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Catalyst solutions delivering value in water gas shift

Johnson Matthey

Reprint from Nitrogen+Syngas January/February 2022



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The water gas shift conversion is an important aspect to the economic operation of an ammonia plant. The reaction has a key role in the generation of hydrogen (15-20% of the hydrogen is generated via water gas shift) and also converts carbon monoxide to carbon dioxide which is more readily removed from the process:



The minimisation of the carbon monoxide slip means that there is less hydrogen consumed in the methanation of carbon oxides, and lower methane flows to the synthesis loop reducing the required purge flow. The exothermic nature of the reaction also generates heat which can be recovered into boiler feed water or steam systems

The water gas shift process is divided between two unit operations: a high temperature shift (HTS) and a low temperature shift (LTS). Since greater equilibrium conversion of carbon monoxide is favoured at lower temperatures, a compromise is required between achievable conversion and kinetic rate. The HTS is used to do the bulk of the carbon monoxide conversion at a faster rate at higher temperatures. The LTS is then used for the final 5% of the hydrogen generation at conditions more favourable to the equilibrium.

A by-product of the water gas shift process is methanol. Methanol is undesirable since its formation consumes hydrogen that could otherwise be used for ammonia synthesis, and methanol emissions from the process can be a serious environmental concern.

High temperature shift

The first stage of the water gas process in an ammonia plant is the high temperature shift (HTS). The HTS operates at an inlet temperature of around 350°C and reduces the mole fraction of CO in the syngas to 2-4%.

High temperature shift catalysts

HTS catalysts consist of iron and chromium, promoted with copper. This formulation is selected for its thermal stability at HTS conditions. The incorporation of chromium oxide creates an intimate mix in the iron structure, which limits deactivation. This allows ironchrome HTS catalysts, such as KATALCO™ 71-series, to operate at high temperatures without deactivation compromising the performance at lower temperatures. The KATALCO 71-series contains a very low proportion of hexavalent chrome. This is particularly important in reducing the hazards of catalyst handling. In service, the trace amounts of hexavalent chrome are converted to

trivalent chrome, and formation of hexavalent chrome at shutdown can be minimised by carefully following plant shutdown procedures.

Diffusion limitations are an important factor in the catalysis of the HTS reaction. Therefore, the pore structure of the catalyst pellet is key in its performance. The structure of the KATALCO 71-series catalysts incorporate patented structural promoters that broaden the pore-size distribution which increases the activity. The benefits of the pore structure and better diffusion characteristics mean that KATALCO 71-series catalysts can be operated at lower temperatures without performance being limited by pore diffusion.

Pressure drop

Minimising the pressure drop is an important consideration in the overall process economics. The pressure drop characteristics of a catalyst is dictated by the pellet design. The design of the KATALCO 71-series pellets optimise the aspect ratio to achieve high voidage in a packed bed to deliver the best combination of pressure drop, strength and activity. Utilising patented developments in pellet design that have shown the benefits of shaped pellets, such as KATALCO 71-5F, JM can offer improved pressure drop and conversion over unshaped pellets.

The catalyst should also be able to tolerate plant upsets and retain its low pressure drop characteristics. Unplanned events that impact the HTS are likely to be wetting incidents related to boiler leaks, which can lead to increased pressure drop from the build-up of boiler solids. Robust catalysts, like the KATALCO 71-series, have good strength and open pore structure to withstand rapid cycles of wetting and drying.

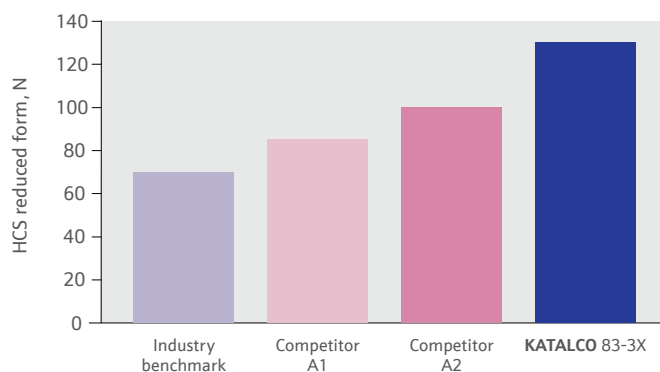


Figure 1: Horizontal crush strength (HCS) of LTS catalysts in-service reduced form

Case study

A hydrogen plant in North America experienced a boiler leak of an estimated 45,000 kg/hr of water onto the catalyst for a three-month period. However, the **KATALCO** 71-series catalyst did not fail catastrophically as might be expected under such conditions. It continued to operate, allowing the customer to produce hydrogen until an appropriate shutdown could be planned and taken. This not only saved the plant the costs of an unplanned shutdown, but also ensured that other operations were not unduly affected. This reliability and managing of other hydrogen consumer production was valued in the millions of US dollars.

Poisoning

JM's latest development in technology combines strong purification expertise with the design of low pressure drop systems for shift reactors to develop **PURASPEC™** 2272 – a new purification tool for use in the HTS to help protect and extend downstream LTS catalyst life.

PURASPEC 2272 support media is a patented technology solution of JM to improve the water gas shift process. It utilises a low pressure drop active adsorbent support media that replaces the inert support media at the bottom of the HTS reactor. **PURASPEC** 2272 actively captures chloride which would otherwise poison the low temperature shift (LTS) catalyst downstream.

JM has used its expertise in purification science along with its proven STREAMLINE engineering skills to develop **PURASPEC** 2272 – an innovative new product which combines the functions of a low pressure drop support with that of a chloride trap.

Start-up exotherms

In some cases of high temperature shift operation exotherms can be observed when introducing steam to fresh catalyst charges. The cause of this was first identified by Johnson Matthey as the rehydration of catalyst, not, as was believed by some, the formation of hexavalent chrome. If the catalyst is held under a nitrogen purge at relatively high temperature, the surface can become dehydrated.

Then, on introduction of steam, the surface rehydrates resulting in an exotherm. Johnson Matthey can identify the conditions under which this is most likely to occur and advise a start-up procedure to avoid high temperatures. If high temperatures are seen, it again highlights the need for thermal stability in HTS catalyst, and practical experience shows that **KATALCO** 71-series catalysts can survive these incidents without any detrimental effects.

Initial desulphurisation

All HTS catalysts contain some residual sulphate. This is converted to H₂S during the reduction of the catalyst and has the potential to poison downstream catalysts. **KATALCO** 71-series catalysts are manufactured via a nitrate route whereas other catalysts may be made via sulphate routes. For catalysts manufactured via the nitrate routes, any sulphur present is not intimately bound in the pore structure of the catalyst but tends to be present at the surface. This means that the sulphur is easily reduced and removed in the fastest start-up time. For catalysts formed by a sulphate route, the sulphur in the finished catalyst is concentrated in the bulk of the structure, and the desulphurisation of these materials is slower.

Low temperature shift

Following the high temperature shift, the remaining carbon dioxide conversion is carried out in the low temperature shift (LTS). The LTS operates at an inlet temperature of around 200°C and reduces the mole fraction of CO in the syngas to 0.2-0.4%.

Low temperature shift catalysts

LTS catalysts consist of copper with zinc oxide and alumina, and other components, such as alkali metals, that can be used to alter selectivity reducing the by-product methanol make. This formulation is selected for its activity. Though it has good activity, it is not thermally stable enough to be suitable for high temperature shift conversion and is therefore only used in the LTS duty.

Catalytic activity at low temperature is an important catalyst parameter. Since the equilibrium of the water gas shift reaction dictates that higher CO conversion is achieved at lower temperatures, activity at low temperatures is key. For example, the **KATALCO** 83-series catalysts show activity such that the equilibrium can be achieved below 200°C and an approach to equilibrium close to zero can be achieved through the catalyst life. **KATALCO** 83-series catalysts have been operated at inlet temperatures as low as 190°C, and the operating temperature is often dictated by the dew point of the inlet gas rather than the catalytic activity.

Pressure drop

Pressure drop is an important parameter relating to the economics of the syngas generation train. Catalyst pellet design can improve the pressure drop of an LTS reactor, and catalyst strength throughout its lifetime is as important as the strength of the fresh pellet. The high strength of **KATALCO** 83-series catalysts minimises the rate of increase of pressure drop during operation, and its

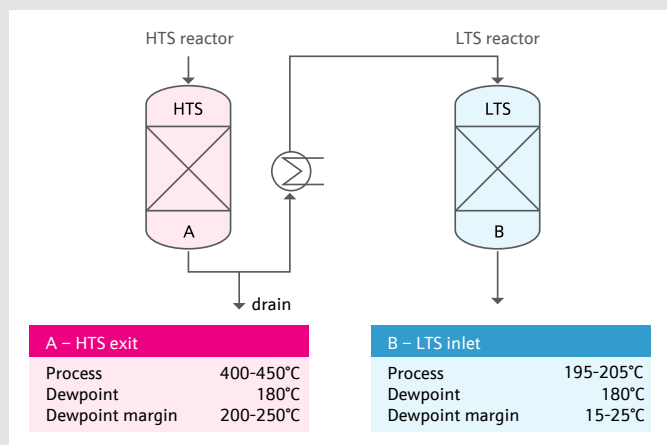


Figure 2: Shift process conditions and dewpoint margins

formulation gives high strength after reduction, steaming and any unplanned wetting events.

The relevant strength of any LTS catalyst is that in the reduced state since that is the state of the catalyst in service. The horizontal (or side) crush strength of **KATALCO** LTS catalyst is compared to both the industry benchmark and recent competitive advances above in Fig.1. This clearly shows why JM LTS is the most reliable option if an increase in pressure drop, and the losses that arise from lower rates are something that an operator wants to avoid.

Condensation on the catalyst or wetting from an upstream water quench system are the most common operational upsets in the running of an LTS. An LTS catalyst should therefore be resistant to these conditions and retain its activity and strength. Reduced catalyst strength is important. Some low temperature shift catalysts can be too weak. **KATALCO** 83-3X is the optimum choice for maximum level of mechanical strength after reduction.

The outstanding mechanical stability of **KATALCO** 83-3 series catalysts deliver a benefit of lower pressure drop increase with time on-line and consequently a longer lifetime. There is also a much lower exposure to risk of production losses caused by pressure drop where deformation of weaker pellets can lead a resistance to flow. There are many incidents in industry where weaker LTS catalysts have caused incidents causing pressure drop losses that can be measured in one to tens of millions of dollars.

Methanol formation

Low temperature shift conditions and catalysts can result in the formation of methanol as a by-product. Methanol emissions can cause plants to exceed the consent limits

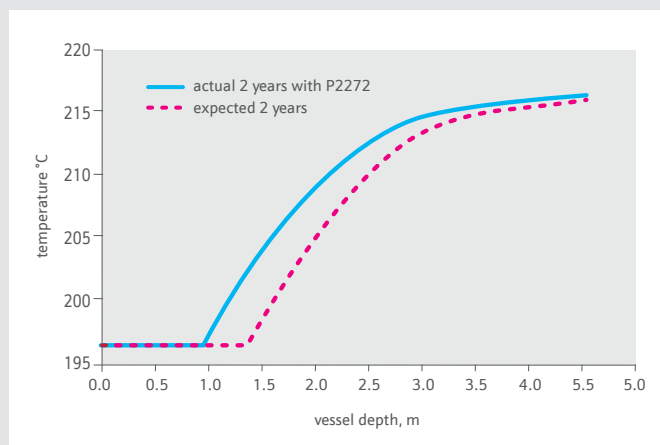


Figure 3: Low temperature shift temperature profiles for expected operation and actual operation when **PURASPEC** 2272 is installed

under environmental legislation and can cause problems in the treatment of process condensate. In addition, the formation of methanol removes hydrogen from the process, which would reduce the capacity for ammonia synthesis. The formation of 1 tonne of methanol equates to the loss of production of 1.05 tonnes of ammonia.

To avoid the formation of methanol, LTS catalysts can incorporate alkali promoters which inhibit the methanol synthesis reaction, such as **KATALCO** 83-3X which includes carefully optimised levels of alkali, which retains the shift activity of the catalyst while minimising the methanol production.

Poisoning

The lifetime of the LTS catalyst is most often determined by the capacity of the catalyst to absorb sulphur and chloride poisons that are present in the process gas. The temperature of the LTS is low enough that thermal deactivation does not show as significant an effect as the poisoning. It is unavoidable that low levels of sulphur and chloride are present at the LTS, and therefore the catalyst must be designed to tolerate and accommodate them.

It is important that the LTS catalyst shows good poison retention. In this way, catalysts such as **KATALCO** 83-3 and **KATALCO** 83-3X show good self-guarding properties, retaining the poisons at the front of the bed. This means that over the lifetime the poisons accumulate in a defined poisoned section at the top of the bed, meaning that the catalyst below still demonstrates excellent activity. Throughout the life of the catalyst, the front of the poisoned section moves through the bed until there is insufficient active catalyst remaining and the bed must be changed.

LTS bed life	Base case	Guarded case	CO reduction	Energy saved	Annual value	Annual value
Year	LTSexit CO%	LTSexit CO%	Delta CO%	million Btu	\$ @ \$4/million Btu gas	\$ @ \$20/million Btu gas
0	0.21	0.21	0	0	-	-
1	0.22	0.215	0.005	0.0055	12,045	60,225
3	0.25	0.24	0.01	0.011	24,090	120,450
4	0.33	0.29	0.04	0.044	96,360	481,800
5	0.52	0.425	0.095	0.1045	228,855	1,144,275
6	0.95	0.735	0.215	0.2365	517,935	2,589,675

Assumptions: 1,500 t/d plant predicted LTS performance; 0.1% CO increase, reduces efficiency by 0.11 million Btu/t with H2 recovery.

Table 1: The energy saving benefits gained for a 1,500 t/d plant for various gas costs

It is also possible to operate with an LTS guard reactor. This is a relatively small vessel that contains a sacrificial bed of catalyst designed to collect the poisons and allow the main catalyst to operate downstream. The guard reactor can then be replaced more frequently to extend the life of the main bed. It is even more important that a guard catalyst should have a sharp front of the poisoned section to maximise the poisons capacity and avoid poisons slipping to the main bed.

Although **KATALCO** 83-3 series catalysts are self-guarding and have a high capacity for chloride poisons, the fact is that chloro-ride poisons are highly mobile in an LTS if the bed is wetted. LTS beds operate with a low margin of 15-25°C against dewpoint meaning wetting can occur and result in chloride washing into the bed (Fig. 2).

The use of **PURASPEC** 2272 at a location below the HTS gives several benefits including keeping chlorides from the LTS reactor, and in the event of wetting allowing chlorides to leave via a drain rather than entering the LTS.

Typical results from an ammonia plant utilising **PURASPEC** 2272 upstream of an LTS charge are shown in Fig. 3. The reaction profile clearly shows that when using the **PURASPEC** 2272 solution the deactivation rate is lower than is typical.

In addition, providing chloride protection and extending the life of the catalyst, **PURASPEC** 2272 can provide significant protection against potentially damaging events such as unexpected transient events causing condensation. The value from this protection can be seen in the following energy saving benefits gained for a 1,500 t/d plant for various gas costs (Table 1).

Case study

A large North American hydrogen plant experienced short catalyst lives due to chloride poisoning. During a 5-year period, it replaced a competitive LTS catalyst and its associated guard material five times. Catalyst lives averaged just one year. The plant then changed to a full bed of **KATALCO** 83-3X, which gave excellent performance for more than three years. This saved the operator both replacement catalyst and unscheduled shutdown costs, estimated to be worth at least \$600,000. In addition to the cost savings achieved by the plant operator, this case study also demonstrates the excellent inherent poisons resistance of **KATALCO** 83-3X products.

These benefits could be further enhanced by use of **PURASPEC** 2272, further increasing the life of the LTS and allowing flexibility on extending turn-around intervals while delivering increasing value through the lifetime through lower CO slip, and significantly lowering the risk of chloride migration in any wetting incidents.

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