

JM

Methanation catalysts

KATALCO 11 series



Johnson Matthey
Inspiring science, enhancing life

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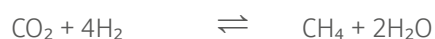
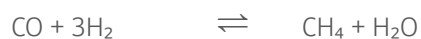


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Introduction

Most modern ammonia plants use the simple and convenient methanation reaction to remove traces of carbon oxides from the process gas. This involves the conversion of carbon oxides to methane and water by the use of a nickel catalyst:



The methanation reaction has been well-known for more than 70 years and applied to a variety of industrial processes. It was not until the 1950s, however, when hydrocarbon steam reforming was being introduced, that methanation could be used more extensively in the ammonia process. Relatively low levels of carbon oxides limited the temperature rise during reaction and extended catalyst life. Now that even better catalysts are available, low temperature carbon monoxide conversion followed by removal of carbon dioxide and methanation is the most widely used process gas purification procedure.

Although the major use of methanation catalysts is in ammonia synthesis and hydrogen plant purification, several other important applications have been developed. Examples include the production of substitute natural gas from a variety of feedstocks and removal of carbon oxides from hydrogen-rich off-gas streams in olefin crackers and oil refineries.

Features and benefits



Catalyst features

- High stable activity
- Maintains high strength and low pressure drop
- Available in 2 sizes for optimum performance
- Can be back-washed to remove contaminants
- Unaffected by high temperature excursions
- Operates with high water vapour content
- Available in pre-reduced form for maximum activity

Operational benefits

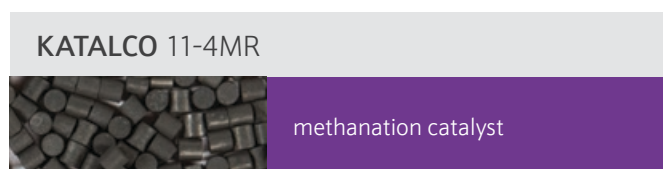
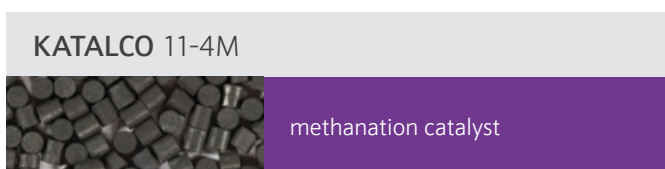
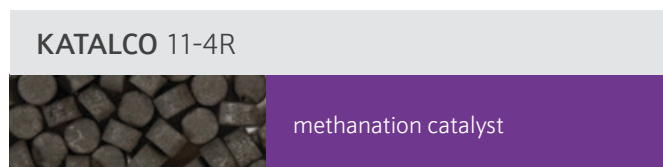
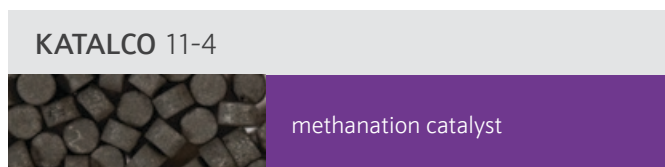
- Reliable and trouble-free operation
- Minimum carbon oxides slip
- Long lives
- Economic performance

Johnson Matthey experience

- 60 years experience in production and operation
- Unique range of reliable products
- Superior performance in all applications
- Comprehensive technical support available
- Quality assured to international standard

Catalyst characteristics

KATALCO™ 11-series



Composition

KATALCO 83-3 & 83-3M:
nickel oxide and promoters combined with a calcium aluminate cement support.

KATALCO 83-3X & 83-3MX:
nickel and promoters combined with a calcium aluminate cement support.

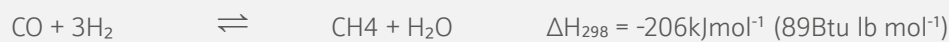
Physical properties (typical)

Catalyst	11-4	11-4R	11-4M	11-4MR
Form	cylindrical pellets	cylindrical pellets	cylindrical pellets	cylindrical pellets
Diameter (mm)	5.4	5.4	3.1	3.1
Length (mm)	3.6	3.6	3.6	3.6
Typical nickel content (% Ni as NiO / % Ni)	35 / -	- / 30	35 / -	- / 30
Charged bulk density (kg/l / lb/ft ³)	1.23 / 77	1.1 / 69	1.23 / 77	30 1.1 / 69
Mean axial crush strength (kgf / lbf)	130 / 290	90 / 200	45 / 100	30 / 70

The pre-reduced catalysts **KATALCO 11-4R** and **11-4MR** have been reduced and stabilised with an oxide layer which makes the catalyst stable in air and prevents further re-oxidation. These catalysts require no activation stage and initiate methanation at maximum activity as soon as reaction conditions are established.

The methanation reaction

The two methanation reactions are strongly exothermic. Because operation is at relatively low temperatures and only small amounts of water are present, thermodynamics does not control conversion in ammonia plant duties.

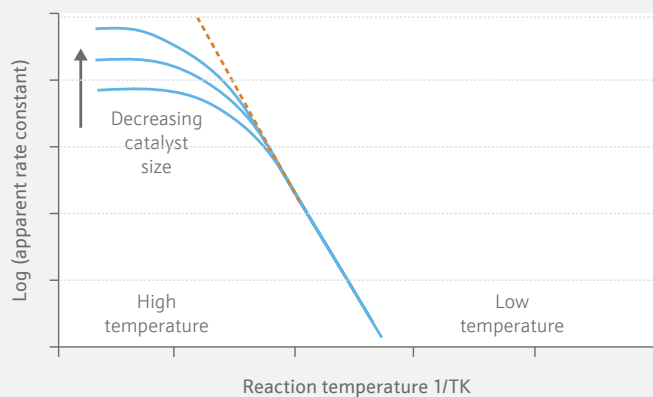


In practice it is unlikely that side reactions will have an adverse effect during operation and the conversion of carbon oxides will be virtually complete.

The temperature rise for typical methanator gas compositions in ammonia plants is about 74°C (133°F) for each 1% of carbon monoxide converted and 60°C (108°F) for each 1% of carbon dioxide converted.

At higher temperatures, the intrinsic rates of both methanation reactions can become sufficiently fast for diffusion effects to become important as shown below.

Graph showing progressive diffusion limitation at higher temperatures



Under these conditions, film diffusion controls the overall rate of reaction. Diffusion limitations can be overcome to some extent by the use of a smaller particle size, such as **KATALCO 11-4M**, to provide a higher geometric surface area to enhance mass transfer.

The methanation process

Methanation is the final stage in the purification of ammonia synthesis gas when small amounts of carbon monoxide or carbon dioxide (0.1-1.0% total) are removed by reaction with hydrogen using a nickel catalyst.

A simple adiabatic reactor is used downstream of the conventional carbon dioxide removal step. Most methanators tend to run at an inlet temperature between 260 and 320°C (500-610°F) with space velocities around 5000 - 9000hr⁻¹. **KATALCO 11-4** is formulated to perform over this range of conditions and 10 year lifetimes are well-known with some examples almost double this.

As a result of the very high activity it demonstrates **KATALCO 11-4R** can operate at even lower inlet temperature or higher space velocities. There are examples of **KATALCO 11-4R** running at an inlet temperature of 250°C (482°F) after 10 years and still exhibiting the same sharp temperature profile they had at start of run.

KATALCO 11-4M and **KATALCO 11-4MR** both have proportionally higher activity as a result of their smaller size and are designed for use in smaller beds or where the higher activity is of more benefit than the penalty incurred due to extra pressure drop.

Methanation must be almost 100% complete to ensure that the ammonia synthesis catalyst maintains its maximum productivity because synthesis catalyst is rapidly poisoned by carbon oxides and its long term activity is severely affected.

The presence of carbon dioxide in ammonia synthesis gas may also lead to the formation of solid ammonium carbamate if make-up gas meets circulating gas which contains ammonia. This can restrict gas flow and foul the compressor. The presence of carbon oxides in hydrogen streams must also be avoided to prevent deactivation of downstream hydrogenation catalysts.

The concentration of carbon oxides is usually reduced to less than 5ppm in process gas leaving the methanator. Methane formed during methanation does not cause problems and simply acts as an inert diluent.

Typical process gas compositions and conditions for ammonia plant methanation reactors

	Inlet	Outlet
Composition (%)		
CO	0.4	} <5ppm
CO ₂	0.2	
H ₂	74.7	74.1
CH ₄	0.25	0.95
N ₂	24.1	24.7
Ar	0.3	0.3
Temperature		
(°C)	300	347
(°F)	572	657

Catalyst formulation

Almost all industrial methanation catalysts are based on nickel oxide supported by various refractory oxides, such as alumina-silica-lime-magnesia, often strengthened with calcium aluminate cement. Nickel oxide must be reduced to nickel metal in the plant reactor before use. Successful catalysts must, therefore, be easily reduced, have a high, stable activity and retain a high strength for long periods. This is achieved with **KATALCO** 11-Series catalysts by forming a NiO-MgO solid solution to provide a structure in which crystallite growth (sintering) of nickel oxide during manufacture, or nickel metal during operation, is negligible. The only significant form of de-activation during operation is poisoning.

High strength in **KATALCO** 11-Series catalysts is provided by calcium aluminate cement binders which set after forming the pellets. As a result, no strength is lost during the nickel oxide reduction, and the pellets neither shrink nor break up during use.

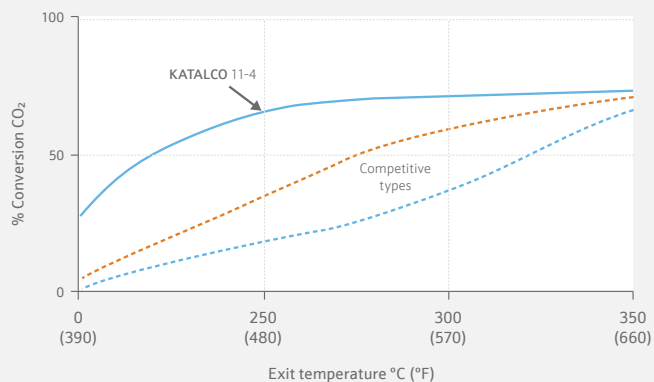
The formulation of methanation catalysts is discussed in more detail by Bridger and Woodward, "Methanation of Synthesis Gas", Advances in Chemistry Series, No. 146, 1975.

Lives of more than ten years are commonly obtained from charges of **KATALCO** 11-Series catalysts, depending on the operating temperature and on the poisons present in the ammonia synthesis gas.

JM methanation catalysts have been formulated to give high, stable activities. This has been demonstrated by semi-technical scale experiments in our Research Laboratories. Catalysts are operated under severe test conditions, in order to illustrate differences in activity.

The graph below shows results for carbon dioxide conversion, which is normally less complete than for carbon monoxide.

Comparative CO₂ methanation activities



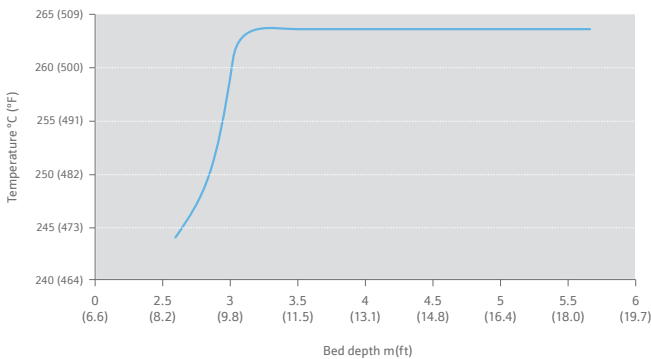
Operating experience

Long life with stable activity

JM has many charges of **KATALCO 11-Series** catalyst installed around the world. Operating experience with these catalysts has demonstrated that extremely long reliable lives are achieved with reasonable care in operation. The catalyst activity remains virtually constant and aged catalyst can be run at the same inlet temperature as when initially installed and still exhibit a sharp temperature profile, typically in the first 25% of the bed.

The methanation reaction is strongly exothermic so that there is a sharp rise in temperature across the reaction zone in the catalyst bed. Most methanation reactors are designed with a number of thermocouples to monitor the position of the exotherm. A strong indicator of the amount and rate of methanation catalyst deactivation is the position of the temperature profile in the catalyst bed and its rate of movement over time.

Temperature profile in an European 1000 MTPD ammonia plant (20m³/710 ft³ catalyst)



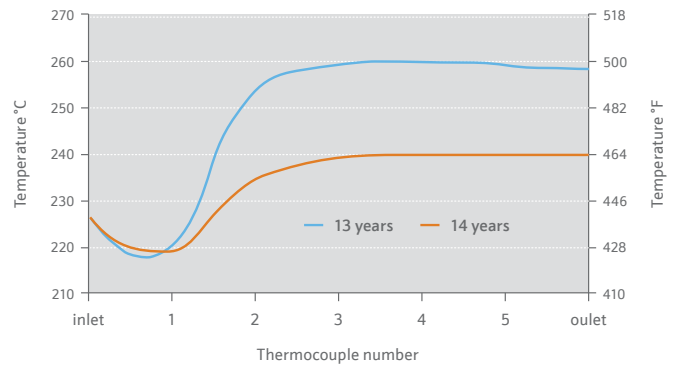
KATALCO 11-Series catalysts have demonstrated that lives well in excess of ten years can be achieved as shown in the following examples which also demonstrate other features of the catalysts.

Low temperature activity

A particular feature of the **KATALCO 11-Series** catalysts is the low strike temperature which, combined with the high stable activity, allows continuous operation at low inlet temperatures, down to 240°C (464°F) or lower. There are examples of operation at inlet temperatures as low as 200°C (392°F) for long periods.

An excellent example is a charge that has been installed in a refinery hydrogen plant in the Middle East since the mid-1980s.

KATALCO 11-Series stable after 14 years



The temperature profile after 13 and 14 years continuous operation showed no movement of the profile in the year, and the required < 10 ppm carbon oxides slip has been maintained throughout and the inlet temperature is still only 220°C (428°F).

The exotherm peaking between the 3rd and 4th thermocouple confirms the long term stability of the catalyst. The decrease in the magnitude of the exotherm was a result of the renewal of the upstream low temperature shift catalyst and the resultant decrease in CO inlet the methanator actually makes the methanation duty more difficult.

Robust performance

There are many examples of the rugged nature of **KATALCO** 11-Series catalysts and their ability to withstand a variety of operational upsets.

Case 1

A plant operator was running with a very high level of water (7%) in the feed to the methanator and 3 charges of competitive catalysts all failed to achieve the design carbon oxides slip of 5ppm. Each charge was discharged after less than one year's operation. **KATALCO** 11-Series catalyst was installed and ran for 7 years at 120% of design rate and achieving below 5ppm carbon oxides slip.

Case 2

In a further instance, an operator suffered gross carry-over of Benfield solution from the CO₂ removal system and successfully back-washed the 5 year old **KATALCO** 11-Series catalyst with demineralized water before returning it to service. The procedure was repeated following a second carry-over onto the same catalyst several months later and the catalyst was once again successfully brought back into service. The high strength and rugged nature of the catalyst were amply demonstrated by the minimal increase in pressure drop over the life of the catalyst.

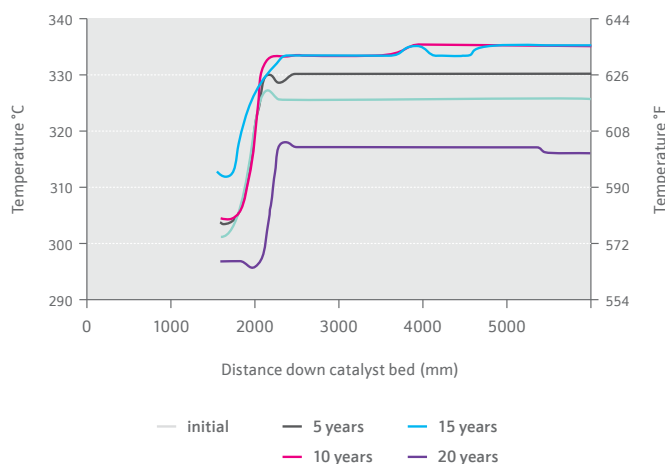
KATALCO 11-3 Series catalysts can last for more than 20 years!

One example which demonstrates all of the features of the KATALCO 11-Series catalysts comes from a plant which has now been operating the same charge of catalysts for 21 1/2 years!

The plant has operated continuously at high loads with an exit carbon oxides level of less than 5ppm while the inlet carbon oxides were varying between 0.16-0.46% depending on the condition of the low temperature shift reactor.

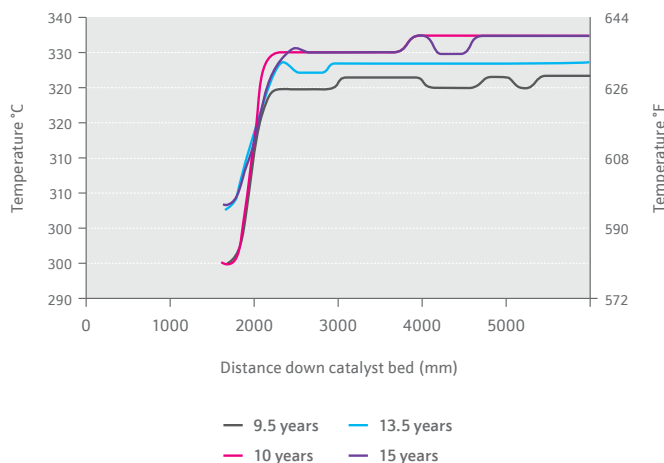
Temperature profiles at 5 yearly intervals in its life are shown below and the sharp exotherm profile and the lack of movement of the profile clearly demonstrate the high stable activity.

KATALCO 11-Series catalysts can last for more than 20 years



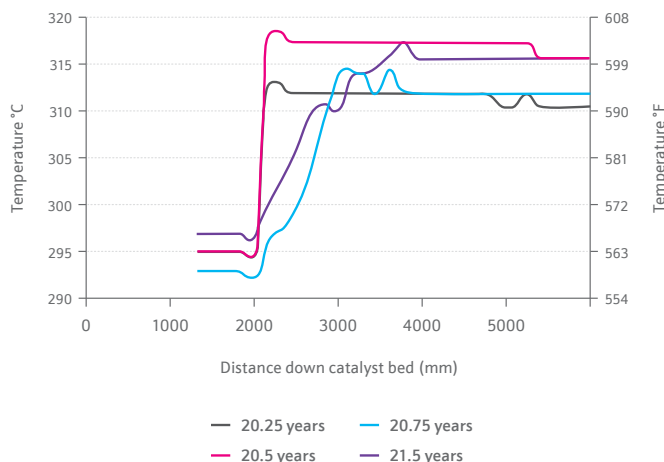
But this does not tell the complete story! In 1989, when the catalyst had been in operation for 10 years, the methanation vessel was due for a mechanical inspection. This required the catalyst to be discharged in the reduced state. Since the temperature profiles were sharp and in the top 30% of the catalyst bed, Johnson Matthey (JM) suggested reusing the same catalyst after the inspection. The operator agreed and the catalyst was discharged under nitrogen, sieved and recharged under the supervision of JM personnel. On recharging the catalyst was returned as far as possible to the position in the bed occupied prior to discharge. The small amount of catalyst lost by breakage during the operation was replaced with fresh catalyst charged on the top of the bed. The plant restarted with the same sharp profile which was maintained a further 10 years.

Activity maintained after discharge and recharge



In May 1999, after more than 20 years' operation of the catalyst, the plant had a problem with Benfield solution carry-over from the CO₂ removal system and the pressure drop increased rapidly. Back-washing with hot water to remove solid deposits is a well-proven and reliable way to recover most of the activity and reduce pressure drop. This was done with JM supervision and the catalyst warmed slowly to dry it out. The catalyst was then put back on line and has been operated successfully for a further year. The graph below shows that the catalyst activity was not completely restored and there is a slightly less sharp profile, but the plant is still readily achieving the required exit level of a maximum of 5ppm carbon oxides.

Temperature profiles before and after back-washing



Catalyst poisons

Methanation catalysts are not usually deactivated by thermal sintering and the principal reason for any loss of activity is poisoning. Sulphur compounds will poison methanation catalyst but they are not usually present in process gas unless the low temperature shift catalyst is bypassed. The poisons most likely to occur under normal operating conditions are those originating from

the carbon dioxide removal system which precedes the methanator. Carry-over of a small amount of liquid into the methanator is not serious. Large volumes of liquid will have a serious effect, particularly if the liquid contains arsenic or sulphur, because irreversible loss of activity results.

Poisoning effect of liquids used in CO₂ removal systems

Process	Chemical	Effect
Benfield	Aqueous potassium carbonate	Blocks pores of catalyst by evaporation of K ₂ CO ₃ solution.
Vetrocoke	Aqueous potassium carbonate plus arsenious oxide.	Blocks pores of catalyst by evaporation of K ₂ CO ₃ solution. As ₂ O ₃ is also a poison - 0.5% of As on the catalyst will reduce its activity by 50%.
Benfield DEA	Aqueous potassium carbonate with 3% diethanolamine.	Blocks pores of catalyst by evaporation of K ₂ CO ₃ solution. (DEA is harmless).
Sulphinol	Sulpholane, water, di-2-propanolamine	Sulpholane will decompose and cause sulphur poisoning.
MEA, DEA	Mono- or di-ethanolamine in aqueous solution.	None
MDEA	Aqueous solution of Methyl-di-ethanolamine and activators	None
Rectisol	Methanol.	None
Catacarb	Aqueous potassium carbonate with borate additive	Blocks pores of catalyst by evaporation of K ₂ CO ₃ solution.
Selexol	Dimethyl ether of polyethylene glycol.	None

When only potassium carbonate or organic solvents are used the effects are less important. Potassium carbonate blocks the catalyst pores, and can be removed by washing with water to restore normal performance.

Methanation catalysts can be protected from poisons by installing a guard bed of zinc oxide absorbent. This will remove traces of sulphur and droplets of liquid from the carbon dioxide removal system.

Methanator design

The operating life of **KATALCO** 11-Series catalysts is usually longer than the lives of other upstream catalysts in an ammonia plant. Providing that there are no major plant upsets, such as gross carry-over of liquor from the carbon dioxide removal system, it is unlikely that **KATALCO** 11-Series catalysts will need to be changed before the design life of 4-6 years has been completed. **KATALCO** 11-Series catalysts are, in fact, more likely to survive until the statutory vessel inspection. The normal rate of deactivation simply depends on any poisons present in the process gas which enter the catalyst bed. These cannot be anticipated from the plant design and a record of the temperature profile must be kept to detect any movement during the first 1-2 years of operation. An estimate of future life can then be made.

The optimum catalyst volume for each plant depends upon the operating conditions, in particular the inlet gas composition, gas flow rate, operating temperature and pressure and the required carbon oxides content in the outlet gas. From a wide design and operating experience, JM will always make recommendations on the optimum catalyst volume to suit each customer's requirement.

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