JM

High temperature shift catalysts

Johnson Matthey
Inspiring science, enhancing life

Contents

Introduction

The high temperature shift (HTS) converter plays a key role in ammonia and hydrogen plants, producing 10-15% of the hydrogen formed in these units. At the same time, it also generates heat due to the exothermic nature of the reaction, which is typically recovered in boiler feed water or steam systems (0.5MW for a 1,000 te/day ammonia or 75MMSCFD hydrogen plant).

The water gas shift reaction is shown below:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \Delta H = -131.2 \text{ kJ/mol}$$

Long catalyst lives are usually achieved in the HTS converter and Johnson Matthey recommends the **KATALCO**™ 71-series catalysts for this duty. The formulation used for the **KATALCO** 71-series products is particularly active, as well as being resistant to normal plant poisons. All of the **KATALCO** 71-series products are promoted for high activity and operation at low steam-to-carbon ratios without by-product hydrocarbon formation. Some plant operators have realized savings of more than US$300,000 by installing **KATALCO** 71-series products through a combination of reduced catalyst volumes and longer catalyst lives.

Boiler leaks on some plants can limit the catalyst life due to solids build-up, or wetting and drying cycles. For these applications, Johnson Matthey has introduced **KATALCO** 71-6, which offers our customers unmatched in-service strength. Savings of more than US$1,000,000 in catalyst, turn-around and lost production costs can result by avoiding a catalyst change due to a boiler leak. **KATALCO** 71-6M is also the preferred product for radial flow reactors due to its exceptionally high activity and virtually zero shrinkage.

Many plants look to lower operational costs by reducing the pressure drop across the plant. Savings of up to US$90,000 per year can be achieved with **STREAMLINE**™ from **KATALCO PERFORMANCE**. This is a unique pressure drop reduction system that is suitable for installation in many shift converters. In addition to this, the standard Johnson Matthey HTS catalyst (nominal size 9 mm x 5mm) provides lower pressure drop than standard catalysts (nominal size 6mm x 6mm) available elsewhere. This is typically worth US$50,000 throughout the life of a catalyst charge.

KATALCO PERFORMANCE adds value to your plant: Case studies

At Johnson Matthey, we believe that world-leading catalysts only give world-beating performance with the right loading, operation and process optimisation. That is why we have introduced **KATALCO PERFORMANCE**.

Through **KATALCO PERFORMANCE** we offer a wide range of services, addressing the key areas of concern to plant operators: Efficiency, Reliability, Throughput, Safety and the Environment.

The following case studies demonstrate how choosing **KATALCO** catalysts, and our expertise have made a real difference to plant operations.

Case study 1 - Short loading with KATALCO 71-series catalysts

Installation of a short load of **KATALCO** 71-5 in an ammonia plant extends the time between reloads while maintaining a low CO slip.

An ammonia plant operating at 1,000 te/day (11, 00 stpd) changed to **KATALCO** 71-5 after poor performance of the previous charge. Figure 1 compares the actual CO slip for a short load of **KATALCO** 71-5 with the previous charge of high temperature shift catalyst from another supplier. The previous catalyst was closely monitored throughout its life and was discharged after 28 months on-line.

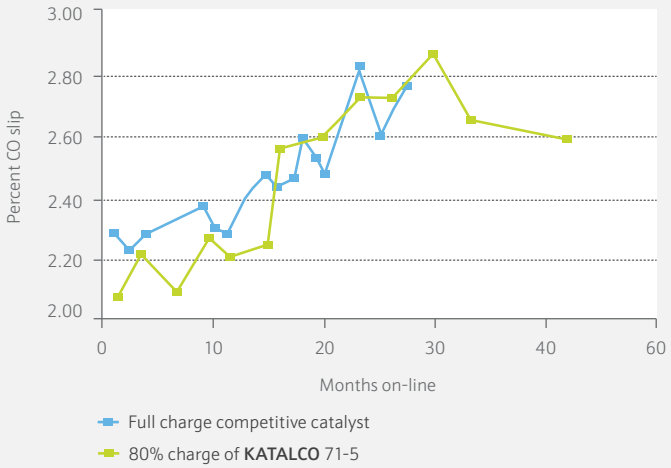

Figure 1: Performance of **KATALCO** 71-5

The customer then reloaded 80% of the reactor volume with **KATALCO** 71-5 and continued to closely monitor the performance. Reaction conditions for the two charges were identical for the first 14 months of operation, during which the performance of the short-loaded **KATALCO** 71-5 was considerably better than the previous competitive charge. After 14 months on-line, the steam ratio was reduced for the **KATALCO** 71-5, thus increasing the CO slip. Nevertheless, the smaller volume of **KATALCO** 71-5 continued to achieve the CO levels of the previous full load of competitive product. Furthermore, the short-loaded **KATALCO** 71-5 also achieved a 30% increase in life.

Case study 2 - **KATALCO** catalyst gives longer life

Installation of a short load of **KATALCO** 71-5 saves an operator at least US$ 330,000.

A1,000 te/day Kellogg ammonia plant in Europe has run with a charge of **KATALCO** 71-5 for more than 7 years following a charge of competitive material that had run for 4.5 years.

The **KATALCO** 71-5 longer life was achieved with just 70% of the catalyst volume, demonstrating the superior activity and stability of **KATALCO** 71-5. Minimal adjustment of the inlet temperature was required to maintain a low CO slip throughout this long life. The saving to this plant was US$170,000 on initial catalyst investment and a further US$160,000 for extended catalyst life..

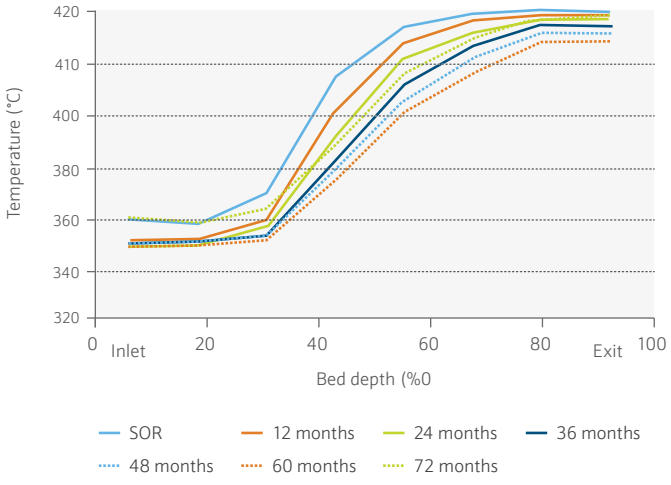

Figure 2: **KATALCO** 71-5 temperature profiles

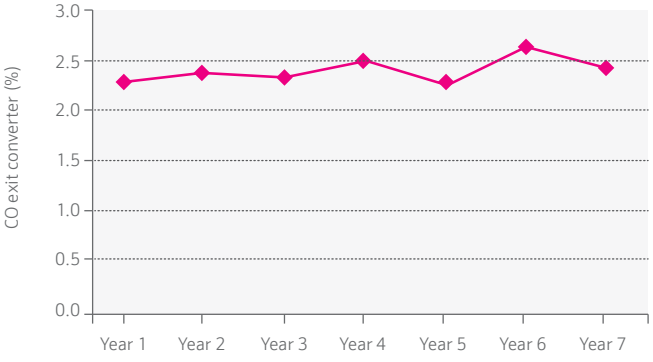

Figure 3: **KATALCO** 71-5 CO performance

Case study 3 - Johnson Matthey oxygen burners give outstanding performance

Installation of **KATALCO** 71-6 saves an operator US$1,300,000.

Due to the strength and robustness of KATALCOJM 71-6, it was able to withstand a full-bore tube leak without any detectable detriment to its activity or performance.

Figure 4 below compares the temperature profile throughout the catalyst bed before the failure of the tube, as well as after repairs had been conducted and the plant restarted. As shown, the temperature profile after the wetting incident and subsequent drying out are the same as before the event. The pressure drop across the catalyst bed before and after this incident was unchanged at 0.13bar (1.9psi).

By installing **KATALCO** 71-6, the operator saved US$500,000 in catalyst and turnaround costs and avoided lost production worth US$800,000.

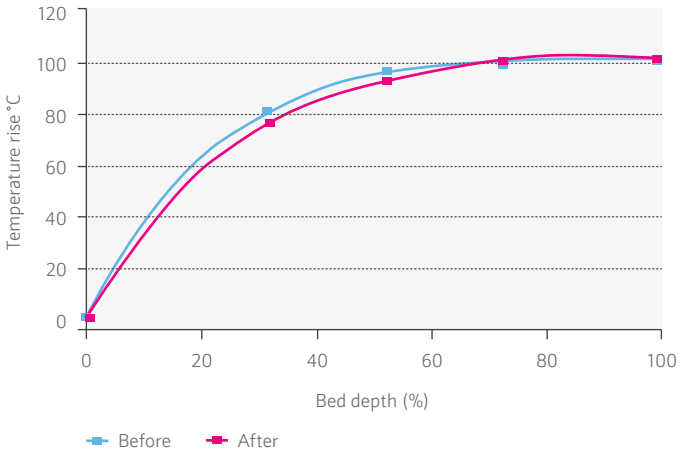

Figure 4: **KATALCO** 71-6 temperature profile before and after tube leak

Case study 4 - **STREAMLINE** delivers lower pressure drop and enables use of higher activity (mini) catalyst

This plant realized pressure drop savings of US$30,000 per year (US$150,000 during a 5-year period) and delayed purchase of US$200,000 of replacement HTS catalyst using a combination of the **STREAMLINE** pressure drop reduction system and **KATALCO** 71-6M catalyst.

Although this plant had the advantage of two high temperature shift beds, the catalyst in both was at end of run.

Johnson Matthey identified the opportunity to reduce the exit header pressure losses in this plant through use of an improved exit collector. This pressure drop reduction was great enough that the more active **KATALCO** 71-6M was specified, even though its pressure drop would be higher than that of the previous charge of 6 mm x 6 mm material.

Hence, with the STREAMLINE exit collector, the smaller pellet size **KATALCO** 71-6M could be installed and still give a lower pressure drop than the previous charge of standard size material. With the higher activity of **KATALCO** 71-6M, the plant could run with just one HTS reactor.

The net effect was that the overall pressure drop was reduced from 0.57bar to 0.37bar (8.3psi to 5.4psi) despite moving to a smaller pellet size. The efficiency saving from this reduced pressure drop is more than US$30,000 per year.

The plant was also able to delay purchase of catalyst for the second bed, saving US$200,000.

Case study 5 - **KATALCO PERFORMANCE** ATR retrofit design

One of the features of **KATALCO** 71-series catalysts is the lack of the so-called "temperature set" phenomenon. This results in additional hydrogen production from the converter, and can be worth US$000's over the life of the catalyst.

A hydrogen plant in North America installed a charge of **KATALCO** 71-5. Initially the inlet temperature was at 335°C (635 °F) but constraints in the early stages of operation forced the operator to raise the inlet temperature to 390–400°C (730 –750°F) for three months until these constraints were resolved.

At the end of this time the HTS inlet was restored to the start of run level of 335°C (635°F). The CO slip returned to the start of run level, confirming that **KATALCO** 71-5 resists thermal sintering effectively and does not suffer from the temperature set phenomenon seen in competitive HTS catalysts. This resulted in an additional 1% hydrogen make for the plant, which will equate to more than 1,000mmscf during the lifetime of the catalyst.

Case study 6 - **KATALCO** 71-series catalysts withstand wetting incidents

While **KATALCO** 71-6 has been specifically designed for use in highly stressed ammonia plants where boiler leaks are commonplace, standard **KATALCO** 71-series catalysts can operate under boiler failure conditions. This allows plants to schedule a shutdown to repair damage and replace catalyst.

One such example is a hydrogen plant in North America. The plant experienced a boiler leak of an estimated 100,000 lbs/hr of water onto the catalyst for a three-month period. However, the 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 at US$ MMs.

Advantages of choosing **KATALCO** high temperature shift catalyst

Operational benefits

Low CO slip close to thermodynamic minimum

Low CO slip is primarily important because it corresponds to high hydrogen generation In most plants, operation of the HTS reactor at low inlet temperature and high conversion aids plant efficiency through increased steam generation.

Achieving low CO slip requires a stable, high-activity catalyst that retains its high activity throughout its life. Retaining catalyst activity requires both thermal stability and resistance to poisons. The **KATALCO** 71-series displays all of these attributes.

High activity

KATALCO 71-series catalysts are unique compared to products offered by most major suppliers in that they are made via a nitrate route. This produces a high surface area precursor that leads to high conversion activity. The activity is further enhanced by reduced diffusion limitations that are achieved with a patented structural promoter that broadens the pore-size distribution.

These benefits in pore structure mean that **KATALCO** 71-series catalysts can be operated at lower temperatures than competitive catalysts without performance being limited by pore diffusion.

Thermal Stability

Chromium oxide is incorporated into HTS catalysts to provide thermal stability. Due to the catalyst production route, the catalyst benefits from simultaneous precipitation of the iron and chrome. This produces an intimate mixture that enables incorporation of chromium into specific sites in the inverse spinel lattice of magnetite. This structure inhibits thermal deactivation, hence delivering superior thermal stability.

The superior thermal stability of **KATALCO** 71-series catalysts is demonstrated by its ability to operate for periods at high temperature without detriment. Other products show what is referred to as "temperature set". This is where the catalyst deactivates during periods of high-temperature operation and cannot achieve the same results at the lower temperature again.

Commercial operating experience confirms that **KATALCO** 71-series catalysts do not show a 'temperature set' effect. This data demonstrates the high thermal stability and robustness of **KATALCO** 71-series products.

Poison resistance

KATALCO 71-series catalysts are resistant to the normal poisons found in syngas plants. The sulphur from the frontend desulphurisation system that eventually slips through the reforming stage does not have any measurable impact.

In practice, silica is the poison of most concern to operators. Silica poisoning is easily avoided through correct selection of upstream refractory materials and catalyst bed support/ hold-down media.

Option to short load

The high activity of the **KATALCO** 71-series makes it possible to either short load the HTS converter or run at a lower inlet temperature to improve the CO equilibrium. In both cases, the cost of converting carbon monoxide to hydrogen and carbon dioxide is substantially reduced in comparison to other high temperature shift catalysts.

The excellent performance of the short-load option for **KATALCO** 71-5 is demonstrated in our case studies.

Resistance to plant upsets and boiler leaks

Resistance to plant upsets requires physical strength to withstand increased pressure drop from build-up of boiler solids, as well as combined physical strength and open pore structure to allow rapid wetting/drying cycles without damaging the pellets.

KATALCO 71-series products provide excellent in-service strength. This has been achieved through the use of a structural promoter that reinforces the microstructure of the catalyst in much the same way as reinforcing bars in concrete. The result is a more rugged product with greater resistance to process upsets, such as upstream boiler leaks.

Figure 5 demonstrates the superiority of **KATALCO** 71-series catalysts when subjected to an upstream boiler leak. With a conventional copper-promoted catalyst, the pressure drop increases steadily to 2 bar (30 psi) due to initial fouling of the catalyst, after which the catalyst pellets start to break.

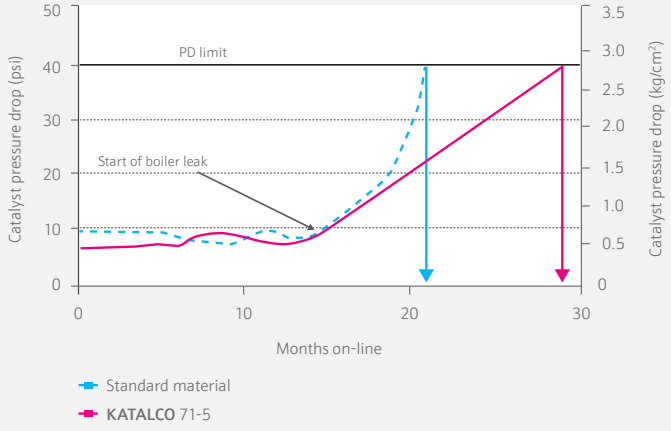

Figure 5: Robustness of KATALCO 71-5 extends life

With the more robust **KATALCO** 71-5, the steady boiler leak can be tolerated for much longer because the catalyst is better able to resist the crushing forces in the vessel. In this example, the maximum pressure drop for the support grid was 2.8 bar (40 psi), and, within this limitation, **KATALCO** 71-5 is able to extend the run time by 10 months.

For plants that operate under very highly stressed conditions (e.g., ammonia plants that have been significantly uprated), **KATALCO** 71-6 gives even greater resistance to boiler leaks. Commercial experience is discussed in one of the case studies.

Low pressure drop

Low pressure drop is achieved through pellet design and the ability of the catalyst to tolerate plant upsets, as covered above.

The **KATALCO** 71-series pellets are designed for low pressure drop. The 1.5-1.8 pellet aspect ratio (diameter/length) creates high voidage to produce more area for flow. This ratio has been optimized to deliver the best combination of pressure drop, strength and activity.

In addition to the aspect ratio, the standard Johnson Matthey Catalysts size is a nominal 9 mm x 5 mm that provides lower pressure-drop than 6 mm x 6 mm alternatives. The reduction is typically 0.07 bar (1 psi), saving US$ 50,000 during a 5 year life.

Easy to operate

KATALCO 71-5 and **KATALCO** 71-6 ranges of catalysts are the latest in the **KATALCO** 71-series of products, and, as such, they include all the benefits of their predecessors.

Low hexavalent chrome

The **KATALCO** 71-5 and 71-6 ranges of catalysts contain a very low proportion of water-soluble hexavalent chrome. This is particularly important in reducing the hazards to those handling the catalyst. Once in service, the trace amounts are converted to trivalent chrome. Carefully following plant shut-down procedures is required at end of run to minimize the formation of hexavalent chrome prior to discharge.

Operation at low steam ratio without by-product formation

The **KATALCO** 71-5 and 71-6 ranges of catalysts are copper promoted and are structurally designed to enhance activity and enable operation at low steam ratio without by-product formation.

Avoiding start-up exotherms

Johnson Matthey was the first to correctly diagnose the apparently random exotherms that occurred when introducing steam to fresh catalyst charges. This had been incorrectly attributed by some to hexavalent chrome formation. The cause is dehydration, usually from extended nitrogen purge at relatively high temperature that causes the catalyst surface to become 'super dry'.

Johnson Matthey's operating procedures both identify when this is likely to occur and advise a start-up procedure to avoid high temperatures. In any case, should an exotherm occur, practical experience shows that **KATALCO** 71-series catalysts survive these incidents without any detrimental effect. This is another demonstration of the excellent thermal stability of our products.

Rapid desulphurisation during initial start-up

KATALCO 71-series catalysts are manufactured by a nitrate route, whereas other commercially available high temperature shift catalysts are made via sulphate routes. These differing manufacturing techniques produce different characteristics in the finished product. By using the nitrate route to produce the **KATALCO** 71-series, any sulphur that is present in the catalysts is loosely attached and does not have the opportunity to become intimately bound up in the pore structure of the catalyst.

Typical desulphurisation profiles for new catalysts are shown below..

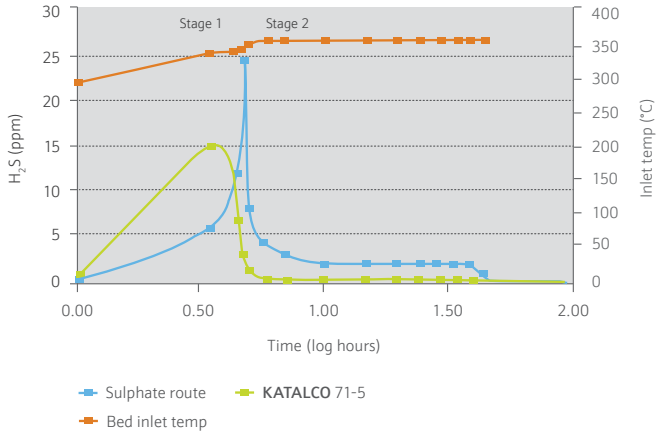

Figure 6: Desulphurisation of HTS catalysts

The H_2S evolved during stage one represents removal of the easily reduced sulphur that migrates to the surface, whereas that in stage two comes from sulphur that remains locked into the bulk of the structure (i.e. occluded species). Thus, stage two represents the rate determining — or slowest — step, and the time required for initial desulphurisation is largely dependent on the quantity of sulphur present in the bulk of the catalyst.

The majority of the sulphur in **KATALCO** 71-series catalysts is in an easily reduced form that is removed during the first five hours on-line, giving a profile typical of stage one. In catalysts produced by the sulphate route, the easily reduced sulphur species are removed during the final stages of manufacture, leaving behind those locked in the bulk of the structure. Thus, desulphiding of sulphate-route materials is slower because sulphur species bound up in the catalyst structure must be removed.

By employing the nitrate manufacturing route for all **KATALCO** 71-series catalysts, Johnson Matthey ensures the fastest start-up time is achieved.

Additional capability with **KATALCO PERFORMANCE**

STREAMLINE pressure drop reduction system

Many operators, particularly of ammonia plants, want to minimize pressure drop. The value of reduced pressure drop is typically US$10,000per psi or US$150,000 per 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 resulted from a thorough study of all of the pressure drop contributors in a shift converter. The 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 (01. 5psi) with **STREAMLINE** installed.
The saving from **STREAMLINE** in these cases is US$75,000per year, or US$375,000 during a five year life.

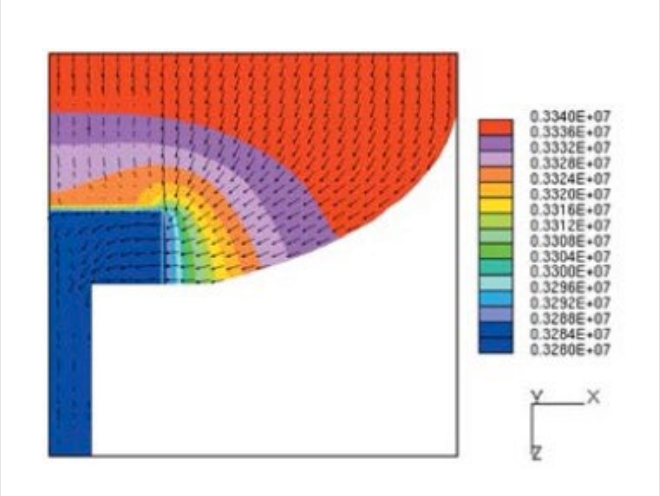

Figure 7: Pressure drop across a standard Kellogg shift reactor

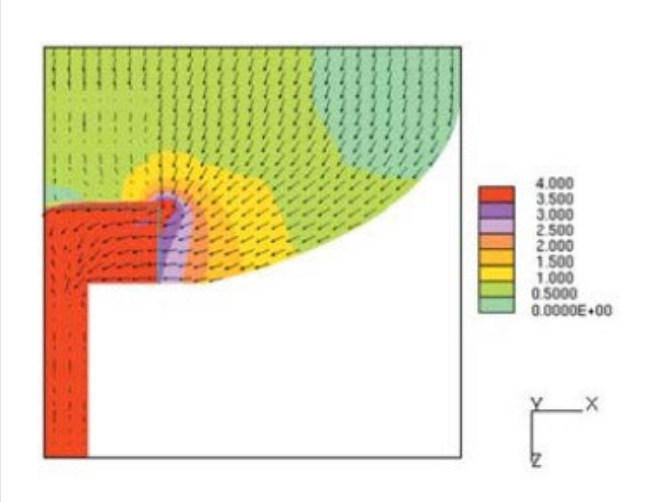

Figure 8: Pressure drop across a standard Kellogg shift reactor with STREAMLINE

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.

KATALCO catalyst selector

JM manufactures a range of high temperature shift catalysts, allowing the optimal choice for every plant's requirements.

KATALCO 71-5

This is the standard product for most applications and offers high, stable activity, low pressure drop and high in-service strength.

KATALCO 71-5M

This is a smaller (mini) size version with enhanced activity for use where a small pressure drop increase is acceptable. Note that reducing the catalyst volume in combination with installation of a **STREAMLINE** lower pressure drop gas collector system can reduce the overall pressure drop, despite using a smaller size catalyst.

KATALCO 71-6

The **KATALCO** 71-6 range delivers the highest activity, highest in-service strength and lowest pressure drop of any product available today. This is particularly beneficial to help resist damage from upstream boiler leaks, which are a significant risk on plants with high-pressure steam systems.

KATALCO 71-6M

This is a smaller (mini) size version of **KATALCO** 71-6 that exhibits outstanding activity and is ideal for use in radial flow reactors and where a small pressure drop increase is acceptable. Note that reducing the catalyst volume in combination with installation of a **STREAMLINE** lower pressure drop gas collector system can reduce the overall pressure drop, despite using a smaller size catalyst.

SHIFTSHIELD

Additional protection against boiler leaks can be gained through use of a layer of guard material. **SHIFTSHIELD** is a high surface area, high voidage inert support that is ideally suited for capturing boiler solids.

Johnson Matthey will make detailed recommendations about the optimal type and volume of catalyst for your application. The excellent performance of **KATALCO** 71-series products often exceeds the original plant design requirements, so a lower catalyst volume might be required to achieve the target number of turnaround cycles between catalyst change-outs.

STREAMLINE

Johnson Matthey developed **STREAMLINE** to help plants with high pressure drop across the HTS reactor. High pressure drops are usually due to either poorly designed exit collector arrangements or increased plant rate. **STREAMLINE** is a simple modification that, in many cases, gives a rapid return on investment.

Catalyst characteristics

KATALCO 71-5

High temperature shift catalyst

KATALCO 71-6

High temperature shift catalyst

KATALCO 71-5M

High temperature shift catalyst

KATALCO 71-6M

High temperature shift catalyst

Composition

KATALCO 71-5, 71-5M Iron/chrome with copper promoter and structure enhancer

KATALCO 71-6, 71-6M Iron/chrome with copper promoter and structural enhancer

Physical properties (typical)

Catalyst	71-5	71-5M	71-6	71-6M
Form	pellets	pellets	pellets	pellets
Diameter (mm)	8.5	5.4	8.3	5.2
Length (mm)	4.9	3.6	4.7	3.4
Typical loaded density (kg/m^3 / lb/ft^3)	1220 / 76	1220 / 76	1230 / 76	1250 / 76

Designed and produced by www.houseoftype.co.uk

For further information on Johnson Matthey, please contact your local sales representative or visit our website.

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