Global Emissions Management

Volume 3, Issue 1
November 2010

Selective Catalytic Reduction: The NO_x Removal Method of Choice from Passenger Cars to Power Plants

There is continued focus on controlling the emissions of pollutants from engines around the world. The Three Way Catalyst (TWC) has been successfully removing carbon monoxide (CO), hydrocarbon (HC) and nitrogen oxide (NO_x) emissions from gasoline engines since the early 1970s. These catalysts operate under so-called stoichiometric conditions, in which there is a balance between the respective concentrations of oxidising and reducing species in the vehicle exhaust. This means that both oxidation (CO to CO_2 and HC to CO_2 and water) and reduction (NO_x to nitrogen) reactions can be carried out simultaneously, leading to the very high conversions (over 90%) seen in these systems.

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Background

The control of emissions from diesel engines presents additional challenges, since the gaseous environment in which the catalyst needs to operate is strongly oxidising. This means that, providing the temperature is high enough, the oxidation of CO and HC are both strongly favoured, but the reduction of NO_x is not. This challenge of NO_x reduction under highly oxidising conditions has led to the development of two sets of catalyst, both capable of carrying out this function.

In NO_x adsorber catalyst (NAC, also called lean NO_x traps) operation it is acknowledged that it is easier to reduce NO_x under reducing conditions. These catalysts store NO_x (as nitrate species) on the catalyst during normal (oxidising) engine operation, and then reduce it to nitrogen by moving the engine operation for a short time (a couple of seconds or so) to a state in which it emits a net reducing gas stream. The high levels of hydrogen, CO and HC emitted during this engine mode react and reduce the NO_x species on the catalyst, generating nitrogen. This strategy was successfully introduced by Cummins in the 2007 diesel-powered Chrysler Dodge Ram vehicle in North America, using Johnson Matthey catalysts. The alternative approach, which continues to find more widespread application, is selective catalytic reduction (SCR). This strategy uses a reductant species that prefers to react with NO_x rather than the far more plentiful oxygen – hence "selective reduction". The reductants normally present in the exhaust from diesel engines (hydrogen, CO and HC) strongly prefer to react with oxygen, so these are not suitable species, especially when high NO_x conversions are required. However, many years ago it was discovered that, over certain catalysts, ammonia is highly reactive with NO_x, even when excess oxygen is present. This reaction proceeds as outlined in Equation 1:

$4NH_3 + 4NO + O2 -> 4N_2 + 6H_2O$

This approach has been used, in association with vanadium-based catalysts, to control NO_x emissions from power plants for many years. In coal-fired power plants the exhaust can contain a significant amount of fly ash, which can lead to catalyst abrasion and blockage, thereby increasing backpressure. These are significant problems when conventional coated catalysts (in which a relatively thin layer of catalyst is coated onto an inert substrate, such as the cordierite used in automotive applications) are used. There are other options. One is to use a plate catalyst, a coated steel substrate which is then shaped and stacked in a manner that optimises catalytic activity to pressure drop. A second approach is to use extruded catalysts, in which the whole catalyst is made of active material. In these extruded catalysts if the top layer of catalyst is abraded away it simply reveals further active material below, which greatly increases catalyst longevity. A further benefit of using extruded catalysts is that they have a higher specific activity, since there is more effective catalyst volume per unit volume than is the case in conventional coated products.

These extruded vanadium-based catalysts are also used to control NO_x emissions in a wide range of applications including: industrial processes ranging from cement kilns to coffee processing to green houses; power generation including coal, waste and biomass-fired power plants; gas turbines; stationary engines running on diesel, gas or bio oil; and ship propulsion using large engines or boilers.

Large coal fired power plants are the most significant point sources of air pollution. To remove more than 90% of NO_x from the exhaust, SCR is required, which has the synergistic effect of oxidising mercury, making it easier to contain. The move towards renewable fuels, combusting biomass and waste, have brought new challenges, but JM and its partners have designed catalyst systems to successfully deal with this. In commercial greenhouses all the main products of diesel engine combustion, CO_2, heat and electricity are utilised. Valuable green electricity is exported to the grid whilst the heat from the engine helps maintain optimum temperature for growth. The CO_2 acts as a feed, although NO_x, CO and unburned fuel cause problems such as spoilage and are removed from the exhaust by a combination of oxidation and SCR catalysts.

Ships continue to use fuel with high levels of sulphur and produce significant emissions of NO_x and SO_x (oxides of sulphur). European studies have predicted that emissions from marine sources will overtake those on land by 2020. Regulatory bodies and the IMO (International Maritime Organisation) have acted and by 2016 new build vessels operating in Emission Control Areas will have to reduce their SO_x and NO_xemissions significantly. The use of lower sulphur fuels will solve the SO_x problem but aftertreatment such as SCR will be required for the 80% reduction in NO_x. Norway, whose coastline is particularly vulnerable, established the "NO_x Fond" to reduce emissions in 2007. This has stimulated an early market for marine SCR, with hundreds of vessels from tankers to fishing vessels being fitted – many with Johnson Matthey's SINO$_x$® systems and catalysts.

Vanadium-based catalysts are very effective, since they enable high conversions of NO_x over a wide operating temperature range, as shown in Figure 1. In addition, they are highly resistant to inhibition from the other gas phase species present in exhaust streams, such as CO and HC, and they are

Figure 1: Typical Operating Temperature Window of Vanadium-based SCR Catalysts

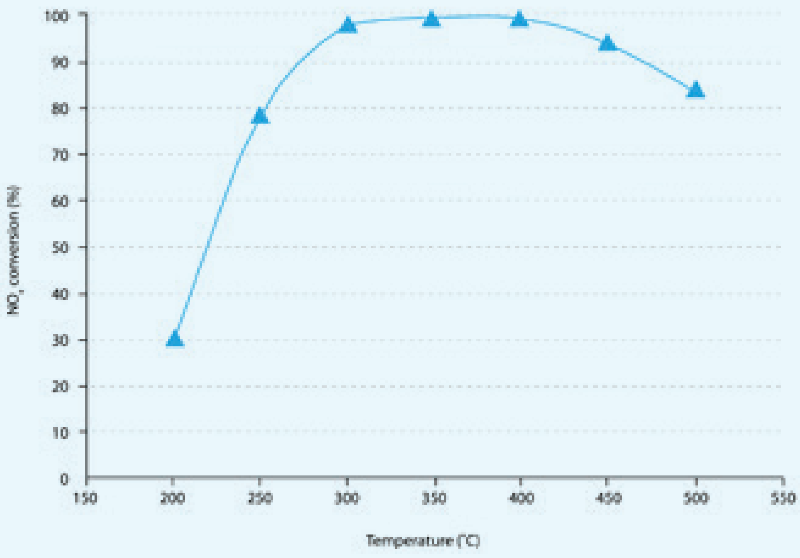
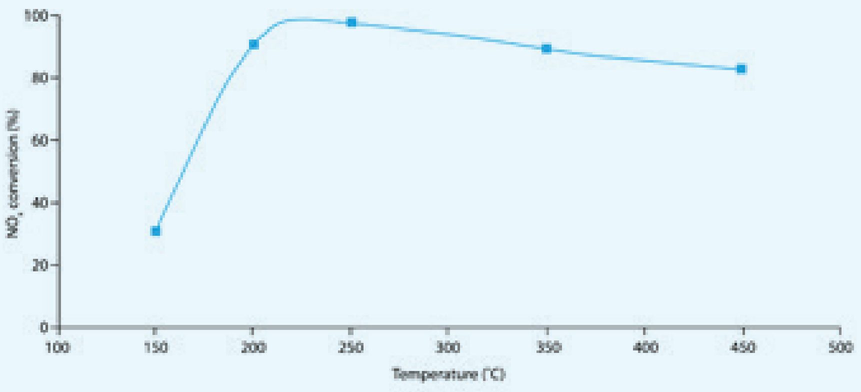


Figure 2: SCR Performance of Cu/Zeolite SCR Catalyst Following Ageing at 670°C for 64 hrs



also tolerant of the sulphur species that can be present at high concentrations in some applications (e.g. marine).

In 2005 the Euro IV regulations were introduced for heavy duty diesel (HDD) vehicles in Europe, requiring significant reductions in both NO_x and particulate matter (PM, also called diesel soot). The majority of engine manufacturers met these emission standards by calibrating their engines to emit very low levels of PM and using vanadium-based SCR catalysts to reduce the NO_x emissions. Such engine calibrations also result in optimum engine fuel economy, which is both good for the operator and for the vehicle's CO_2 emissions (which are also minimised). Both coated and extruded vanadium-based catalysts were used to meet these Euro IV and the subsequent Euro V (2008) HDD emission regulations. Successful operation for one million kilometres has been demonstrated by such systems [1].

Since engines do not emit ammonia, the ammonia for these applications is derived from aqueous urea, which is carried in a separate tank on board the vehicle. In HDD applications this tank is replenished periodically by the driver, at the thousands of outlets of aqueous urea at vehicle depots, service centres and gas stations globally. Ammonia is generated from urea as outlined in Equation 2.

$(NH_2)2CO + H_2O \text{ -> } 2NH_3 + CO_2$

In North America the EPA introduced its 2010 (EPA10) emission regulations for both light and heavy duty diesel applications. These regulations are met by using a combination of diesel particulate filters (DPFs) to control PM emissions and SCR to remove NO_x. Filters generally use high temperature active regeneration to remove the soot that builds up in the DPF during normal operation. This active regeneration involves raising the temperature of the DPF to around 600°C, at which temperature the oxygen in the exhaust reacts rapidly with the trapped soot to clean the filter and to form CO_2. As a consequence of this DPF active regeneration process, the SCR catalysts used in such combined DPF + SCR systems need to be able to withstand very high temperatures.

Vanadium-based products do not have the required thermal durability, so alternative SCR catalysts based on iron and copper zeolite are used. As an example, Figure 2 shows that copper zeolite catalysts have outstanding activity even following prolonged exposure to high temperature.

These combined DPF + SCR systems, which will also be used to meet future HDD and light duty diesel emissions regulations in Europe, are able to remove all four major pollutants, CO, HC, NO_x and PM, with efficiencies exceeding 90%. An additional benefit of combining DPFs with SCR is that the oxidation catalysts that form an integral part of the DPF system convert some of the engine-out NO into NO_2, and this NO_2 promotes the low temperature performance of the downstream SCR catalyst, by the reaction shown in Equation 3, as illustrated in Figure 3 for an Fe/Zeolite catalyst.

$2NH_3 + NO + NO_2 \text{ -> } 2N_2 + 3H_2O$

In conclusion, it is clear that SCR systems are pivotal technology for present and future NO_x control systems, and will be used for years to come in a wide range of applications from passenger cars, through trucks and buses, to power plants, locomotives and ocean-going ships. Johnson Matthey has invested in world class facilities for development and manufacture of coated, extruded and plate SCR catalysts, and is well positioned to play a key role as demands from these sectors increase over the coming years.

Produced by Johnson Matthey's Emission Control Technologies business. For further information visit www.jmect.com or email ECTsalesUK@matthey.com

Figure 3: Promoting Effect of NO_2 on the SCR Reaction Over Fe/Zeolite SCR Catalyst