JM

Catalysts for olefin processes

A range of performance catalysts and absorbents for use across the olefins value chain.

Johnson Matthey
Inspiring science, enhancing life

Why Johnson Matthey?

We have been leaders in our field for more than 200 years, applying unrivalled scientific expertise to enable cleaner air, improved health whilst making more efficient use of our planet's natural resources. Through continued investment in sound research and development, we are tackling the world's big challenges into our third century and beyond.

As the global population grows and demographics change, consumer expectations are putting pressure on chemical producers to produce more for less. Johnson Matthey (JM) has continued to supply and adapt our high performance catalysts and technology to rapidly changing customer requirements.

High performance catalysts

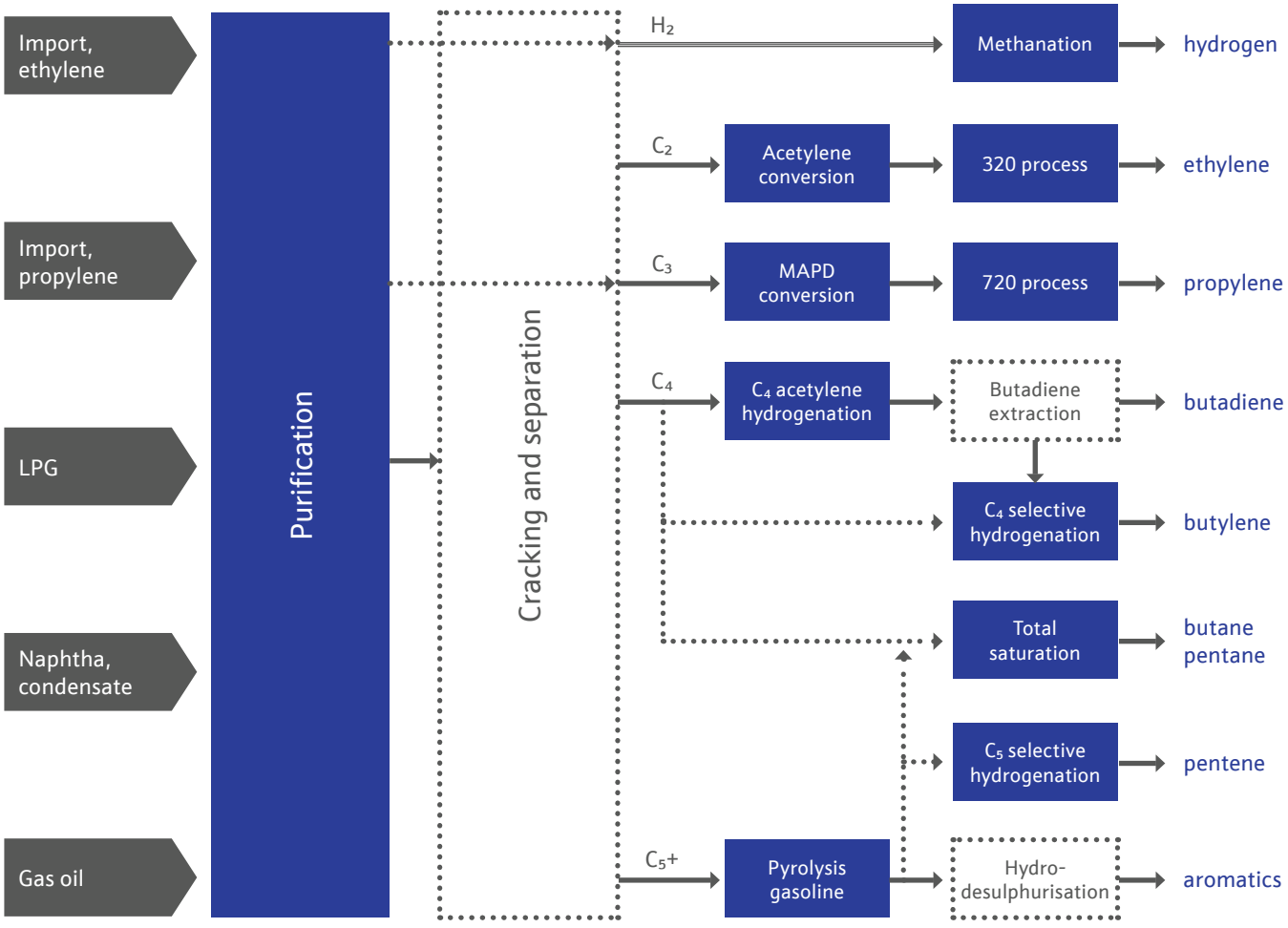
Our customer focus enables us to maintain prominent positions in catalyst supply and new product development for the petrochemical, syngas, refining, gas processing and purification industries.

Olefins are key components within the industrial chemicals sector. Our **PRICAT™**, **HTC™**, **PURASPEC™** and **KATALCO™** ranges of catalysts have been developed, demonstrated, scaled-up and commercialised across a range of duties and have been designed to deliver maximum selectivity and enhanced lifetimes, ensuring product quality, reliability and cost effectiveness.

JM has a dedicated team of scientists developing leading selective hydrogenation catalysts for use across the olefins value chain. Combining our research and development capability with our vast experience in process engineering, technical services and catalyst manufacturing we can help our existing and new customers extract more value from their operations.

Olefins value chain

JM offers a portfolio of catalysts designed for the olefins value chain. Additionally, we actively collaborate with customers and partners to develop tailored solutions for process specific duties.



■ Blue areas indicate the JM offering

Acetylene conversion

Global industry requirements demand acetylene to be reduced to less than 1 ppm. JM offers catalysts for selective hydrogenation, for both ethylene plant configurations: front-end and tail-end.

Front-end configuration

The **PRICAT** PD 308 catalyst series is formulated to ensure complete acetylene removal in front-end converters whilst avoiding significant ethylene hydrogenation. All versions of **PRICAT** PD 308 are designed to reduce the acetylene concentration to less than 1 ppm.

The front-end acetylene converter is located upstream of the cold box prior to the separation of hydrogen from the olefins. In addition to acetylene and ethylene, the feed contains various amounts of hydrogen, carbon monoxide and heavier hydrocarbons, depending on the distillation configuration.

	PRICAT PD 308/1	PRICAT PD 308/4	PRICAT PD 308/6	PRICAT PD 308/7
Active metal	Pd	Pd	Pd	Pd
Promoted	yes	yes	yes	yes
Size (mm)	3 x 3	3 x 3	3 x 3	3 x 3
Shape	tablet	tablet	tablet	tablet
Support	alumina	alumina	alumina	alumina
Service				
de-ethaniser	-	-	yes	-
de-propaniser	-	-	yes	yes
raw gas	yes	yes	-	-

PRICAT PD 308/6 is suitable for low CO concentrations.

Tail-end configuration

The tail-end acetylene converter is located downstream of the cold box and de-ethaniser. The feed contains acetylene, ethylene, ethane and only a trace of lighter and heavier compounds. A controlled amount of hydrogen is added to effect the selective hydrogenation of acetylene.

The **PRICAT** PD 608 series has been formulated to achieve complete acetylene removal in tail-end converters whilst retaining a high selectivity to ethylene. Carbon monoxide is not required for the operation of the 608 series but with it selectivity gains can be made and green oil formation rates are minimised.

	PRICAT PD 608/1
Active metal	Pd
Promoted	yes
Size (mm)	2 - 4
Shape	sphere
Support	alumina
Service	
lead bed	yes
middle bed	yes
clean-up bed	yes

MAPD conversion

Selective hydrogenation can be used in the C_3 (propylene) cut from the steam cracking operation. Although a co-product itself, propylene streams from cracking can carry up to 2% methyl acetylene (MA) and 1.5% propadiene (PD). By employing selective hydrogenation we can convert these impurities to chemical grade propylene. This route offers considerable efficiencies compared to processes which downgrade to propane instead. This selective hydrogenation unit can be located on the distillate of the depropaniser or the bottoms of the de-ethaniser, depending on the main plant configuration. We offer catalysts for MAPD converters configured as liquid phase reactors.

Liquid phase converter

The liquid C_3 cut is pressurised and a controlled amount of hydrogen is added to effect the selective hydrogenation of MAPD. **PRICAT** PD 309/3 and **PRICAT** PD 468 are formulated to ensure complete MAPD removal whilst avoiding significant propylene hydrogenation through high selectivity operation.

	PRICAT PD 309/3	PRICAT PD 468
Active metal	Pd	Pd
Promoted	no	yes
Size (mm)	2 - 4	2 - 4
Shape	trilobe extrudate	sphere
Support	alumina	alumina
Service	liquid phase	liquid phase

PRICAT PD 309/3 is suitable in high LHSV situations; high recycle rate lead beds.

PRICAT PD 468 is formulated to minimise propylene hydrogenation.

Hydrogenation

C_4 acetylene hydrogenation

The modern specification for combined C_4 acetylenes in butadiene product is less than 10 ppm. C_4 acetylene can be separated from butadiene as part of the extraction process, however considerable efficiencies are available by converting vinyl acetylene to butadiene and ethyl acetylene to 1-butene instead of downgrading to fuel.

This selective hydrogenation unit can be located downstream of the debutaniser as part of the steam cracker complex or upstream of the first extractor in the butadiene extraction unit.

JM offers combined engineering and catalyst packages for C_4 streams.

C_4 selective hydrogenation

Butylene yield can be improved by selective hydrogenation of the co-produced acetylenes and butadiene to butylene.

After butadiene extraction, the butylene rich raffinate contains up to 1% butadiene which must be reduced to 100 ppm or less via selective hydrogenation.

A single, liquid phase adiabatic reactor is suitable for feed containing up to 1% butadiene. For a higher feed concentration liquid recycle may be required.

Our range of **PRICAT** PD catalysts cater for different applications and customer requirements, our technical service team can discuss these with each customer and advise on which of the range would be most suitable for the desired C_4 duties.

C_5 selective hydrogenation

After the first stage of pyrolysis gasoline processing, the pentenes rich distillate may contain up to 1% dienes which must be reduced to 100 ppm or less via selective hydrogenation for most downstream processes.

PRICAT PD catalysts cater for different applications and customer requirements, our technical service team discuss these with each customer and advise on which of the range would be most suitable for the desired C_5 duties.

Total saturation

The yield of C_4 and C_5 unsaturates from ethane and propane is normally less than 100 kg per MT of ethylene produced. Many ethylene plant operators prefer to saturate and recycle back to the cracker instead of shipping offsite for further processing.

Cracker feeds should contain less than 5% unsaturates in order to maximise ethylene yield and minimise heater coking. LPG products should contain less than 0.5% unsaturates.

We support our customers in catalyst selection for total saturation duties by considering the feed composition and operating parameters, we then determine the optimal catalyst from the **PRICAT** and **HTC** series.

Pyrolysis gasoline

Raw pyrolysis gasoline contains a high level of unsaturated hydrocarbons (olefins and aromatics) making it an excellent source of aromatics and high octane gasoline components, but it must be hydrotreated before further processing. Eliminating acetylenes, dienes and aromatic olefins in this pyrolysis gasoline can produce a number of important benefits:

- improve the induction period and colour,
- reduce gum content of gasoline blending components,
- reduce fouling in the downstream hydrodesulphurisation unit.

HTC NI 200 is the leading nickel catalyst for all designs of pyrolysis gasoline hydrogenation units. **HTC** NI 400 is a higher activity product to handle higher feed rates, more stringent product specifications and higher olefin saturation.

PRICAT PD 309/6 is a palladium catalyst formulated for operation in palladium duties.

Nickel vs. palladium

Two-thirds of all pyrolysis gasoline units were designed to operate with palladium catalysts. The **PRICAT** PD 309/6 catalysts offer simple activation, high aromatic selectivity and high olefin selectivity. Lower olefin saturation results in lower hydrogen consumption and higher octane C_5 and C_9+ cuts. Enhanced olefin saturation is available with **PRICAT** PD 309/6 by formulating with higher palladium content or operating at an elevated temperature.

HTC NI catalysts have an order of magnitude higher tolerance for heavy metals and sulphur in the feed than any palladium based catalyst. There is no detectable aromatic loss with properly activated **HTC** NI catalysts.

HTC NI products come in three types to suit different activation situations. Once activated, all forms exhibit equally good performance characteristics. RPS catalysts are activated within the normal operating temperature range of the unit without the addition of sulphur.

Pyrolysis gasoline catalysts

	HTC NI 200	HTC NI 400	PRICAT PD 309/6
Active metal	Ni	Ni	Pd
Promoted	no	no	no
Size (mm)	2.5	2.5	2.5
Shape	trilobe extrudate	trilobe extrudate	trilobe extrudate
Support	alumina	alumina	alumina

Types of HTC NI catalysts

	OX	OXS	RPS
Reduction temperature	high	moderate	lowest
Sulphur action	standard	none	none

Purification

Feedstock purification

The new generation of **PURASPEC** absorbents have been shown to effectively remove contaminants and improve operating and long life without impacting product quality.

Feedstocks are being sought from alternate sources in order to increase the profitability of plants. These feedstocks bring with them new contaminant challenges.

Mercury is found in an ever-increasing number of hydrocarbons worldwide. The level of mercury can vary significantly depending on location. Complete removal of mercury is advisable to avoid catastrophic failures in cryogenic equipment, to prevent poisoning of process catalysts and for health and safety reasons.

Crude olefin streams from refinery sources can bring elevated levels of carbonyl sulphide, chloride and arsine which can affect the performance of catalysts and equipment.

PURASPEC series for olefin plant feed purification

Removal	Mercury removal	COS removal	Arsine removal	Chloride removal	H_2S and COS
LPG feed	**PURASPEC** 5158	**PURASPEC** 5312	-	**PURASPEC** 5110	**PURASPEC** 5040
Naphtha, condensate	**PURASPEC** 5158	-	-	-	-
Import ethylene	-	-	-	**PURASPEC** 3110	**PURASPEC** 3020
Import propylene	-	**PURASPEC** 7312	**PURASPEC** 7151	**PURASPEC** 7110	**PURASPEC** 7085
C_3 and C_4 fraction	**PURASPEC** 7168	-	-	-	-

The above table contains a sample of materials available for purification duties. We will provide advice on which products are most suitable for individual applications.

Monomer purification

Several **PURASPEC** products have been developed to meet the most demanding purity requirements of polyethylene producers, polypropylene producers and other users of high purity ethylene and propylene.

We can provide a full range of products to ensure an economic purification solution.

PURASPEC 3020	Hydrogen sulphide is reduced to less than 0.1 ppm
PURASPEC 3410	Acetylene is reduced to less than 0.5 ppm in a bed A small amount of hydrogen is added to effect the reaction
PURASPEC 3450	Carbon monoxide is reduced to less than 0.1 ppm by operating in the oxide form Oxygen is reduced to less than 0.1 ppm by operating in the reduced form
PURASPEC 7110	Hydrogen chloride is reduced to less than 0.1 ppmw
PURASPEC 7312	Carbonyl sulphide is converted to hydrogen sulphide to facilitate sulphur removal A small amount of water is added to the feed to effect this reaction
PURASPEC 7040	Hydrogen sulphide and carbonyl sulphide are reduced to less than 0.1 ppmw total sulphur
PURASPEC 7151	Arsine is reduced to less than 50 ppbw

Methanation

Hydrogen produced as a by-product of ethylene production contains 500 to 5,000 ppm carbon monoxide. The concentration of carbon monoxide must be reduced to less than 10 ppm prior to use in reactors containing palladium or platinum based catalysts. The most common method of carbon monoxide reduction is nickel catalyst based methanation. Purification using pressure swing adsorption, cryogenic ethane wash and low temperature ruthenium catalysts are also used.

KATALCO 11-4 is the widely suitable replacement catalyst for all designs of methanators. **KATALCO** 11-4M provides higher activity for higher GHSV operation with a slight increase in pressure drop.

The pre-reduced catalysts **KATALCO** 11-4R and **KATALCO** 11-4MR have been reduced and stabilised with an oxide layer which makes the catalyst stable in air and prevents further reoxidation.

These catalysts require no activation stage and initiate methanation at maximum activity as soon as reaction conditions are established.

Methanation catalysts

	KATALCO 11-4R	**KATALCO 11-4MR**	**Type 146**
Active metal	Ni	Ni	Ru
Promoted	yes	yes	-
Size (mm)	5.4 x 3.6	3.1 x 3.6	3 x 3
Shape	tablet	tablet	tablet
Support	refractory oxides	refractory oxides	refractory oxides
Pre-reduced	yes	yes	n/a

Designed and produced by www.houseoftype.co.uk

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