NO_x Adsorber Developments for Diesel Emissions Control

For light and heavy-duty diesels, catalytic systems can supplement the nitrogen oxides (NO_x) control offered by engine-related measures. So called NO_x Adsorber Catalysts (NAC) can offer NO_x conversion efficiencies in excess of 90% over a wide temperature window. This article summarises a Johnson Matthey technical paper presented at the SAE World Congress, which outlines improvements in NAC performance.

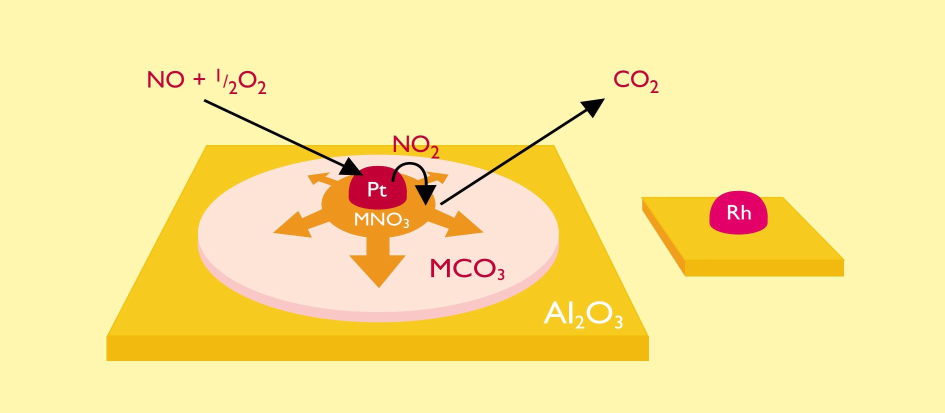
The chemical principles behind NO_x Adsorber Catalysts (NACs), also known as Lean NO_x Traps, are well documented. Under lean conditions, the NAC promotes NO_x adsorption as illustrated by reactions 1 and 2, where M is the NO_x adsorbing element, MCO_3 is the adsorber material, and MNO_3 is the stable NO_x containing compound.

(1) $NO + {}^{1}/_{2}O_2 \Rightarrow NO_2$

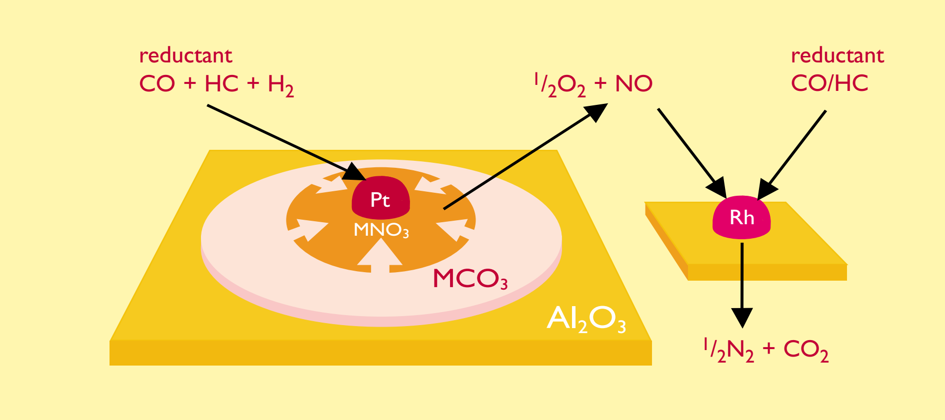
(2) $NO_2 + MCO_3 \Rightarrow MNO_3 + CO_2$

Under fuel-rich conditions, the NAC promotes decomposition of the nitrate phase to release the stored NO_x (reaction 3). The NAC then catalyses the reduction of NO_x to form N_2 (reaction 4).

Lean Conditions



Rich Conditions



(3) $MNO_3 \Rightarrow MO + {}^{1}/_{2}O_2 + NO$

(4) $NO + CO/HC \Rightarrow {}^{1}/_{2}N_2 + CO_2$

The drawback of these catalysts has been their sensitivity to fuel sulfur. NO_x adsorber materials are very efficient adsorbers of sulfur oxides, ultimately forming sulfate. Unfortunately sulfur blocks the adsorption sites and consumes adsorber by forming stable sulfate (reaction 7), thereby reducing the efficiency by which the NAC adsorbs NO_x.

(5) $MO + CO_2 \Rightarrow MCO_3$

(6) $SO_2 + {}^{1}/_{2}O_2 \Rightarrow SO_3$

(7) $SO_3 + MCO_3 \Rightarrow MSO_4 + CO_2$

Under rich conditions, the adsorbed sulfur can be desorbed but this requires a higher temperature than that required for the NO_x release. So, unless the engine operates on sulfur-free diesel, the successful application of a NAC within an emissions management system depends on the impact of temperature on the performance of the NAC, both in terms of NO_x adsorbtion efficiency and NAC durability after high temperature operation.

The NAC functions by forming chemical compounds that store the NO_x. The performance of an emissions control system incorporating a NAC is significantly influenced by the temperatures at which these compounds form and decompose. By using appropriate adsorber materials, NO_x storage can be enhanced at both low and high temperatures, helping to broaden the effective operating temperature window within which NO_x is controlled.

NAC durability

A NAC must be able to maintain its activity whilst withstanding high temperatures. This is because emissions management systems are under development for light-duty diesels that employ a NAC in conjunction with a particulate filter. The trapping function of the particulate filter must be regenerated, which involves periodically injecting fuel, either in-cylinder by engine management techniques or directly into the exhaust gas, to raise the temperature to around 600°C to burn away the soot in the filter. Likewise, when desulfating the NAC under rich conditions, the NAC can be exposed to even higher temperatures.

Thermal durability can be demonstrated for the latest NAC formulations by measuring NO_x conversion efficiency on aged samples after repeated sulfation and desulfation cycles.

Figure 1 illustrates that NAC activity does fall after the first and second sulfation and desulfation but is stable thereafter. Repeated testing confirmed the reproducibility of this effect. This stable sulfation-desulfation behaviour is important for the long-term durability of a NAC system in actual use on a vehicle.

Low and High Temperature NAC Performance

The potential application of NAC on European passenger cars requires that the NAC give good performance at exhaust gas temperatures below 250°C, reflecting urban driving. However, the exhaust gas temperatures generated by these same diesels can be significantly higher when the cars are motorway driving. Figure 2 shows NAC formulation A, which gives good low temperature performance, and a modified formulation, NAC B, which gives better high temperature performance. Formulation B's good high temperature activity makes it suitable for heavy-duty diesel applications, where high engine loads make relatively high exhaust gas temperatures a common occurrence.

NAC System Design

The first step in the NO_x storage process is the oxidation of NO to NO_2 (reaction 1). This reaction is catalysed by platinum incorporated into the NO_x Trap. Under some operating conditions this NO oxidation reaction can be inhibited and there are advantages in employing an optimised NO_x oxidation catalyst (NOC) upstream of the NAC to provide additional NO_2, particularly at low temperatures.

Figure 3 summarises the NO_x conversions obtained for NAC A with and without an upstream NOC and with the various cycle timings employed, ranging from 120 seconds lean and 2 seconds rich to 60 seconds lean and 8 seconds rich operation. The benefit of a NOC is apparent regardless of the cycle timing.

A further benefit of using a NOC in the system is seen in tailpipe HC emissions. For NAC-based systems, controlling HC emissions can be a challenge, particularly during the rich pulse where extra fuel is injected at the same time as oxygen is depleted. During the rich pulse, HC emissions were 80% lower when an upstream NOC was employed.

Low Temperature Performance Revisited

Having demonstrated improved high temperature performance with NAC B compared with NAC A, further developments led to a new C formulation which gave equivalent high temperature activity (> 280°C) to NAC B but superior low temperature activity (< 280°C) as shown in Figure 4. The very wide activity window demonstrated by NAC C will allow greater system design flexibility, and very high NO_x conversions over a comprehensive range of diesel applications.

Conclusions

Commenting of the results, Johnson Matthey Technology Director Dr Martyn Twigg said "Given the NO_x conversions achievable it is understandable why there is intense interest in using NO_x adsorber catalyst (NAC) technology for light-duty and heavy-duty diesel applications. The key to improving NAC performance lies in the capability of the catalyst designer to widen the operating window whilst retaining activity and thermal durability. These results demonstrate very good progress is being made in this direction."

Figure 1: NAC Activity After Sulfation and Desulfation

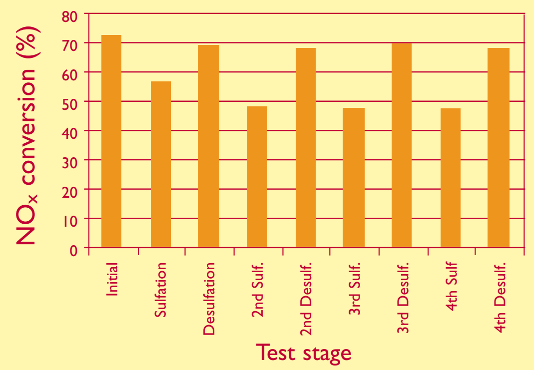


Figure 2: Activity of NAC A and B showing improved high temperature activity of NAC B

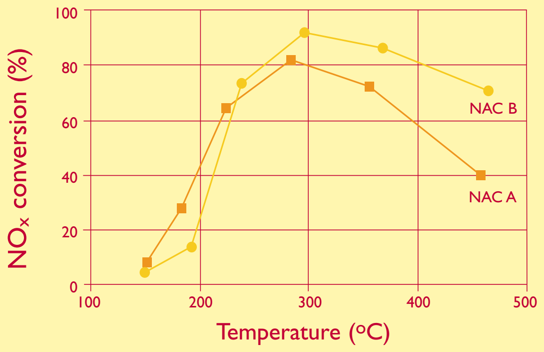


Figure 3: Effect of lean/rich cycle timings on system activity at 350°C for NAC A, with and without an upstream NOC

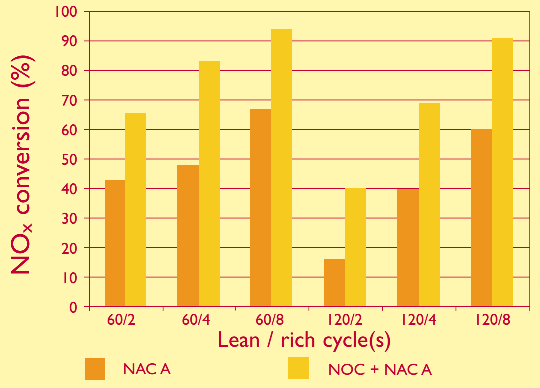


Figure 4: Comparison of the NO_x conversions of NACs A, B and C