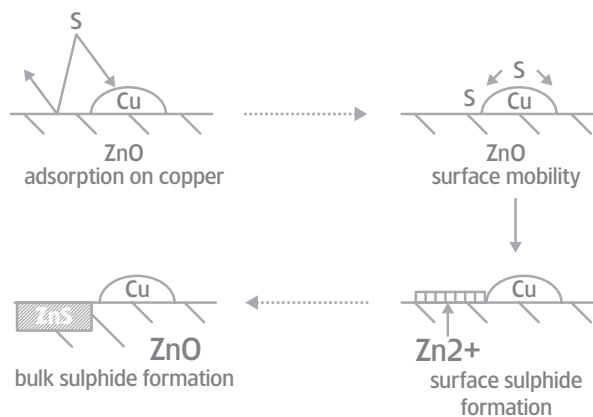


Figure 3: Mechanism for absorption of sulphur onto LTS catalyst

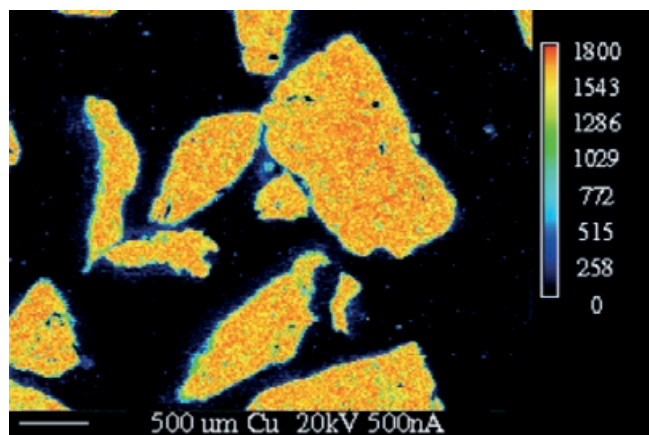


Figure 4a: EPMA scan showing Cu

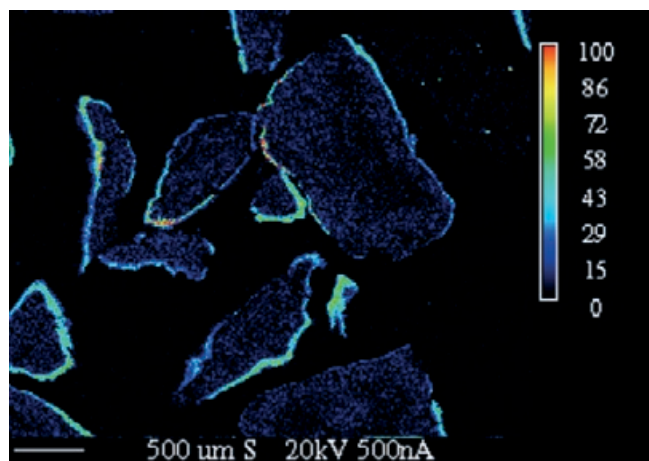


Figure 4b: EPMA scan showing S on surface

In comparison to sulphur, chloride is a very severe poison, even low levels of chloride will result in loss of catalyst activity and compromise the ability of the catalyst to remove sulphur poisons. Its severity arises from the fact that it can react with the copper and zinc oxide components of the catalyst to form low melting point chlorides.

The mechanism of chloride poisoning of LTS catalysts has been determined using radio-labelled  $^{35}\text{Cl}$  which illustrated that chloride will react with the copper surface of the catalyst to form  $\text{CuCl}$ . Chlorides will also react with the zinc oxide surface of the catalyst to form zinc chloride, which may cause disruption of the catalyst lattice, inhibiting the impact of the zinc oxide stabiliser. This can lead to a loss in surface area of the catalyst, which impacts on the ability of the catalyst to remove sulphur.

Once formed, both  $\text{CuCl}$  and  $\text{ZnCl}_2$  are low melting point solids. Cupric chloride has a melting point of  $430^\circ\text{C}$  ( $806^\circ\text{F}$ ) compared to a melting point of  $1063^\circ\text{C}$  ( $1945^\circ\text{F}$ ) for copper metal. The typical LTS operating temperature is above the Tammann temperature of this compound and it is therefore a very mobile species sintering rapidly and causing a concomitant loss in catalyst activity.



The solubility of the chlorides formed is also a significant issue for catalyst operation. Both cuprous and zinc chloride are soluble in water, hence condensation on the catalyst during start up, shutdown or normal operation can move the chlorides further down the bed resulting in further poisoning of the catalyst.

Many industrial catalysts, like the **KATALCO** 83-series, due to the manufacturing route possess self guarding properties with respect to typical poisons, i.e. S and Cl. However to maximise the resistance to poisons, especially for chlorides the use of an alkali promoted LTS catalyst, such as **KATALCO** 83-3X is recommended. The alkali in the catalyst is able to trap very low levels of chloride without disrupting the  $\text{Cu/ZnO}$  lattice of the catalyst. The melting points of these chlorides are much higher than those of copper and zinc chlorides. The chloride is therefore trapped and does not move around the crystal lattice preventing sintering of the active copper component of the catalyst and loss of surface area by formation of zinc chloride. Because of the ability of the catalyst to retain surface area in the presence of chloride, resistance to sulphur poisoning is also improved.

However simply incorporating alkali in to the catalyst is not sufficient as the alkali must also be accessible. This is ultimately determined by the method of manufacture and therefore the total alkali content of a catalyst is not a reliable indicator of poison resistance.







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