

# Carbon Formation in Steam Reforming and Effect of Potassium Promotion

## Potassium dopants prevent carbon formation and aid catalyst recovery

**By Mikael Carlsson**

Johnson Matthey Plc,  
PO Box 1, Belasis Avenue, Billingham TS23 1LB, UK

Email: [mikael.carlsson@matthey.com](mailto:mikael.carlsson@matthey.com)

---

### Introduction

When choosing a reformer catalyst, there are a number of important things to consider. Steam reforming of methane is an endothermic reversible reaction, whilst steam reforming of higher hydrocarbons is not reversible. The activity of the catalyst installed is critical in determining the reaction rate within the reformer. However, the steam reforming reaction is diffusion limited, so the geometric surface area of the installed catalyst is directly related to the catalyst activity. This article will show the mechanisms by which carbon can form on a catalyst and how a potassium dopant can prevent this and aid catalyst recovery following carbon formation (1).

Because the reaction is endothermic, the transfer of heat from the burners to the catalyst is just as important as the activity. Whilst within the reformer itself the primary heat transfer mechanism is radiation, within the tube it is convection and conduction. The hottest point inside the tube is the internal tube wall. The size and shape of the catalyst will impact on the tube-side laminar film layer and therefore on the overall heat transfer coefficient as represented in **Figure 1**.

Due to the temperatures at which steam reformers operate, carbon is constantly being formed from the hydrocarbon feedstock, with the primary route being through cracking reactions. However, there are also carbon removal (or gasification) reactions that simultaneously occur which remove the carbon laid down, meaning there is no net accumulation of carbon in a well-run plant. With a given catalyst loading in the reformer, the rate of gasification is fixed by the catalyst type and the process conditions. However, the rate of carbon laydown is a function of a number of conditions such as the catalyst activity, degree of sulfur poisoning and heat input to the tubes. The rate of laydown is therefore more likely to vary compared to the rate of gasification. The selected catalyst should have appropriate activity or alkali promoters to ensure that the carbon removal rate is faster than the carbon formation rate, which would result in no net carbon laydown.

Finally, the catalyst should allow for the lowest possible pressure drop, as this will enable the highest possible plant throughput before compressor limits are reached. However the catalyst breakage characteristics are also important as all pelleted steam reforming catalysts will break due to the forces exerted on them when reformer tubes expand in operation and then contract during plant shutdowns, which will lead to an increase in pressure drop.

### Carbon Formation

The three main reactions for carbon formation are hydrocarbon cracking (Equations (i) and (ii)), carbon

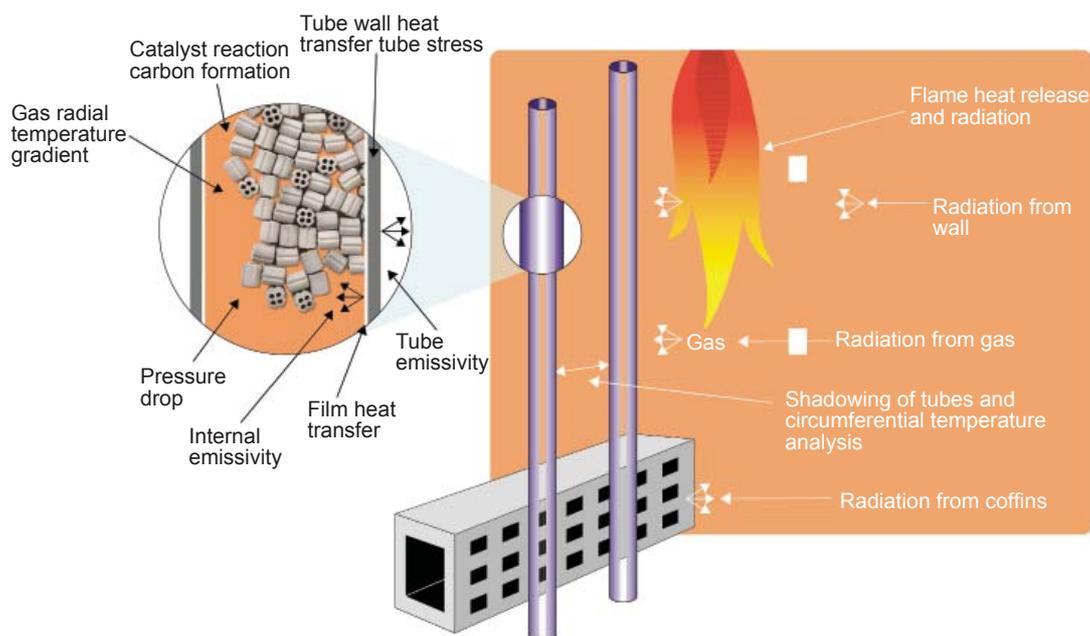


Fig. 1. Heat transfer balance inside a steam reformer box from flames to reactant stream

monoxide disproportionation (the Boudouard reaction) (Equation (iii)) and carbon monoxide reduction (Equation (iv)).



Cracking or decomposition of hydrocarbons is favoured at temperatures above approximately 620°C (1148°F) depending on the hydrocarbon species. The reaction with methane is reversible but with the heavier hydrocarbons they are not.

Both the carbon monoxide reduction and disproportionation reactions are more prevalent at lower temperatures but at those temperatures the concentrations of carbon monoxide would normally be low, depending on recycle rates, so the cracking reactions are normally the most important to consider. However, any combination of these reactions can lead to detrimental effects on catalyst activity and, if left untreated, eventually lead to permanent damage and carbon build-up.

There are three catalyst parameters that can be altered to prevent carbon formation. These are the activity, the inherent heat transfer coefficient and the catalyst alkali promoter content.

Increasing the catalytic activity can be achieved by using a higher surface area catalyst due to the diffusion limited nature of the reaction mentioned previously. This has a threefold effect; firstly, as there is more reforming reaction near the inlet of the tube, there is a lower process gas temperature due to the increased heat of reaction required. Secondly, the hydrocarbon content of the process gas is reduced. And finally as more hydrogen is produced carbon formation is suppressed.

By improving the heat transfer characteristics of the reforming catalyst, the rate of heat transfer within the tube can be increased. Intuitively this would appear to increase the process gas temperature thereby making the carbon forming potential worse. However since carbon is most likely formed on the inside tube wall which is the hottest part of the process, increasing the heat transfer characteristics of the catalyst reduces this temperature by transferring heat to the bulk of the catalyst. The additional heat transferred will in turn increase the reaction rate, which will also reduce the hydrocarbon content of the process gas making carbon formation less likely. The process gas temperature is

also reduced. Overall, this has a similar effect to that seen by installing a highly active catalyst.

Another way of preventing the formation of carbon is to include a promoter in the catalyst to help increase the rate of carbon gasification; one such promoter is potassium.

### Potassium Promotion

It is well known that carbon formation on a surface, whether the support or catalyst, is affected by the acidity of that surface. Positively charged acidic sites on a surface will increase the rate of carbon formation, which is partly due to acidic sites catalysing the cracking reaction. Alpha alumina, which is a common catalytic support, contains acidic sites and adding Group 2 metals such as magnesium or calcium neutralises these making the surface less acidic.

For a supported nickel catalyst the steam ratio at which a catalyst would run without forming carbon can be decreased by approximately 16% compared to an undoped alumina through the addition of dopants such as calcium or magnesium. A way to further increase the surface basicity is to add a potassium-containing compound such as potash as a dopant, which will lead to an increased prevention of carbon formation. For alkalis calcium aluminate catalyst the steam ratio can be reduced by approximately 65% without forming carbon compared to an undoped alumina. The reason for this is due to both the acceleration of the carbon gasification reaction and the suppression of carbon formation reactions.

In addition to increasing the surface basicity, the potassium will form hydroxide species in the presence

of steam and these will aid in any removal of carbon that is formed on the surface. As highlighted earlier, depending on the conditions, there are locations within the reformer where carbon will form on hot surfaces, for example, the inner tube wall. This is especially likely if heavier species slip further down the tube where the wall is hotter. That carbon will have to be removed at a faster rate than it is formed in order to prevent any build-up.

The history of potassium promoted catalysts goes back to 1975 when a trial was carried out on the No 1 Low Pressure Ammonia Plant in Billingham, UK, (2). During the trial it was shown that the promoted catalyst, where the potassium was incorporated in the support, was successful in the suppression of hot bands that had been seen for the previous charge of unpromoted catalyst. These hot bands associated with carbon formation appeared after only a few months of operation and it was thought at the time that they were due to a plant uprate. Alkali metals were known to inhibit the steam reforming reaction, but during the plant trial no such inhibition was seen due to the way in which the potassium was incorporated into the support. The effect was confirmed by laboratory experimental testing. After nine months of operation the reformer was inspected and the tubes containing potassium promoted catalyst were running cooler with a more uniform temperature than adjacent tubes, which contained unpromoted catalyst. The material was discharged and when examined only a very limited potassium loss was detected.

The Johnson Matthey KATALCO<sub>JM</sub> catalyst range available today has been designed with different amounts of promoter for various operations. As can be seen in **Table I** the range spans from unpromoted

Table I Range of Johnson Matthey KATALCO <sub>JM</sub> Catalysts with Different Potassium Promotion		
K <sub>2</sub> O, wt%	Series	Feedstock/carbon protection requirement
0	KATALCO <sub>JM</sub> 23-4 or 57 series	
1.5–2.5	KATALCO <sub>JM</sub> 25-4 series	
4–5	KATALCO <sub>JM</sub> 47 series	
6–7	KATALCO <sub>JM</sub> 46-3	
		Heavy feed/high C protection

KATALCO<sub>JM</sub> 23 and 57 series which are used for light feedstocks such as methane in combination with a low heat flux, up to KATALCO<sub>JM</sub> 46-3 which contains much higher levels of potassium for operations with heavy naphtha. The two catalysts series with intermediate levels of potassium promotion are for operations where the feed composition is heavier than methane but lighter than heavy naphtha, for example, liquid petroleum gas (LPG). In reality this summary is slightly oversimplified as both the steam-to-carbon ratio and the overall heat flux also affect the amount of carbon protection required.

Potassium is incorporated into the catalyst in ceramic phase reservoirs with a precise stability to regulate the rate of release onto the surface. This leads to the right level of potassium and hydroxide species on the surface to ensure gasification of carbon from all nickel sites throughout the catalyst's lifetime.

The potassium-containing phases present in Johnson Matthey catalysts depends on the series but typically they are either a potassium-aluminosilicate or potassium-aluminate which is incorporated in the support. The use of a range of phases allows for the release of potassium at an appropriate rate under a range of process conditions and maintains high activity in terms of carbon removal. This also ensures that any adverse effect on the steam reforming activity is minimised.

**Figure 2** shows an electron probe microanalysis (EPMA) of a potassium-promoted catalyst which clearly

shows areas which are rich in aluminium (**Figure 2(a)**) and potassium (**Figure 2(b)**). What can be seen is that where there is a high abundance of potassium there is also high aluminium content. This clearly indicates that there are areas of potassium-aluminates which act as potassium reservoirs for the catalyst.

Froment *et al.* examined different potassium loadings on a nickel catalyst and found that in conditions where methane cracking was taking place the presence of potassium seemed to have three effects on the carbon formation (3): (a) it reduced the final level of carbon formed; (b) it reduced the rate of carbon formation; and (c) it apparently delayed the onset of carbon formation, which is speculated to be the result of decreasing the nucleation rate on the catalyst surface. Furthermore, the gasification rate of filamentous carbon that had been deposited is also affected by the presence of potassium as shown in **Figure 3**. The rate of gasification by steam as a function of the potassium content exhibits a maximum of around 1.6–2.0 wt% potassium oxide (K<sub>2</sub>O) for this catalyst system.

The presence of a potassium dopant will promote the adsorption of water which will in turn increase the carbon gasification (4). The potassium will also affect the gasification kinetics and increase the carbon monoxide production rate and, as steam adsorbs dissociatively, there could be an increase in oxygen on the surface as a result of the increased number of sites for water adsorption on an alkalisated catalyst, which leads to an increase of the rate of gasification.

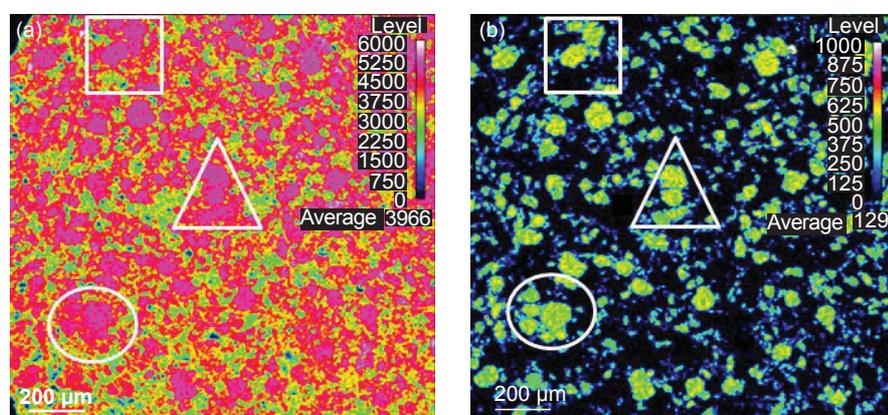


Fig. 2. EMPA images showing: (a) aluminium; (b) potassium distribution in a catalyst support highlighting areas of K-Al reservoirs

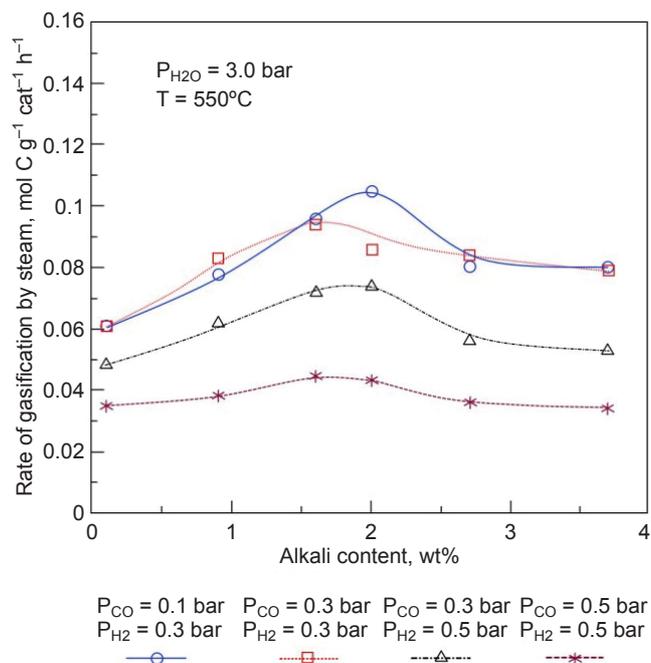


Fig. 3. Carbon gasification rate as a function of potassium loading. (Reprinted with permission from (2). Copyright (2002) American Chemical Society)

### Carbon Formation Case Study

Figures 4–6 demonstrate the use of a potassium promoted catalyst to aid recovery after a carbon incident in a reformer on a European ammonia plant.

Figure 4 shows hot bands on the reformer tubes that appeared following a carbon incident due to LPG condensate trapped in a line being inadvertently fed into the reformer. This carbon led to an increase in pressure drop from 3.6 to 5.0 bar (52.2 to 72.5 psi) across the reformer.

Although carbon had been formed, the presence of potassium promoted catalyst limited the severity of this incident and a full shutdown was averted. As the plant needed to keep running the operators decided that it would be run at a higher steam-to-carbon ratio in an attempt to promote carbon gasification. Over the following months the pressure drop was decreased to 4.7 bar (68.1 psi) and the extent of hot bands on the tubes decreased, which can be seen in Figure 5. The measurement of the tube wall temperature revealed a decrease of up to 30°C (54°F). This highlights the effect of carbon removal that is promoted by the potassium containing catalyst.

After two months of running at an increased steam-to-carbon ratio the plant tripped, providing an opportunity to steam the catalyst prior to restart. When the plant

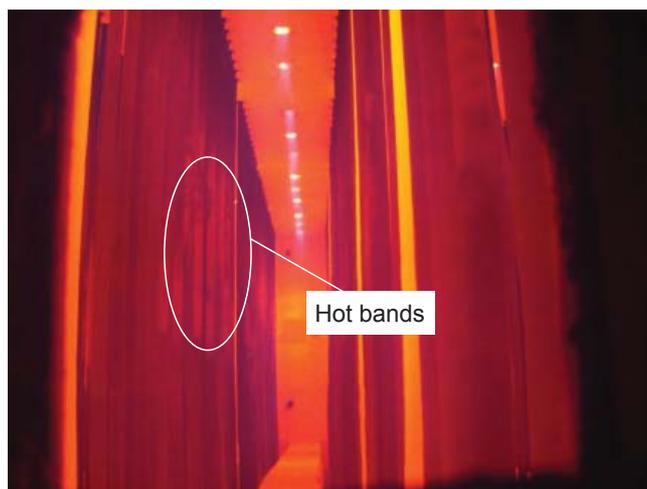


Fig. 4. Hot bands shown on tubes after a carbon forming incident



Fig. 5. Tube appearance two months after the carbon incident, illustrating some improvement



Fig. 6. Tube appearance after plant shutdown and steaming showing conditions returning to normal

was restarted no hot bands were observed (as can be seen in **Figure 6**) and operation was back to normal with pressure drop at 3.8 bar (52.2 psi). This case study illustrates both how the KATALCO<sub>JM</sub> catalyst can slowly recover during normal operation and also the dramatic return to normal operating conditions after steaming.

## Conclusion

There are a number of mechanisms by which carbon formation can occur on a nickel-based steam reforming catalyst, with the cracking of hydrocarbons most prevalent. Carbon deposition happens when the formation rate is greater than the removal rate which is a function of surface chemistry and the addition of promoters to reduce carbon formation. It is important that the potassium dopant is added to the catalyst in optimised phases with appropriate hydrothermal stability to give a controlled release rate. The

release and mobility of the potassium are required to keep tube walls free from carbon and also assist in recovery from plant upset conditions resulting in carbon formation.

## References

- 1 "Catalyst Handbook", 2nd Edn., ed. M. V. Twigg, Manson Publishing Ltd, London, UK, 1996
- 2 L. W. Lord, ICI Internal Report RD/CC430, 1976
- 3 J.-W. Snoeck, G. F. Froment and M. Fowles, *Ind. Eng. Chem. Res.*, 2002, **41**, (15), 3548
- 4 R. A. Hadden, J. C. Howe and K. C. Waugh, 'Hydrocarbon Steam Reforming Catalysts - Alkali Induced Resistance to Carbon Formation', Catalyst Deactivation 1991, Illinois, USA, 24th–26th June, 1991, "Proceedings of the 5th International Symposium", eds. C. H. Bartholomew and J. B. Butt, Studies in Surface Science and Catalysis, Vol. 68, Elsevier Science Publishing Co, New York, USA, 1991, pp. 177–184

---

## The Author



Mikael Carlsson joined Syntex/ICI in 2002 after graduating from Napier University in Edinburgh, UK, with a MSc degree in Materials Technology. He also has a BSc in Chemical Engineering from Chalmers University of Technology, Sweden. Mikael has for the last nine years been developing catalysts for the steam reforming area and currently works as Reforming Technical Development Manager.