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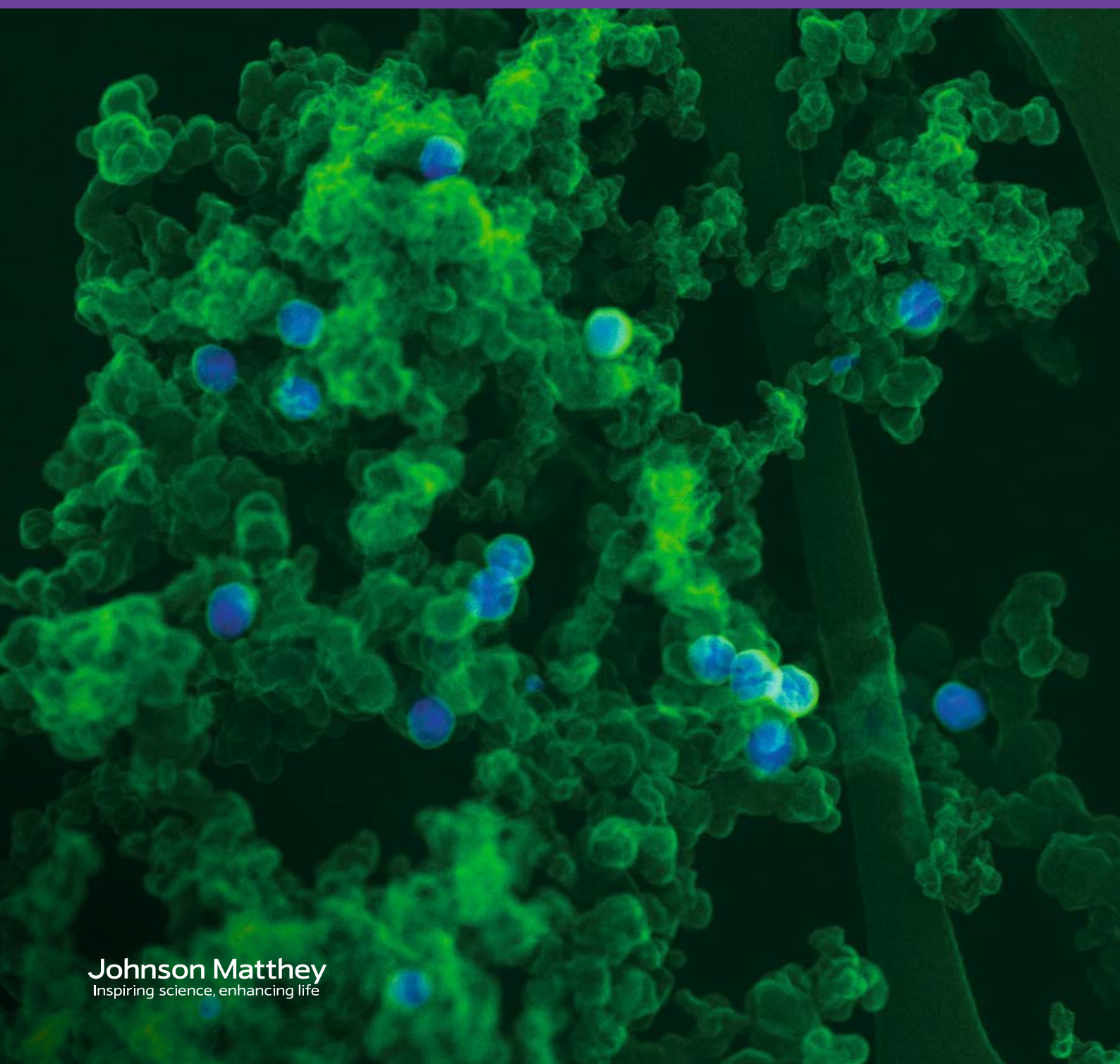Inspiring science, enhancing life

White paper

Maximising performance through understanding supported PGM catalyst deactivation

Dr Steve Wainwright

Product Specialist, Heterogeneous Catalysts

Johnson Matthey

Steve studied at the University of York, UK, completing his MChem degree in 2006 and MSc in Liquid Crystals and Nanoscience in 2007. This was followed by an EPSRC funded PhD in heterogeneous PGM catalysts, completed in 2012 at the University of York. He then joined Syngenta as a Physical Chemist for 2 years researching co-crystals of APIs.

In 2014, Steve joined Johnson Matthey as a Development Chemist, focusing on developing new industrial heterogeneous PGM catalysts for petrochemical and bio-renewable applications from inception, through scale-up and manufacture.

In his current role as Product Specialist, Steve is responsible for a portfolio of heterogeneous catalysts, supporting the development and manufacture of new and existing catalysts within the business.

Dr Danny Mortimer

Global Technical Service Leader

Johnson Matthey

Danny studied at the University of York, UK, completing his MChem degree in 2007. This was followed by a GSK funded PhD in organic chemistry completed in 2011 at the University of Sheffield. He subsequently spent a year at Argenta and Biofocus as a Medicinal Chemist.

In 2012, Danny joined Johnson Matthey as a Research Chemist, working as part of a research team that combines organic chemistry evaluation for the design, preparation, and development of new supported platinum group metal heterogenous catalyst powders. Following this, he worked as a Product Specialist, managing the heterogeneous PGM catalyst portfolio.

His current role is Global Technical Service Leader for Johnson Matthey's Catalyst Technologies business, which specialises in the application of PGM heterogeneous catalysts for fixed-bed and slurry reactors used in the downstream petrochemical and fine chemical industries.

How Johnson Matthey can work with you

- Johnson Matthey (JM) can provide expert insight into identifying optimal catalysts for your processes
- Our experts perform parallel screening experiments to assist in defining optimum process parameters
- We optimise unit operations for catalytic steps, improved catalyst mileage, reduced metal inventory, and improved impurity profile

JM is committed to building strong relationships by providing a flexible approach that meets the specific needs of our customers. With our cutting-edge global manufacturing capabilities – and expertise in closed loop supply through precious metal refining – we can streamline your catalytic processes to maximise profit.

Heterogeneous supported PGM catalysts

Chemical catalysis by platinum group metal (PGM) based materials is an essential synthetic technology in the fine chemical industry. The role of a catalyst is to accelerate the rate of a reaction, while not itself being consumed in the reaction. This allows target molecule production to be both efficient and economically viable. Heterogeneous supported PGM catalysts used in fine chemical reactions are made of platinum group metal particles (Pd, Pt, Ru, Rh) immobilised on a porous support, e.g. activated carbon, oxides, graphite. Their reactivity is controlled by a range of factors including the size and shape of the crystallites, their dispersion on the support, doping with other metals (e.g. Pb, Fe, Cu), the metal oxidation state and the nature of the support itself. Supported heterogeneous PGM catalysts are employed in a different phase to the reactants and are routinely used to carry out liquid phase hydrogenations (hydrogen gas – liquid – solid) in a batch reactor setup (Figure 1a). A catalyst powder slurried with liquid phase reactants in a batch or continuous process (e.g. stirred tank or bus loop reactor) can be easily separated at the end of the reaction by filtration. Alternatively, catalyst particulates can be used in a fixed-bed reactor setup (Figure 1b), through which reactants pass over the catalyst in the gas or liquid phase (e.g. trickle-bed, multi-tubular, up/downflow).
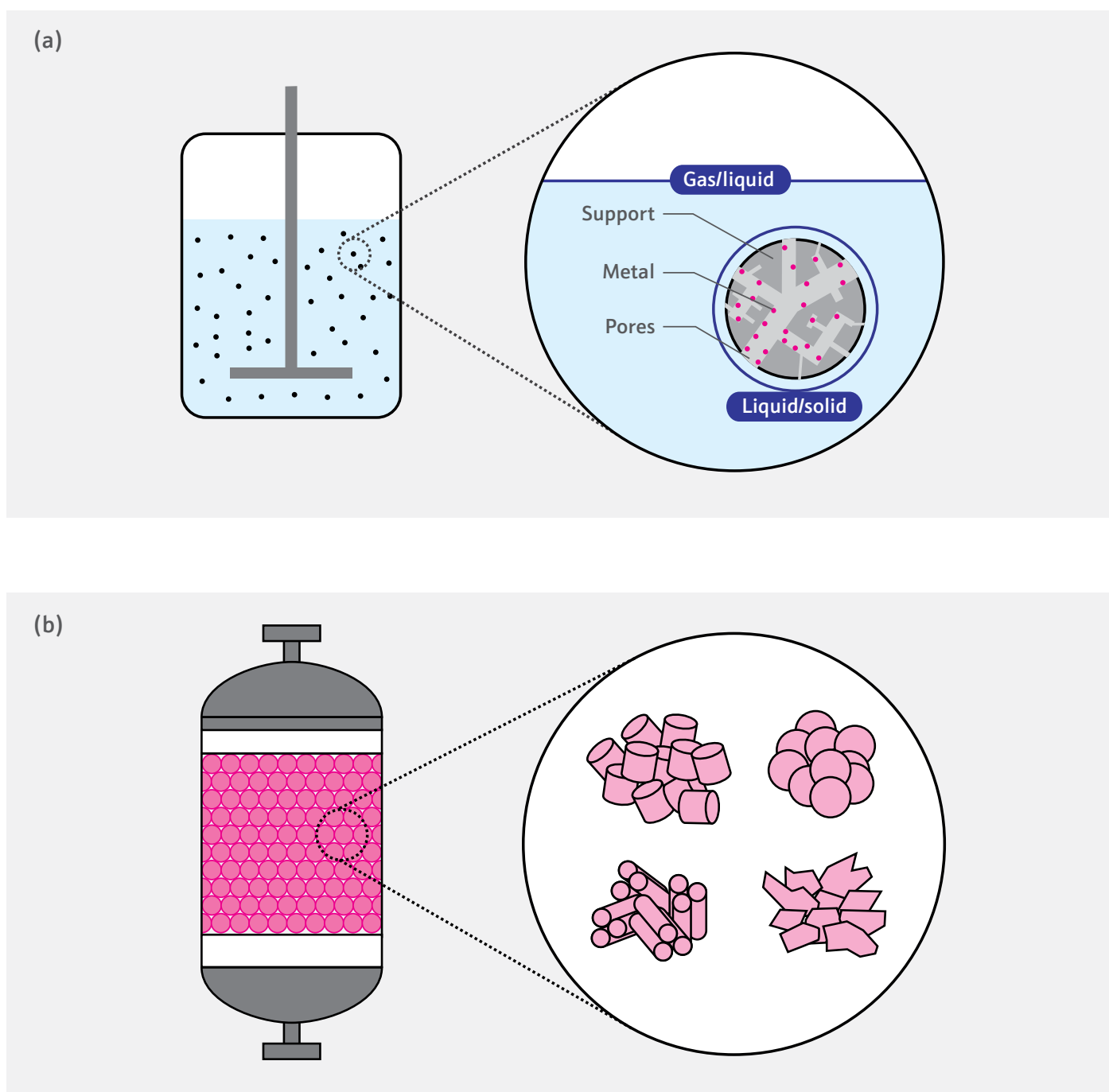

Figure 1. (a) Powder catalyst in slurry batch reactor (b) Particulate catalyst in fixed-bed reactor

Catalyst deactivation

A key consideration in catalyst design is the expected lifetime of the catalyst and the acceptable loss over time of catalytic activity and/or selectivity. It is important to prevent unexpected activity loss wherever possible, as this causes costly unplanned process shutdowns and early catalyst replacement.

While all catalysts will experience a loss in performance, understanding and controlling the mechanisms behind that loss can vastly improve the economics of the process. This white paper will cover each of the main areas of deactivation and provide advice for preventing and/or overcoming deactivation in different catalytic systems.

Catalyst deactivation can occur through a range of mechanical, chemical, and thermal processes. For simplicity, these can be grouped into five mechanistic groups: metal poisoning, metal loss, metal agglomeration, fouling, and support breakdown (Figure 2).

While all forms of deactivation are possible, some affect slurry reactions, while others are more likely to occur in fixed-bed systems depending on the chemistry and process setup. However, all deactivation leads to the loss of available metal surface area and therefore creates an undesirable change to activity or selectivity in catalyst performance.
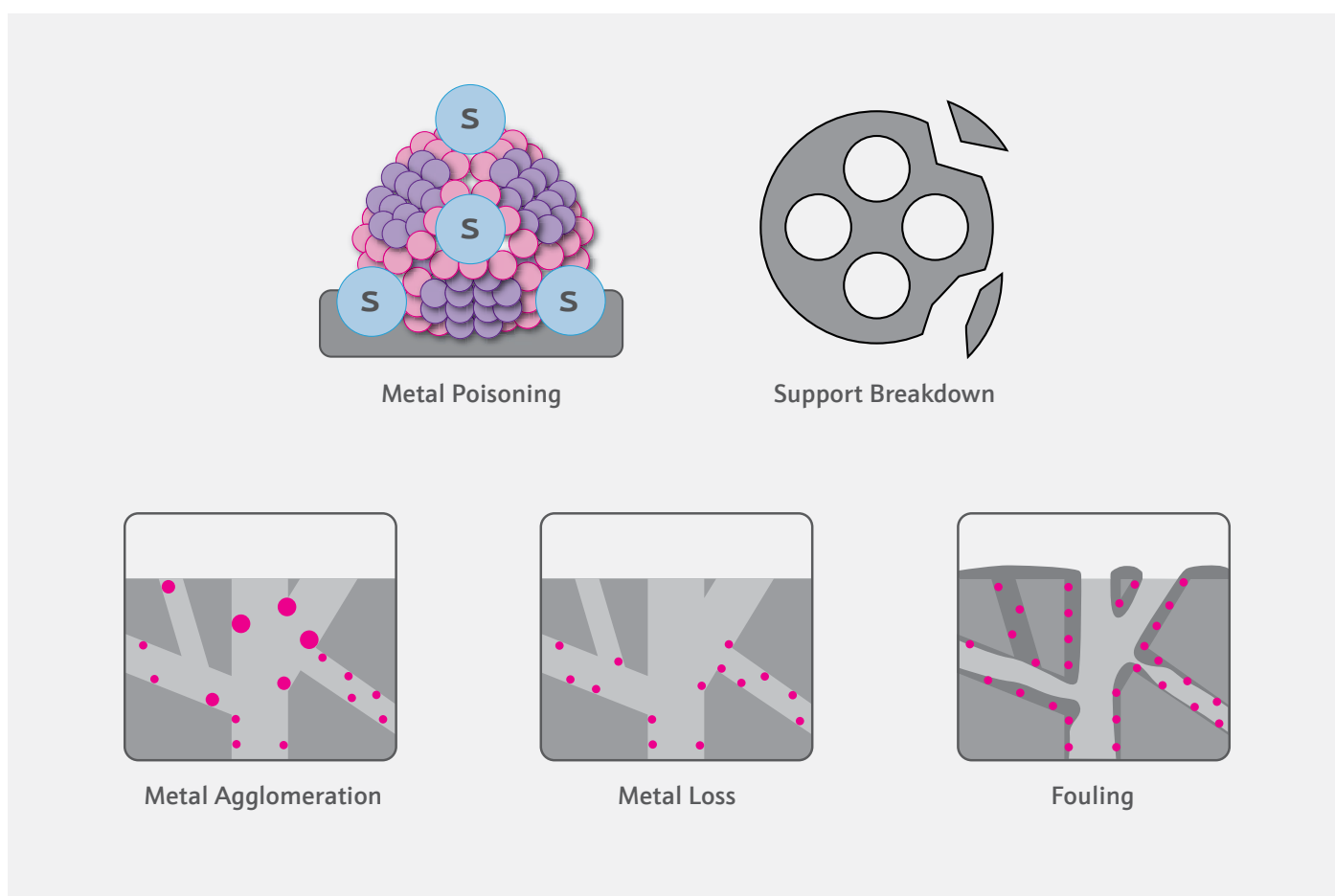

Figure 2. *Mechanisms of catalyst deactivation*

Metal poisoning

Poisoning is caused by the unwanted adsorption of non-substrate species on the metal surface. Such species could include heavy metals, amines, sulphur compounds, arsenic compounds, and carbon monoxide. The poisoning species can be introduced exogenously or be present in the feedstock, then carried through subsequent reaction steps. Variations in feed quality, such as from naturally occurring sources, can result in the loss of process stability, which has a detrimental impact on the catalyst. Equally, this loss of process control can introduce poisons to the catalyst. Poisoning can be reversible or irreversible, depending on the strength of the interaction and if the catalyst and process can tolerate a regeneration stage.

It is important to realise that one atom or molecule of a typical poison may electronically modify more than one surface atom of the active metal and may therefore result in a loss in activity of the neighbouring metal atoms. The implications of this deactivation method for the operational lifetime of an industrial catalyst are profound. Therefore, catalyst tolerances to poison content can be varied depending on the species present (Table 1), even at very low concentration levels.

Understanding which poison is present in the system can help lower the catalyst cost contribution to a process. Preventing the poison from reaching the catalyst will enable the catalyst to operate at its best. A guard bed is therefore often implemented to protect the catalyst from exposure. For example, passing the feed through a guard bed of porous ZnO at 200 °C before it reaches the catalyst can reduce the H_2S concentration to less than 0.1 ppm.

Metal Poisons	Catalyst effects
Organic chlorides	• Modifies catalyst activity
Ketones / aldehydes / alcohols / ethers	• Can compete for active sites • May consume hydrogen
Amines	• Modifies catalyst activity
Polymer / gums	• Blocks catalyst pores / covers active sites • Causes increased pressure drop
Carbon monoxide	• Modifies catalyst activity through competitive adsorption with reactant
Halide salts	• Causes coverage of active sites
Heavy Metals (Hg / As / Pb)	• Reacts with Pd to form salt / alloy • Greatly decreases activity • Severe poison
Iron	• Blocks catalyst pores • Modifies catalyst activity
Si / silicones	• Occlusion of active metal • Can cause growth of silica fibres in pores
Hydrogen sulphide	• Forms bulk PdS • Severe poison
Organic sulphurs	• Moderate poison • Decreases activity
Hydrogen chloride	• Leach metal • Greatly decreases activity • Severe poison

Table 1. Typical metal poisons and implications

Metal-poison interaction

The most potent poisons to PGMs are those that form thermodynamically stable stoichiometric compounds with the catalytically active metal under reaction conditions.
The extent of poisoning is directly proportional to the strength of the chemical bond formed between the poison and the catalytically active metal. It follows that the ease of reversibility of the poisoning effect is inversely proportional to the strength of the chemical bond formed. Species that contain lone electron pairs can form chemical bonds with the metal surface, producing stable metal compounds which are catalytically inactive.

Notable examples of such species are sulphide, thiol, mercaptan and H_2S compounds. These sulphur-containing compounds react with the metal surface to form metal sulphides (Figure 3). Compounds containing amines, phosphines or arsines also poison the surface of a precious metal catalyst by a similar mechanism.
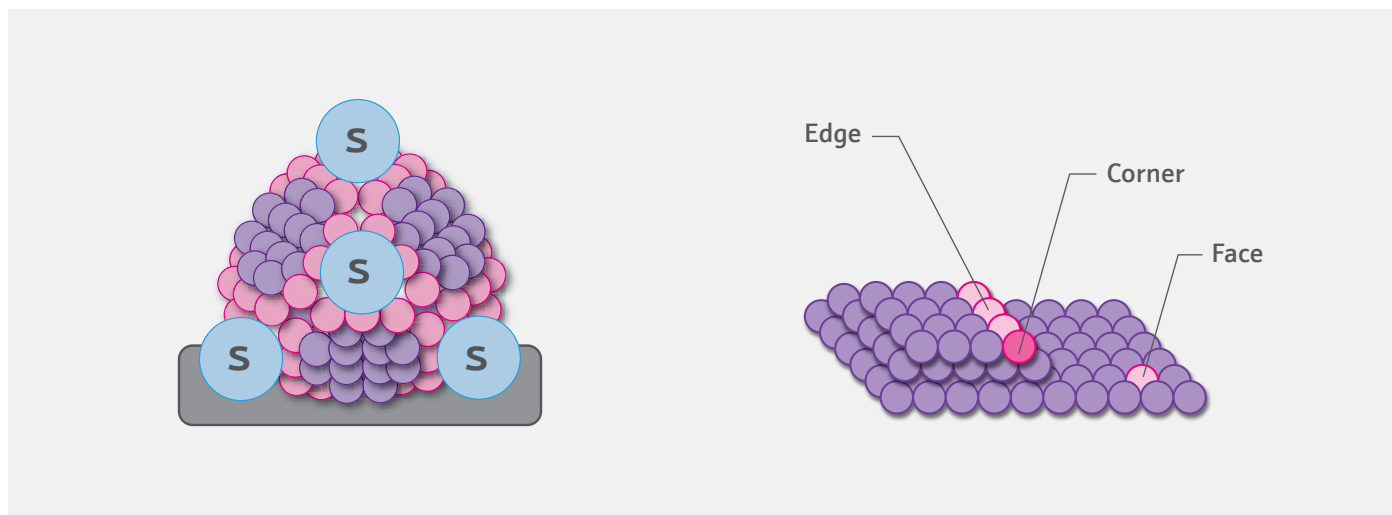

Figure 3. Metal crystallite surface coordination

Catalyst modifiers

It is important to note that the poisoning effect is not always negative. Intentional catalyst modification is a technique that is sometimes used when it is necessary to control catalyst performance, normally targeting positive selective rate enhancement. A modifier is a substance that modifies catalytic effect/rate and could be a promoter, inhibitor, or poison.
The effect on performance depends on concentration.
Most modifiers are inactive as catalysts themselves and tend to be specific to the application.

A common example of this in the petrochemical industry is the treatment of the surface of a fixed-bed Al_2O_3-supported Ni catalyst with organic sulphur compounds. This promotes the selective hydrogenation of diolefin compounds in pyrolysis gasoline streams, rendering the catalyst inactive for aromatics saturation. Al_2O_3-supported Pd fixed-bed catalysts used in the selective hydrogenation of acetylene in ethylene are often treated with CO or a second metal to avoid over hydrogenation of valuable ethylene to produce less valuable ethane.

Metals such as Hg or Pb, which form stable alloy compounds with catalytically active metals such as Pd, are also potent poisons for PGM catalysts. In the pharmaceutical industry, high loading Pd powder catalysts are treated with Pb (the Lindlar catalyst) or nitrogen compounds such as quinolines to modulate selectivity in the hydrogenation of larger molecules containing carbon-carbon triple bonds.

Metal location

Johnson Matthey has developed techniques to deposit the metal selectively at a chosen pore distribution in the particulate or powder support. This allows catalysts to be designed with different metal locations for reactions performed under different conditions of hydrogen pressure and temperature (Figure 4). This customisation is primarily done to optimise the catalyst for performance. For example, eggshell catalysts, in which the metal is located on the exterior surface of the support, would be chosen for higher activity at low hydrogen pressure conditions. However, poison tolerance is also a consideration. Uniform catalysts, in which the metal is evenly dispersed throughout the support structure, may lead to large in−pore diffusion resistance to reactants, but also to poisons.
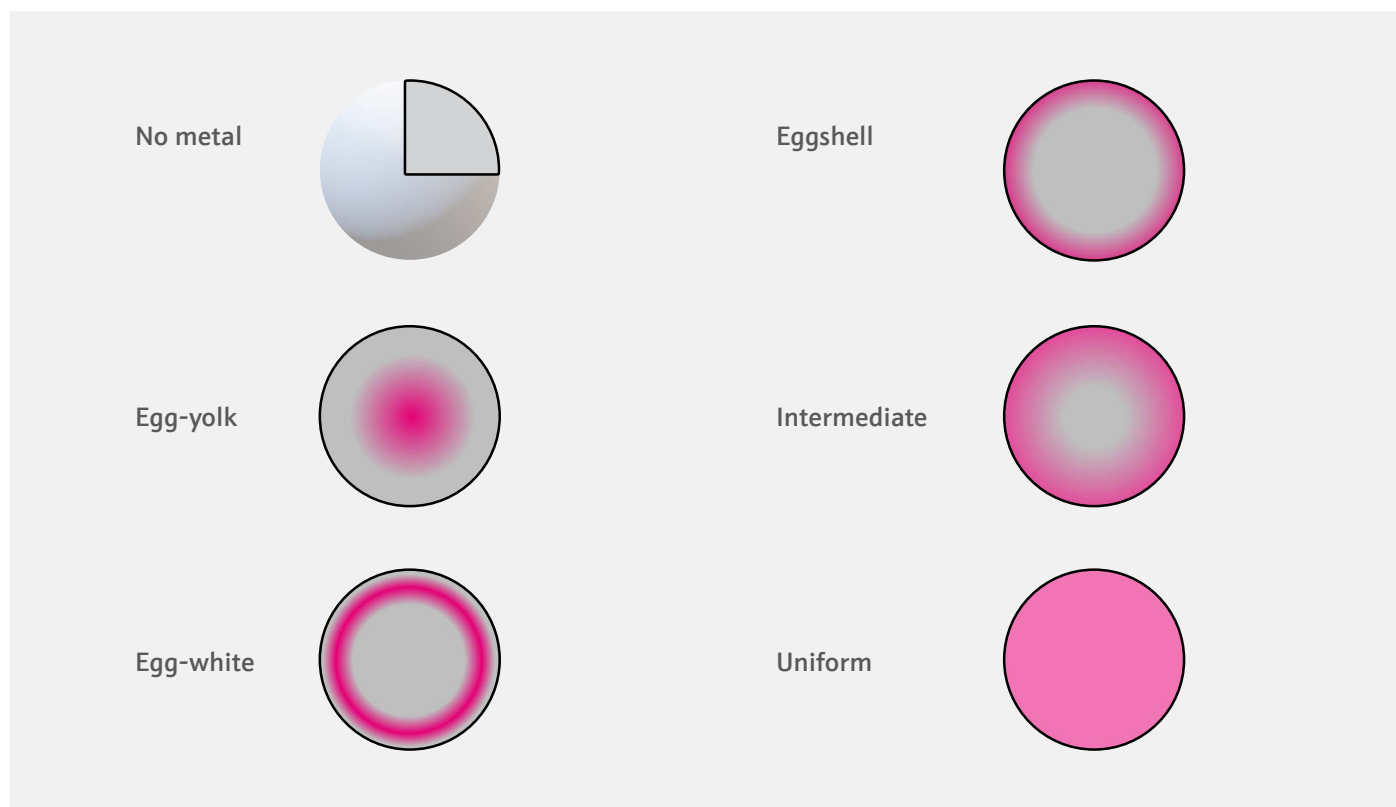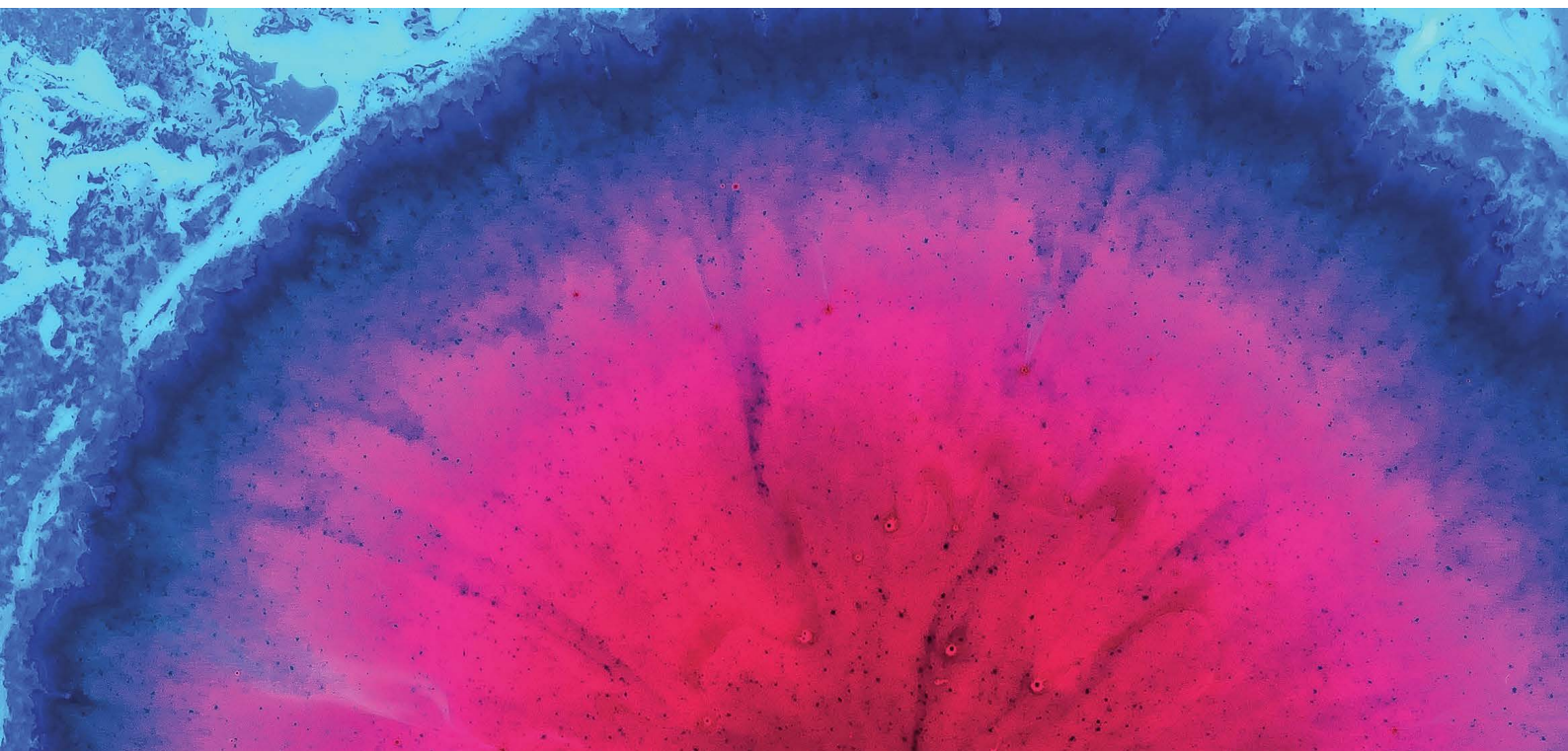

Figure 4. *Cross-section with differing metal pore distributions*

Metal loss

Catalyst deactivation by the physical loss of metal can be caused by structural breakdown, leading to the generation of metal-enriched support fines or by metal leaching (Figure 5). In fixed-bed systems, this can lead to hot-spots and by-product formation. In slurry systems, this can lead to issues with filtration and catalyst recovery. In most cases, the metal loss is irreversible and results in the loss of catalyst activity, as well as the introduction of possible impurities in the final product.

Leaching is where the active metal is mobilised and becomes detached from the catalyst. This is predominately metal crystallite breakdown and can be either mono-atomic or colloidal. The leaching process is highly dependent on the reaction medium environment, which affects the stability of metallic species. Dissolution or etching occurs when the metal is exposed to halides, low pH and chelating functionality from the feedstock. The rate of leaching increases when the metal crystallites are in a hydrogen-starved environment, resulting in a less stable, non-hydritic species.

Leaching is a particularly important factor to consider when using powder catalysts with a slurry reactor setup. In these cases, there is the possibility of hydrogen starvation occurring as a result of mass transfer issues. The rate of mass transport of either gaseous reactant or substrate from the bulk liquid to the external surface of the catalyst particle can be delayed. Most often it is gas to liquid mass transfer, where mixing efficiency or agitation and catalyst metal location will impact hydrogen concentration (Figure 6). The degree of delay will also be influenced by substrate concentration, the weight of the catalyst in the reactor, and catalyst particle size distribution. Encouraging higher hydrogen pressure, using more efficient mixing, and lower catalyst loading will help to reduce metal leaching.

Avoiding or minimising the time the catalyst is in contact with feedstock without or at low hydrogen pressure is key. At the start of the process, before introducing feedstock, pre-reduction (activation) of the catalyst can be beneficial. Or, at the end of the reaction sequence, during filtration, the filtration or settling speed can impact the degree of metal leaching. Powder catalyst properties such as support parameters (surface area, porosity, PSD), initial metal oxidation state, metal location (eggshell, intermediate, uniform), metal dispersion and metal:support ratio, will all contribute to minimising the mass transfer effects.
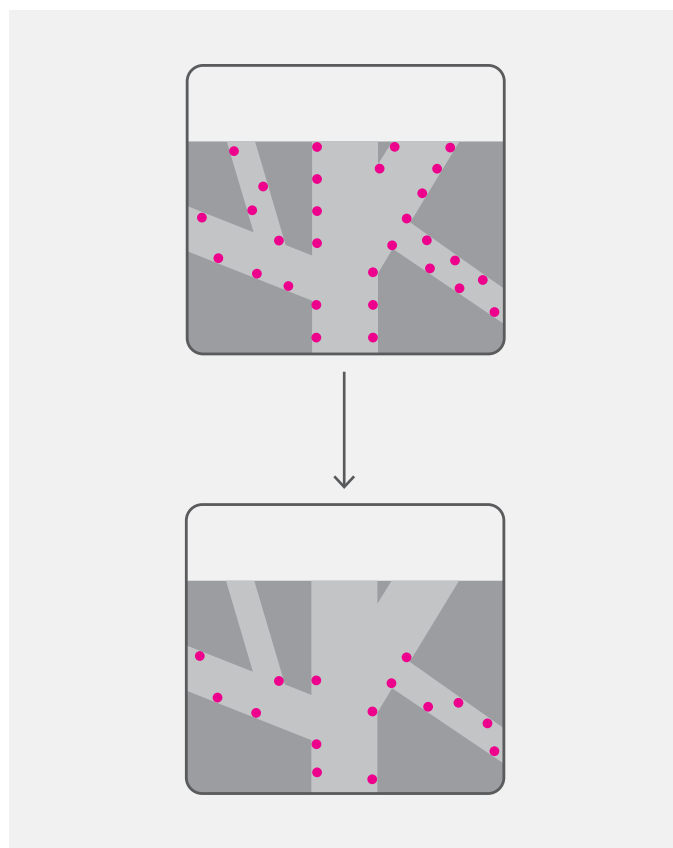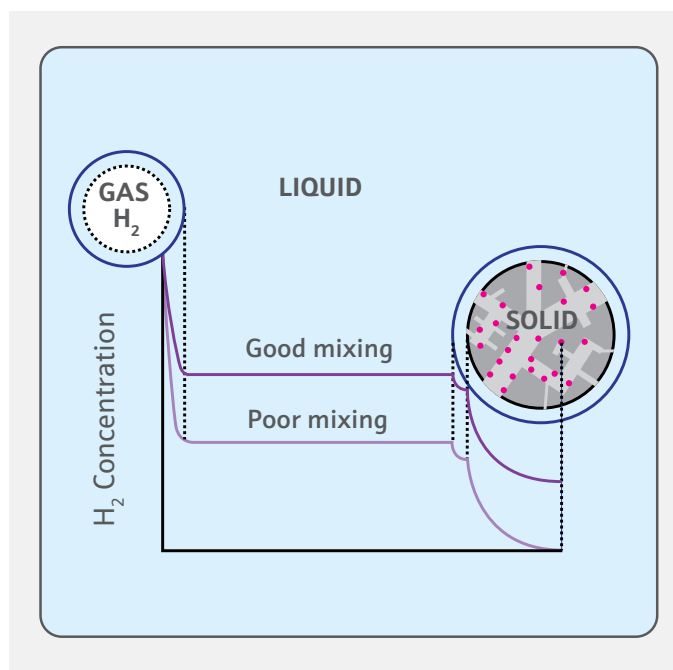
Figure 5. *Schematic of metal loss*

Figure 6. *Hydrogen gas concentration change*

Metal agglomeration

Metal agglomeration (sintering or migration) occurs by crystallite growth of the catalytic metal (Figure 7). This decreases the metal surface area by chemically transforming the catalytic phases into non-catalytic phases. Metal agglomeration can arise by thermal sintering, particularly when operating above the Hüttig Temperature or by a metal dissolution/reprecipitation mechanism. This is generally accelerated by the presence of water vapour. Catalyst deactivation by sintering is usually irreversible as dispersion cannot be recovered. Sintering can be identified through post-mortem analysis of a spent catalyst by examining the metal particle size either directly – by using TEM (transmission electron microscopy) – or by measuring the metal dispersion by chemisorption and comparing against fresh material.

Thermal sintering can sometimes cause the collapse of the support pore structure. One example of this would be the phase transition from gamma to alpha-alumina, resulting in the encapsulation of the metal crystallite. Choosing the right support is therefore crucial for higher temperature reactions.

As the primary cause of sintering is high temperature, the strategy for avoiding sintering is good thermal control of the reaction system, preventing hot spots from occurring. Control can be maintained through efficient mixing for slurry reactors. For fixed-bed setups, flow maldistribution or sub-optimal space velocity profiles should be avoided. Additionally, it is necessary to avoid environments where metal dissolution can occur, such as highly acidic conditions. Promoters or impurities in the metal crystallite can affect sintering and redispersion, either by increasing or decreasing the metal atom mobility on the support. This can be used to resist deactivation of the catalyst.
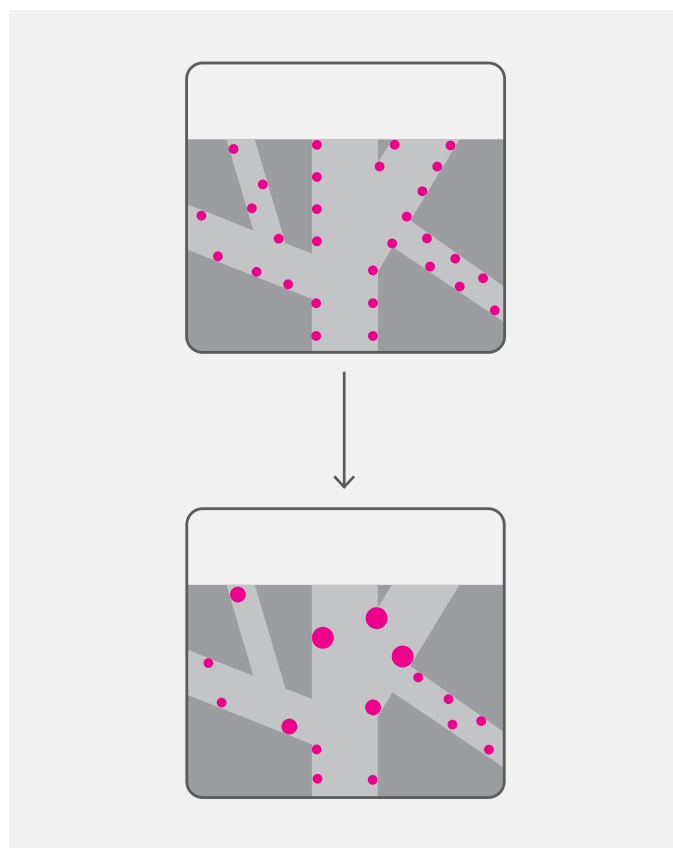

Figure 7. Schematic of metal sintering

Support breakdown

The choice of support is key for catalyst performance. The main function of the support is to immobilise the metal and promote metal dispersion (surface area) through accessible porosity and structural durability. Therefore, the resistance to structural breakdown and the stability of the support to mechanical, thermal, and chemical changes is crucial.

- Mechanical breakdown occurs by either fracture or attrition, depending on the support properties. Attrition is typically the erosion of the catalyst particle size to produce fines, which can occur from bed movement. Fracture is the structural breakdown of catalyst particulates. This can occur during the loading of the catalyst into the reactor. Depending on the type of reactor and environment, breakdown can also occur from crushing due to the load in fixed-bed reactors.

- Thermal-induced breakdown normally occurs as a result of catalyst particles that are heated rapidly, such as localised exotherms in fixed-beds.

- Chemical-induced breakdown can occur due to incompatibility of the support and the feedstock, reagents and/or by-products. This can include hydrothermal stability, which is key for exothermic reactions that produce water (e.g. nitrobenzene hydrogenation to aniline).

For batch reactor setup, the powdered catalyst is slurried with liquid phase reactants. The catalyst is separated by filtration after reaction completion. A well-designed powder catalyst will exhibit high attrition resistance, meaning that it will reduce catalyst losses by fines generation. Similarly, it will display good suspension characteristics, thereby resisting mass transfer effects. Thus, the selected powdered catalyst supports provide a compromise of properties for the catalyst, balancing performance and physical properties.

For fixed-bed reactors, formed particulate supports are used. The shape and size of the catalyst particles are key in maximising activity and heat transfer, as well as minimising fixed pressure drop. The pressure drop impacts plant efficiency, production rates, and profitability. By selecting a catalyst specifically designed to reduce the impact of both fixed and variable pressure drop, higher efficiencies can be achieved for longer times online. One of the main causes of increased pressure drops is support breakdown (Figure 8).

The preparation method and constituent material used for the particulate support, along with the resulting shape and size, dictates the structural and chemical properties. These include crush strength, hardness, geometric surface area, porosity, and thermal/chemical stability. There is typically a balance between support stability and catalyst activity. Stronger support materials have greater breakdown resistance, whilst weaker materials with higher porosity may promote higher metal dispersion and therefore a more active catalyst.
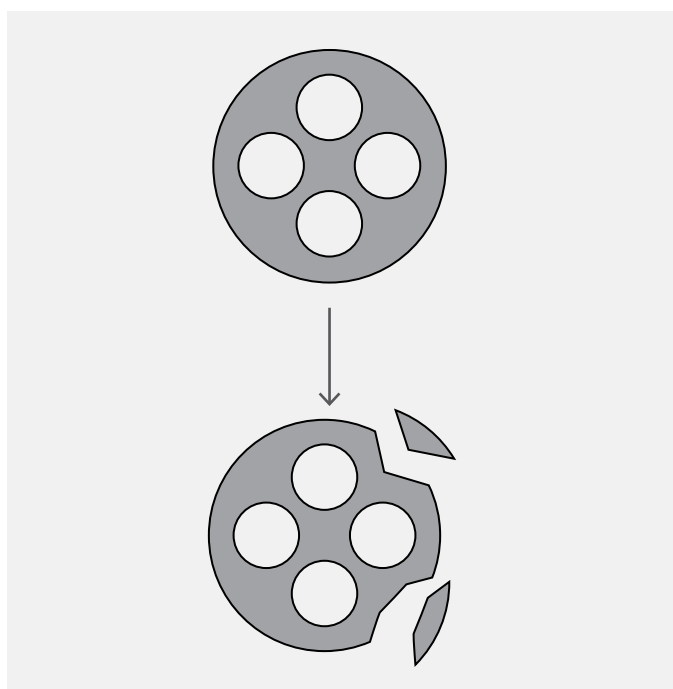

Figure 8. Schematic of catalyst breakdown

Catalyst fouling

Fouling occurs when the catalyst surface is masked by polymeric materials or tars. On fixed-bed particulate catalysts, it is often referred to as "coking". The catalyst activity can also be lost due to the blockage of pores, preventing feedstock from accessing the catalytically active sites (Figure 9). In extreme cases, the fouling may result in breakages of the catalyst support (attrition) and/or plugging of the reactor (increased pressure drop).

Fixed-bed, non-carbon-supported catalysts affected by fouling can be reactivated by controlled combustion of the coke using an inert gas stream and/or steam with a low concentration of air. The combustion exotherm should not exceed sintering temperatures. Powder catalysts can sometimes be reactivated by washing with suitable solvents, treating with oxidising agents to break down the polymeric materials into smaller, more soluble species, and then reactivating the catalyst.

Coke formation depends on the balance between the reactions that produce atomic carbon (or coke precursors) and the reactions of these species with H_2, H_2O or O_2 (which remove them from the catalyst surface). An understanding of these competing processes is crucial to preventing the fouling of catalysts. In conditions favouring the gasification of unwanted species, less coke will be formed on the surface. A catalyst that displays greater selectivity for the desired product will also reduce fouling.
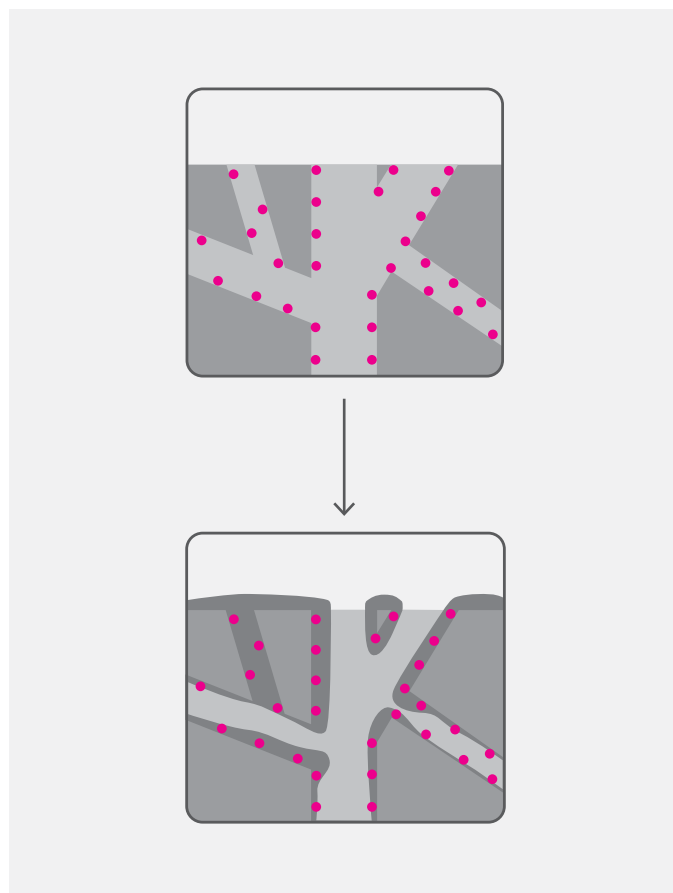

Figure 9. Schematic of catalyst fouling

Conclusion

Each of the mechanistic groups involved in catalyst deactivation have been highlighted for both slurry and fixed-bed supported PGM catalysts. Essentially, all deactivation leads to a reduction in the available surface area of the catalytic metal. Loss of performance, whether activity and/or selectivity, can vary depending on the root cause.

Generally, the deactivation of powdered PGM supported catalysts is irreversible. However, this is only applicable if the catalyst is reused. Commonly for slurry reactions, the catalyst is employed for single use. Robust and predictable performance is therefore key and can be maintained by avoiding deactivation and establishing the correct setup.

The deactivation of catalysts for fixed-bed catalysts can be reversed. However, in cases of irreversible metal poisoning, metal loss, metal agglomeration and support breakdown, the deactivation is seldom reversible.

Understanding the mechanisms of deactivation can help to reduce the catalyst cost contribution to the process. Due to the price of PGMs, it is more cost efficient to prevent catalyst deactivation rather than repair the damage after it is done. Modifying the process through poison capture, purification of feed, or reactor design and/or modifying catalyst choice through support choice, metal location, dispersion and dopants/promoters can all help maximise the performance of the feedstock.

Summary

As is true with most industrial processes, experience and expertise in handling catalytic reactions are essential to optimising process conditions and choosing the ideal catalyst type. Every industrial reaction has varying requirements that must be evaluated on a case-by-case basis.

Johnson Matthey supports its customers in achieving success by providing essential technical services. We utilise our cutting-edge in-house parallel screening experimentation and team of experienced specialists to supply and support the optimal catalyst identification process.

Whether you are looking for an existing catalyst, a new customised solution, or to improve a current process, our highly accessible support team is ready to work with you. We are committed to providing our customers with the best technology to optimise catalytic activity and minimise the catalyst cost contribution factor.

Using our comprehensive portfolio of heterogenous PGM catalysts and range of collaboration models, we are able to produce custom-made solutions at a commercial scale.