

# “Urea-SCR Technology for deNO<sub>x</sub> After Treatment of Diesel Exhausts”

**Edited by Isabella Nova and Enrico Tronconi (Politecnico di Milano, Italy),  
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## **An essay book review by Martyn V. Twigg**

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The introduction and development of catalytic control for exhaust gas emissions from vehicles has been one of the major technical achievements over the last four decades. A huge number of cars were manufactured during this time that provided society with a high degree of personal mobility and without the continuous development of emissions control technologies the atmospheric pollution derived from them would have been overwhelming. Three-way catalysts (TWC) were introduced on traditional gasoline powered cars in the early 1980s to control the emissions of hydrocarbons (HC), carbon monoxide (CO) and nitrogen oxides (NO<sub>x</sub>) and have since been developed so that today tailpipe emissions of these pollutants can be reduced by more than 99.5% and tailpipe emission levels can be less than in the surrounding ambient air. During more recent years, and especially in Europe, the proportion of diesel powered cars has increased rapidly so now about half of new European cars have a diesel engine. Control of their tailpipe emissions has been particularly challenging because of their low exhaust gas temperature and the presence of excess oxygen.

Under these conditions TWCs cannot be used and alternative technologies were developed for the control of HCs and CO by oxidation catalysts. An undesirable characteristic of older diesel engines was the black soot they produced. This was considerably reduced by fuelling and combustion engineering improvements and was effectively eliminated by the use of diesel particulate filters (DPFs) which were introduced a decade ago. The remaining difficult challenge has been the control of NO<sub>x</sub> emissions from both light and heavy duty diesel vehicles. Two technologies have been recently introduced to do this, though only one, ammonia selective catalytic reduction (SCR), appears to be able to provide the necessary performance for future demands under a wide range of driving conditions. The present book is about diesel engine NO<sub>x</sub> emissions control by ammonia (derived from urea) SCR, and before detailing the book's contents some background information is given which provides a suitable context. Because of higher exhaust gas temperatures control of emissions from heavy duty diesel vehicles is less demanding than with light duty ones, so the emphasis here is on diesel cars.

## **1. Background**

### **1.1 Exhaust Gas Temperature**

The control of tailpipe emissions from vehicles powered by traditional stoichiometric gasoline engines with

TWC is now highly advanced and can achieve almost complete removal of the three gaseous pollutants CO, HCs and NOx under normal driving conditions. In practice reductions of more than 99.5% are possible, and a contributing factor for such a good performance is the relatively high temperature of the exhaust gas. In contrast the control of diesel engine exhaust gas emissions under lean conditions has been more problematic for two main reasons. The first problem results from the efficiency of diesel engines that under part load conditions can result in particularly low exhaust gas temperatures. For example, the exhaust gas temperature of a small European car with a gasoline engine may typically be in the region of 350°C to 475°C in the urban part of the European test cycle, whereas the same car with a diesel engine may be around 150°C as shown in **Figure 1**, and designing catalysts to operate efficiently at such low temperatures has been a major challenge, particularly when fuel sulfur levels were higher than they are today!

Heavy duty diesel engines in trucks generally operate under higher engine percentage loads and over appropriate duty cycles they can have much higher exhaust gas temperatures than their passenger car counterparts, typically up to around 400°C. So here there is considerably more scope for catalytic emissions control.

Once diesel fuel sulfur levels were reduced from the very high levels of two decades ago in Europe control of CO and HC emissions from all diesel engines by oxidation catalysts became feasible although special catalysts had to be developed for the low operating temperature cars.

### 1.2 Particulate Control with Filters

This was followed by control of particulate matter (PM or soot) by the introduction of filter technologies that enabled engine measures to further reduce engine-out NOx levels without being overly concerned about increased PM that was handled by the filter system. Traditionally the main approach for controlling NOx from small diesel engines has been *via* engine measures, including the use of exhaust gas recycle (EGR) and improving injection fuelling to produce ever finer sprays *via* multiple smaller injector nozzles and *via* increasing fuel pressures. EGR works by decreasing the amount of oxygen in the combustion charge that reduces the fuel burn rate and the peak temperatures as well as somewhat increasing heat capacity of the combusting charge.

There is a trade-off between NOx and PM. Reducing engine-out NOx normally results in an increase in PM. This is because a higher combustion temperature reduces PM by increased burning of residual

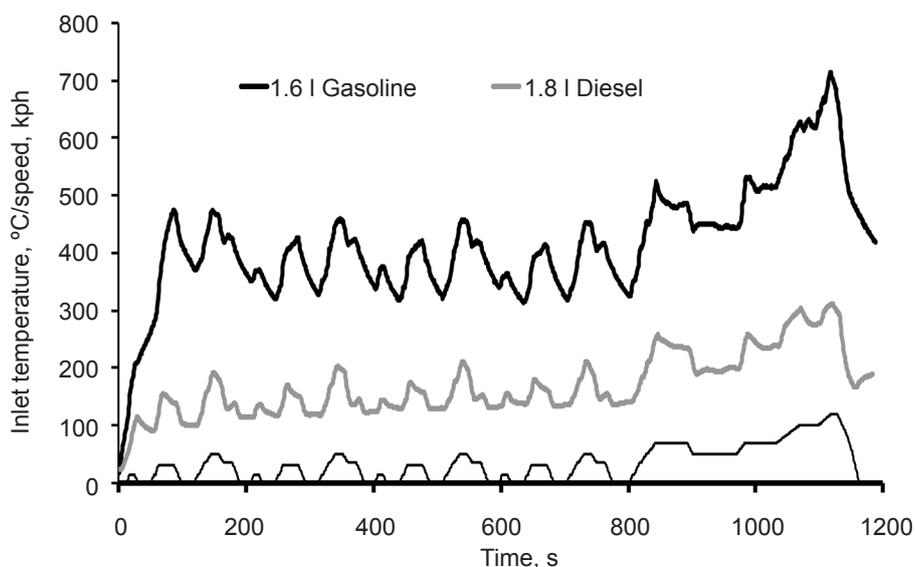


Fig. 1. Exhaust gas temperatures during the European test cycle for the same family size car equipped with a similar displacement gasoline and diesel engine. Throughout the test cycle the exhaust gas temperature is much lower with the diesel engine than that with the gasoline engine

carbonaceous PM but thermodynamically high temperatures favour formation of endothermic NOx (see Figure 2). This trade-off was broken by fitment of DPF that recently enabled achievement of car diesel engines with engine-out NOx levels significantly below 0.1 g km<sup>-1</sup> in the combined European test cycle.

### 1.3 NOx Control Technologies

Notwithstanding the improvements just mentioned, more recently NOx control has become increasingly important, driven by ever more stringent NOx emissions legislation. This legislation requires additional catalytic aftertreatment to meet the NOx standards for diesel vehicles, especially cars, and two approaches have become established.

In the first of these catalytic approaches, NOx trapping, under normal driving lean conditions NO is oxidised to NO<sub>2</sub> as in Equation (i). This undergoes further oxidation as it is stored as a metal nitrate, Equation (ii), followed at intervals by a reductive regeneration that converts the stored NOx to nitrogen. In this process NOx is liberated usually as NO, Equation (iii), that is reduced over a rhodium component in much the same way as a TWC functions on a traditional gasoline car, Equation (iv).



This technology works well on smaller diesel cars, although it has temperature limitations reflecting the thermodynamic stability of the metal nitrates concerned.

The second NOx control technology, and the subject of the present book, is ammonia SCR that involves reaction of NOx with ammonia to form nitrogen and water. Ammonia SCR technology was introduced on power plant applications in Japan in the early 1970s, and some twenty years later it was adopted for use in heavy duty diesel vehicles that have exhaust gas temperatures appropriately high to use the traditional vanadium-based catalysts. Ammonia was derived from urea solution that was injected into the exhaust gas where it hydrolyses forming ammonia and carbon dioxide (see Equation (v)).

However, the temperatures on light duty diesel vehicles are too low for efficient operation of the older SCR vanadium-based catalyst formulations and so after much effort base metal zeolite catalysts were introduced that can operate effectively at remarkably low temperatures and already increasingly large numbers of cars on European roads are equipped with this SCR technology.

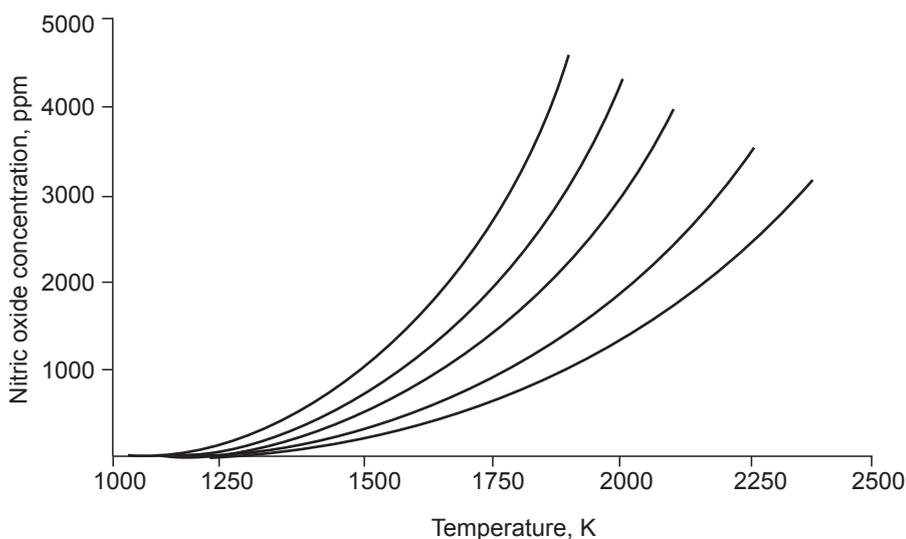


Fig. 2. Concentrations of NO at high temperatures in equilibrium with nitrogen (0.8 bar) and various amounts of oxygen; the highest curve corresponds to 0.2 bar, and subsequent lower curves 0.15, 0.05 and 0.02 bar respectively. Derived from measurements made by W. Nernst (1); modern theoretical values are somewhat higher

More than thirty years ago a very important discovery was made about the effect of the ratio of NO<sub>2</sub> to NO on the rate of the ammonia SCR reaction over vanadium-based catalysts. The reaction is much faster when both are present. The reactions involved when urea ((NH<sub>2</sub>)<sub>2</sub>CO) is the source of ammonia are: urea hydrolysis to give ammonia, shown overall in Equation (v); a rapid reaction when just NO is present, Equation (vi); a particularly slow reaction when NO<sub>2</sub> is present alone, Equation (vii); and an amazingly fast reaction when the ratio of NO<sub>2</sub> to NO is 1:1, that is known as the fast SCR reaction, Equation (viii). Depending on the actual SCR catalyst used it can therefore be important that an appropriate upstream oxidation catalyst provides the SCR catalyst with a suitable mixture of NO and NO<sub>2</sub>, although some modern copper zeolite catalysts are less sensitive to the NO/NO<sub>2</sub> ratio than other catalysts.



There have been extensive studies on the mechanism of ammonia SCR reactions, and by analogy with known reactions of discrete compounds it may be suggested that rapid decomposition of ammonium nitrite (Equation (ix)) is important in the SCR surface catalysed process forming nitrogen. At higher temperatures one route to undesirable nitrous oxide (N<sub>2</sub>O) emissions might be from decomposition of ammonium nitrate-like surface species, Equation (x). The former reaction has been used to prepare chemically pure nitrogen (free of atmospheric argon) and the latter to manufacture N<sub>2</sub>O.



However, the surface SCR reactions are complex and recently nitrate species have been shown to have important roles in the fast SCR reaction. Chapters in this book go a long way to help the reader to unravel some of the mechanistic details.

## 2. Topics Covered

This book has 22 chapters by eminent contributors and is appropriately edited by Professors Isabella Nova and Enrico Tronconi from the Politecnico di Milano, Italy, whose Laboratory of Catalysis and Catalytic Processes (LCCP) has a worldwide reputation for research on the control of NO<sub>x</sub> emissions especially by ammonia SCR reactions. This very well produced book includes some colour illustrations and it is divided into eight parts that are detailed in the following sections.

### 2.1 Part 1. Selective Catalytic Reduction Technology

The first part of the book has two chapters with the first entitled 'Review of Selective Catalytic Reduction (SCR) and Related Technologies for Mobile Applications' by Timothy Johnson (Corning, USA). It provides an overview of relevant legislation and progress in engine developments to reduce engine-out NO<sub>x</sub> levels, before detailing mobile SCR systems using urea in solution as the source of ammonia. This chapter relies heavily on illustrations reproduced from a variety of original publications that appear not to have been redrawn so there is, unfortunately, a lack of style consistency. Notwithstanding this the chapter collects together much valuable and practical information.

The second chapter called 'SCR Technology for Off-highway (Large Diesel Engine) Applications' is by Daniel Chatterjee and Klaus Rusch (MTU Friedrichshafen GmbH, Germany) and is concerned with large diesel engines used in marine applications, mining trucks and trains as well as in electrical power generation units. These engines usually operate under high load conditions so have high temperature exhaust gas, enabling good SCR performance with conventional vanadium-based catalysts, but their fuel invariably contains high sulfur levels and this can cause a variety of problems. For example, newer zeolite-based SCR catalysts are poisoned and do not work well, and at these quite high operating temperatures some sulfur dioxide (SO<sub>2</sub>) can be oxidised to sulfur trioxide (SO<sub>3</sub>), Equation (xi). If any ammonia slip is present this can form particulate ammonium sulfate and/or ammonium bisulfate according to Equations (xii) and (xiii), as well as sulfuric acid mist that can itself cause difficulties, Equation (xiv).





This well-illustrated chapter goes on to discuss combined SCR systems such as SCR/filter combinations, and large scale SCR units, as well the automated control strategies that are usually involved.

## 2.2 Part 2. Catalysts

The second part of the book has four chapters that focus on SCR catalysts, and the first of these by Jonas Jansson (Volvo, Sweden) discusses vanadium-based catalysts used in heavy duty mobile SCR applications and highlights the legislative requirements before considering catalyst properties. Because the vanadium-based catalyst operates in the temperature range of optimum activity (say 300°C–500°C) they have been widely used. Typical catalyst compositions are given as 1%–3%  $\text{V}_2\text{O}_5$  plus about 10% tungsten trioxide ( $\text{WO}_3$ ) impregnated onto a high surface area titania (normally anatase) that is coated onto flow-through substrates. Related extruded catalyst compositions have also been widely used. Practical aspects such as selecting appropriate catalyst size (dimensioning), the effects of space velocity and ageing effects (thermal and poisoning) are considered, and it is clear vanadium catalysts have had and will continue to have a major role in this area. However, with reduced sulfur fuel levels the newer, higher activity zeolite-based catalysts discussed in the following chapter will probably become increasingly important.

Appropriately the next chapter, by Todd J. Toop, John A. Pihl and William P. Partridge (Oak Ridge National Laboratory, USA), is about iron-zeolite SCR catalysts. These were amongst the first metal zeolite catalysts used in SCR applications, and because they can have good high-temperature performance coupled with reasonable stability, they were introduced into gas turbine applications at an early stage. In contrast copper zeolite catalysts usually have better low-temperature activity that falls off at higher temperatures as ammonia is oxidised to  $\text{NO}_x$ . Making sweeping generalisations about the relative performance of SCR catalysts can be problematic because several factors are involved such as: the type of zeolite involved, its silica to alumina ratio, the metal loading and importantly the preparation method. However, in general copper-based catalysts

absorb more ammonia than do iron ones and under dynamic transient conditions this can provide a significant performance advantage.

Because of their superior low-temperature performance copper zeolite catalysts have been adopted for use in car applications and these are discussed in the third chapter in this section by Hai-Ying Chen (Johnson Matthey, USA). The emphasis is on the impact of the nature and physical properties of the zeolite type on catalytic performance, and in particular the size of the zeolite pores classified as small, medium or large. Small pore zeolites such as chabazites and other small pore molecular sieve materials such as the silicon substituted aluminium phosphate SAPO-34 have outstanding hydrothermal stability, excellent SCR activity and importantly they form very low amounts of the undesirable byproduct  $\text{N}_2\text{O}$ . The introduction of these copper molecular sieve SCR catalysts into the series production of diesel cars in Europe was an outstanding technical achievement that will provide a high degree of  $\text{NO}_x$  emissions control into the future. Indeed one might expect that new materials will be discovered that provide the necessary acidity and environment around the copper atoms to provide good SCR activity and durability. However, these features are not unique in providing excellent ammonia SCR performance. Some simple metal oxide catalysts have been shown to perform well and these are the subject of the last chapter in the part on SCR catalysts.

The last chapter in this part on catalysts is the result of a collaboration by Gongshin Qi (General Motors, USA) and Lifeng Wang and Ralf T. Yang (University of Michigan, USA) that deals with low-temperature SCR involving both zeolite and metal oxide ammonia SCR catalysts as well as touching on developments with hydrogen SCR. They highlight the importance of the method of making iron-ZSM5 catalysts. Aqueous impregnation with iron(III) salts does not lead to full metal incorporation into the pores because, it is suggested, the heavily hydrated metal cations are too large for easy penetration, whereas impregnation with iron(II) species makes highly active catalysts. The interpretation of the origin of this effect may be more complex because reduction of catalysts derived from iron(III) salts gives improved activity. Again the importance of small pore acidic molecular sieves is noted, as is the wide range of activities that can be obtained with different copper zeolite catalysts and their dual role in providing acid sites for formation of ammonium cations and metal-based oxidation of  $\text{NO}$

to NO<sub>2</sub>, leading to highly reactive ammonium nitrite-like species that decompose to nitrogen and water. Manganese oxides can have excellent low-temperature ammonia SCR activity, and clearly their oxidation capability is important. A wide variety of promoted oxides have been investigated, but it appears their adoption has been restricted by a lack of tolerance to water and in particular sulfur poisoning. Moreover, increasing activity by using higher manganese loadings appears to result in the formation of more N<sub>2</sub>O. It is noted perhaps the most successful development in this area was made by Shell who in the early 1990s developed a relatively low-temperature ammonia SCR process using a vanadium on titania catalyst promoted by transition metal species.

Hydrogen can be a reductant in NO<sub>x</sub> SCR reactions and over platinum group metal (pgm) catalysts. The reactions that can take place are shown in Equations (xv)–(xvii).



High conversions of NO in the presence of oxygen at low temperatures are possible, although as might be expected, at higher temperatures the direct reaction of hydrogen with oxygen, Equation (xvi), increasingly takes place, and NO conversion decreases because less hydrogen is available for the SCR reaction. As a result an operational temperature window is formed in which NO conversion is optimised. A serious detraction from these hydrogen SCR pgm catalyst systems is the high proportion of N<sub>2</sub>O that can be formed. A better catalyst in this respect appears to be a palladium promoted vanadium on titania/alumina that retains good low-temperature SCR performance and has reduced N<sub>2</sub>O formation although this is probably still too high for practical applications.

### 2.3 Part 3. Mechanistic Aspects

This part of the book is concerned with the mechanistic aspects of SCR reactions and has three chapters, the first of which is by Wolfgang Grunert (Ruhr University Bochum, Germany) on the nature of SCR active sites. The range of available characterisation techniques are first outlined before the surface science techniques that have been used are highlighted. Vanadium-based catalysts are considered first, and there is general

agreement that binary V—O—V moieties including a Brønsted site are the most active structures and a well-accepted mechanism is available for this site. Isolated VO<sup>2+</sup> species exchanged into zeolite structures are also active, apparently *via* a different mechanism. Tungsten promoted vanadium appears to be effective by encouraging formation of isolated V—O—V species. The active sites in iron and copper exchanged zeolites are then considered; here a huge amount of research has been done over several decades trying to identify the intimate mechanistic details and the nature of the active SCR sites. Much of the earlier work involved exchanged ZSM-5, and then more recently beta-zeolite and small pore molecular sieves were studied. As previously noted a key feature is the low temperature performance of the copper catalysts and the higher temperature durability of the iron catalysts. The metal centres may be associated with NO oxidation. An added advantage of the iron catalysts, like the earlier vanadium ones, is tolerance towards sulfur that is in marked contrast to the poison sensitive copper catalysts. Although there has been considerable speculation about the roles of monomeric, dimeric and oligomeric metal active centres their general relative importance is unclear. Brønsted acidic zeolite sites have been thought to be a means of concentrating ammonium ions close to the metal centres, but the importance of this is questioned by more recent work on non-zeolite conventional oxide catalysts some of which can have good performance.

The next chapter by Masaoki Iwasaki (Toyota, Japan), is about mechanistic aspects of the ammonia/NO reaction in excess oxygen, Equation (vi), that is the traditional standard or rapid ammonia SCR reaction. Results are given for reactions involving copper and iron exchanged ZSM-5, a tungsten-promoted vanadium on titania catalyst as well as the acid form of ZSM-5. The expected reaction order of copper was greater than iron and vanadium catalysts. Kinetic parameters such as apparent activation energies and apparent reaction orders were reported for the separate oxidation of ammonia and NO as well as the ammonia-NO-oxygen reaction. Generalising for the ammonia NO SCR reaction the order in NO is positive and close to one, the order in oxygen is fractional and that for ammonia is negative, reflecting its strong adsorption that can result in reaction inhibition. There is a strong correlation between SCR activity and NO oxidation activity. A considerable amount of carefully determined transient

response data is reported and several catalytic cycles are presented. The mechanistic conclusions are similar to those previously noted.

There then follows an important chapter on the role of NO<sub>2</sub> in ammonia SCR reactions by the editors Isabella Nova and Enrico Tronconi (Politecnico di Milano, Italy). The most obvious role of NO<sub>2</sub> is in combination with NO in the fast SCR reaction. Ammonia and NO<sub>2</sub> are strongly adsorbed and interact on the catalyst surface. The reaction of NO<sub>2</sub> with surface oxide ions affords nitrate and nitrite ions, according to Equation (xviii), with the latter being further oxidised by NO<sub>2</sub> to nitrate and NO *via* Equation (xix) so the overall stoichiometry is as shown in Equation (xx). These reactions are in equilibrium and depend on concentration, temperature and catalyst oxidation state.



The intimate mechanism of the SCR process is based on nitrogen redox chemistry. In the standard slow SCR reaction oxygen is the oxidant taking NO to nitrite, and in the fast SCR reaction the more powerful oxidiser NO<sub>2</sub> is available and so the mixed reaction involving NO

and NO<sub>2</sub> is much faster. The overall fast SCR reaction may be considered to go *via* the disproportionation of NO<sub>2</sub> to nitrite, the nitrate oxidation of NO to nitrite and the formation of surface ammonium nitrite that spontaneously decomposes to water and nitrogen. All the steps involved in the fast SCR reaction are summarised in **Table I**. The required oxidant provided by NO<sub>2</sub> in the fast SCR reaction can also be supplied by addition of ammonium nitrate in what is called enhanced SCR.

### 2.4 Part 4. Reaction Kinetics

There are three chapters in the part of the book on the reaction kinetics of ammonia SCR reactions, and fittingly the first is by Isabella Nova and Enrico Tronconi. This is on SCR reactions over vanadium(V) oxide (V<sub>2</sub>O<sub>5</sub>)/WO<sub>3</sub> supported on titania catalyst, and they explain how measured unsteady state kinetic parameters for all of the reactions concerned can be incorporated into a computer model for the control of heavy duty diesel NO<sub>x</sub> control systems. At an intimate mechanism level surface sites are indicated that include a surface redox site at which oxygen is adsorbed, a reaction site at which NO is adsorbed and an acidic site to bond to ammonia. Reduced vanadium centres are reoxidised by nitrate. It is concluded the fast SCR reaction proceeds *via* dimerisation of NO<sub>2</sub> followed

**Table I Summary of the Individual Steps Involved in the Fast SCR Reaction over Vanadium-based and Zeolite Metal Promoted Catalysts**

<b>Involving NO<sub>2</sub> only</b>	
2NO <sub>2</sub> ⇌ N <sub>2</sub> O <sub>4</sub>	NO <sub>2</sub> dimerisation
N <sub>2</sub> O <sub>4</sub> + O <sup>2-</sup> ⇌ NO <sub>2</sub> <sup>-</sup> + NO <sub>3</sub> <sup>-</sup>	Disproportionation
NO <sub>2</sub> + NO <sub>2</sub> <sup>-</sup> ⇌ NO + NO <sub>3</sub> <sup>-</sup>	Nitrite oxidation by NO <sub>2</sub>
<b>In the presence of NH<sub>3</sub></b>	
2NH <sub>3</sub> + H <sub>2</sub> O ⇌ 2NH <sub>4</sub> <sup>+</sup> + O <sup>2-</sup>	NH <sub>3</sub> adsorption
NH <sub>4</sub> <sup>+</sup> + NO <sub>2</sub> <sup>-</sup> ⇌ [NH <sub>4</sub> NO <sub>2</sub> ] → N <sub>2</sub> + 2H <sub>2</sub> O	Nitrite reduction by NH <sub>3</sub>
NH <sub>4</sub> <sup>+</sup> + NO <sub>3</sub> <sup>-</sup> ⇌ NH <sub>4</sub> NO <sub>3</sub>	Formation/dissociation of NH <sub>4</sub> NO <sub>3</sub>
NH <sub>4</sub> NO <sub>3</sub> → N <sub>2</sub> O + 2H <sub>2</sub> O	Formation of N <sub>2</sub> O
<b>In the presence of NO</b>	
NO + NO <sub>3</sub> <sup>-</sup> ⇌ NO <sub>2</sub> + NO <sub>2</sub> <sup>-</sup>	Reduction of nitrate by NO
<b>Fast SCR</b>	
2NH <sub>3</sub> + NO + NO <sub>2</sub> → 2N <sub>2</sub> + 3H <sub>2</sub> O	Overall reaction

by its disproportionation to surface nitrite and nitrate. Ammonium nitrite decomposes to nitrogen while nitrate is reduced by NO to reform NO<sub>2</sub>.

The next chapter by Michael P. Harold (University of Houston, USA) and Parnit Metkar (DuPont, USA) provides a very good overview of the published mechanistic work on ammonia SCR of NO<sub>x</sub>. They consider not only kinetics and mechanisms but also the role of transport effects, especially in reactions over iron exchanged zeolites and layered catalysts comprising separate copper and iron zeolite layers. A number of particularly important points are highlighted. Diffusion limitations can become significant for the fast SCR reaction at temperatures just above 200°C, first diffusion within the catalyst pores; and increasing the amount of ammonia rather than increasing the rate of the standard SCR reaction with NO does not enhance the reaction rate but rather slows it due to strong ammonia adsorption causing site blocking. The reaction orders are one in NO, half in oxygen and -0.3 in ammonia and the corresponding activation energy of around 10 kcal mol<sup>-1</sup> could reflect a relatively low barrier for the rate limiting step since this was estimated under conditions where diffusion effects were thought to be absent. Curiously on iron zeolite NO oxidation is inhibited by water, but the standard SCR reaction is not. However, the results of isotopic labelling experiments are consistent with the decomposition of ammonium nitrite being involved, Equation (ix), and a potentially important route to ammonium nitrite is from NO reduction of the nitrate. It is clear the mechanistic situation for the fast SCR reaction can be significantly complex, and the chapter concludes with an examination of two layer copper zeolite/iron zeolite catalyst arrangement, and aspects of reactor modelling.

The last chapter in this part, by Louise Olsson (Chalmers University, Sweden), complements the previous one because it concerns the kinetic modelling of ammonia SCR reactions over copper zeolite catalysts. An often unappreciated fact, that is highlighted, is under operating conditions the zeolite will adsorb a large amount of water in addition to ammonia with an enthalpy of adsorption of around 100 kJ mol<sup>-1</sup> in the absence of competing adsorbates.

## 2.5 Part 5. Modelling and Control

The first chapter in this part, about reactor models for flow-through and wall-flow converters, is by Dimitrios Karamitros and Grigorios Koltsakis (Aristotle University Thessaloniki, Greece). The arrangement of the different

aftertreatment components are discussed because of the consequences it has on their rate of heating after the engine starts. A number of other interesting aspects are discussed including the complex behaviour of SCR catalysts incorporated into a particulate filter. In the absence of soot in the filter the pressure driven flow of gas through the filter walls containing catalyst provides better performance than the same amount of catalyst on a flow-through substrate because of the absence of diffusion resistances. However, the presence of a substantial layer of soot can modify the situation: there is the potential reaction of NO<sub>2</sub> with soot that reduces the NO<sub>2</sub>/NO ratio which, with some SCR catalysts, can reduce its performance. To compensate for this effect more catalyst will be required. This might not be physically possible and if it were possible more catalyst would increase backpressure across the filter. It is therefore important SCR catalyst incorporated into filters lack NO<sub>2</sub>/NO ratio sensitivity.

The other chapter in this part includes discussion about the understanding and measurements needed for SCR control systems by Ming-Feng Hsieh (Cummins, USA) and Junmin Wang (Ohio State University, USA). SCR control systems have to take into account varying engine NO<sub>x</sub> emissions during real world driving and adopt the urea solution injections accordingly. Forward control strategies have been used which make major assumptions about catalyst ageing and degradation of ammonia capacity, but alone they are not adequate and some degree of feedback control using sensors is necessary. However, the present NO<sub>x</sub> sensors suffer interference from ammonia, and this has to be taken into consideration *via* sophisticated algorithms. In fact NO<sub>x</sub> sensors also have a sensitivity to the NO<sub>2</sub>/NO ratio resulting from the extra oxygen present in NO<sub>2</sub>. Ammonia sensors are being experimented with to overcome some of the practical difficulties, but there remain significant challenges so SCR control system development is an area of much activity.

## 2.6 Part 6. Ammonia Supply

The three chapters in this part are about the production of a spray of urea solution in the exhaust gas flow, its conversion into ammonia gas, storage of ammonia in SCR catalysts and the modelling of these processes. The first chapter by Ryan Floyd (Tenneco, USA) and Levin Michael and Zafar Shaikh (Ford, USA) is about system architecture and includes the design of injectors and mixing devices. The computer-based design of these systems has resulted in reliable production of gaseous

ammonia with minimal deposition of troublesome solids. The second chapter is about ammonia storage and release by Daniel Peitz, Andreas Bernhard (Paul Scherrer Institute, Switzerland) and Oliver Kröcher (EPFL, Switzerland) that focuses attention on the chemical reactions involved in converting urea to ammonia, Equations (xxi) and (xxii), before going on to discuss alternative ammonia sources. While some of these alternatives have some attraction, the use and distribution of urea solution is now so well established it seems unlikely it will be displaced. The third and final chapter in this part is about gas flow modelling by Gianluca Montenegro and Angelo Onorati (Politecnico di Milano). Computational fluid dynamics (CFD) have been used for many years to optimise distributed flow through monolithic honeycomb catalysts and the exhaust system as a whole, and these techniques have been successfully applied to systems involving SCR NOx reduction (Figure 3). A high degree of mixing ammonia with the exhaust gas is essential for high overall performance.



### 2.7 Part 7. Integrated Systems

For performance, space constraints and cost considerations it is desirable to integrate emissions control functionality as much as possible, and the three chapters in this part of the book are about this topic. The first chapter details an experimental and modelling study of dual-layer ammonia slip catalysts (ASCs) by Isabella Nova, Massimo Colombo and Enrico Tronconi (Politecnico di Milano) and Volker Schmeißer, Brigitte Bandl-Konrad and Lisa Zimmermann (Daimler, Germany). The amount of ammonia fed to a SCR catalyst must be sufficient to reduce the varying amounts of NOx produced by the engine while maintaining the quantity of ammonia stored in the catalyst to ensure optimum NOx reduction performance. As highlighted elsewhere in this review, the control systems designed to maintain this situation under dynamic transient

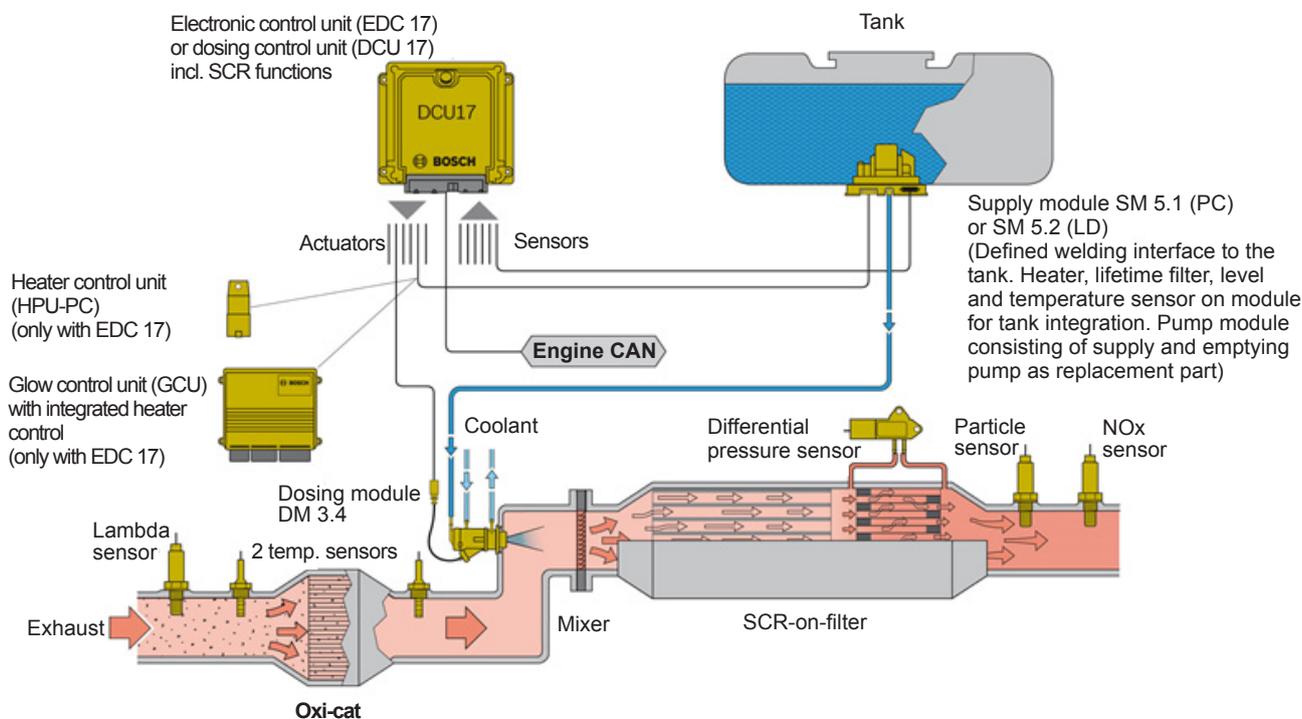


Fig. 3. Schematic diagram of a car exhaust gas emissions control system comprising an oxidation catalyst, wall-flow particulate filter, and flow-through SCR catalyst. Key components include a urea solution tank (heated in cold weather), dosing spray module and static mixer, temperature and NOx sensors. (Source: Robert Bosch GmbH)

conditions can be effective but occasionally in some circumstances excess ammonia may slip from the SCR catalyst, and oxidation catalysts have been developed to control the amount of escaping ammonia by converting it to nitrogen. They need to have high selectivity towards the production of nitrogen, and they can have SCR activity should any NO<sub>x</sub> be present. The situations examined were the traditional arrangement of a separate special oxidation catalyst after a SCR catalyst, a layer of oxidation catalyst above which was a layer of SCR catalyst as well as a physical mixture of the two catalysts. An iron zeolite catalyst was used and when this was present as an upper layer on the oxidation catalyst there was enhanced selectivity to nitrogen and a small amount of additional NO<sub>x</sub> reduction.

The second chapter in this part is about combining NO<sub>x</sub>-trapping catalysts with downstream SCR catalysts on diesel cars and is by Fabien Can, Xavier Courtois and Daniel Duprez (University of Pointiers, France). When a NO<sub>x</sub>-trap is regenerated by periodic enrichment of the exhaust gas ammonia can be formed, and the reactions involved in this process are detailed before giving the fascinating history of the use of this ammonia with a SCR catalyst. The ability of the SCR catalyst to store significant amounts of ammonia enables it to reduce NO<sub>x</sub> that is not retained in the NO<sub>x</sub>-trap during normal lean operation. Although optimised systems have been used on series production cars it seems likely further advances will be made in the future in this important area because it has the practical advantage of not requiring to store and inject urea solution into the exhaust system.

The final chapter in this part is by Thorsten Boger (Corning, Germany) about the integration of SCR catalysts into DPFs. The DPF materials in series production are cordierite, various forms of aluminium titanate, and silicon carbide. To reduce component count, cost and possibly improve performance there has been a move to incorporate catalytic functionality into particulate filters especially those in light duty diesel vehicles. This was first done with oxidation catalyst that removes CO and HCs during normal driving and periodically provides high temperature to initiate filter regeneration. This is done by oxidising partial combustion products from late injection of fuel into the engine. Recently SCR catalyst has been incorporated into filters, and a large amount of catalyst is required so that exceptionally high porosity filters are needed. Having sufficient strength and filtration efficiency with the necessary high porosity material

has been a major challenge that has been overcome and such filters are now in series production on some European diesel cars.

## 2.8 Part 8. Case Histories

There are two chapters in the last part of the book about practical applications of urea SCR systems to series of production vehicles. The first, entitled 'Development of the 2010 Ford Diesel Truck Catalyst System' by Christine Lambert and Giovanni Cavataio (Ford, USA), is a well written contribution with well sized clear illustrations. It provides a nice overview of the SCR work done in Ford since the early 1990s. By 1995 they had demonstrated a SCR NO<sub>x</sub>-control system on a light duty diesel vehicle, and development continued culminating in the USA with the introduction of the 2010 truck system. The evolution of copper zeolite catalysts is detailed and practical aspects such as the importance of durability of the upstream oxidation catalyst to maintain high NO<sub>x</sub> conversion through the then necessary appropriate NO<sub>2</sub> to NO ratio. Also covered is the influence of packaging constraints, backpressure problems, and the temperature requirements for the NO<sub>x</sub> conversions required. It was clear a rapid heating cold start strategy was needed to enhance the exhaust gas temperature so the emissions control system would work efficiently at a sufficiently early stage. The 2011 model year system comprised two oxidation catalysts, urea solution injection, two SCR catalysts, and a silicon carbide particulate filter. The optimisation work included substituting a proportion of the platinum for palladium in the oxidation catalyst as a cost save, although this resulted in poor (if any with an aged catalyst) NO oxidation to NO<sub>2</sub>. This was acceptable because a NO<sub>2</sub> insensitive copper/zeolite catalyst had been selected. Platinum/palladium formulations also had the advantages of reducing potential volatilisation of traces of platinum *via* its oxide that could influence SCR catalyst selectivity, reduced low level emissions of N<sub>2</sub>O and not oxidising traces of SO<sub>2</sub> to the more potent catalyst poison SO<sub>3</sub>. Both the oxidation catalyst and the SCR catalyst had to have high thermal stability because they experience high temperatures during active filter regeneration. The palladium-containing oxidation catalyst had durability, but early copper/zeolite SCR catalysts and even those based on beta zeolite did not have sufficient thermal stability. The availability of SCR catalysts based on small pore zeolites in 2007 provided the required higher thermal stability. The ammonia storage capacity of SCR catalyst with a

suitable urea solution dosing strategy can significantly enhance low temperature NO<sub>x</sub> conversion, although this has to be balanced with the possibility of ammonia slip during high temperature filter regeneration. On the vehicle this requirement was obtained by the control system. Exotherm problems on the SCR catalyst during filter regeneration caused by HC adsorption and carbon formation were all but eliminated with the small pore zeolite SCR catalyst. This chapter illustrates the huge amount of fundamental and development work that goes into the introduction of a successful vehicle emissions control system incorporating urea-based SCR that, of course, continues to be improved upon.

The final chapter in this part, and the last in the book, is by Michel Weibel, Volker Schmeißer and Frank Hofmann (Daimler, Germany) and is a short contribution about computer models for simulation and development of exhaust gas systems incorporating urea-based SCR NO<sub>x</sub> control. Factors such as maintaining the level of ammonia stored in the catalyst are particularly important with copper-based catalysts that operate best with a significant amount of stored ammonia. The urea solution dosing strategy has to satisfy this requirement under most engine operating conditions without there being excess ammonia that would be wasteful and potentially be an emission problem. Independently determined kinetics for each of the catalytic reactions and catalysts involved are parameterised for ease of use in computer modules, and in some instances compiled in data maps. The resulting simulation models are important during the development and optimisation of the individual components and in identifying practical ways of obtaining optimum overall operating performance. This is complex and made more so by a need to take into account the engine operation that determines engine-out NO<sub>x</sub> emissions.

### 3. Conclusions

Ammonia SCR has become the technology of choice for control of NO<sub>x</sub> emissions from all but the smallest diesel vehicles, and its importance is reflected in the

huge number of publications cited in this multi-author book. A wide variety of materials are catalytically active in ammonia SCR reactions, and several high performance catalysts have become established commercially. These have the attributes of high activity, the necessary good selectivity with minimal undesirable formation of N<sub>2</sub>O as well as very good longevity associated with high thermal durability. The book provides an important up-to-date survey of the state of SCR science and technology that over recent years has undergone tremendous advances. Exceptionally high conversions of NO<sub>x</sub> to nitrogen with amazingly high selectivity are now possible at temperatures so low they were thought impossible a decade ago. These improvements resulted from development work targeting low-temperature NO<sub>x</sub> control of emissions from diesel engine powered cars. Development work continues in this area and further exciting developments are likely in the not too distant future that could take the form of substituting urea as a source of ammonia for some other reductant derived from on board sources such as water or diesel fuel.

The lack of consistent illustration style, equation numbering that could have been unified during copyediting are easily criticised, as could the all too brief index that does not for instance have important terms such as chabazite and SAPO. However, these failings do not detract from this book being a mine of information that will be of value to researchers working in the SCR area as well as a reference for students in chemistry, catalysis and chemical engineering. The editors are to be congratulated for bringing together so many eminent contributors and completing such a major endeavour. This book should therefore be made available in academic and industrial research libraries alike.

### Reference

- 1 W. Nernst, *Z. Anorg. Chem.*, 1906, **49**, (1), 213

## The Reviewer



Following Fellowships at the Universities of Toronto and Cambridge Martyn Twigg joined a polymer group at ICI's Corporate Laboratory in the North West of England, and after involvement in projects at Agricultural Division at Billingham moved there in 1977. Martyn worked on catalysts and catalytic processes including synthesis gas production *via* naphtha and natural gas steam reforming, methanol and ammonia synthesis, and proprietary catalysts and processes for herbicide manufacture and environmental protection applications. He studied catalyst activation and built a much used off-site catalyst reduction unit. After managing an international polymerisation project he was head-hunted to work at Johnson Matthey as Technology Director in the autocatalyst area that he successfully led until being appointed Chief Scientist. This provided an opportunity for research diversity that included carbon nanotube manufacture and catalysts for medical applications. He was associated with four Queen's Awards, and was awarded the Royal Society of Chemistry Applied Catalysis Prize. He has more than 200 papers, co-authored books on transition metal mediated organic syntheses and catalytic carbonylation. He produced the "Catalyst Handbook", co-edits the Fundamental and Applied Catalysis series with Michael Spencer, and has 150 published patent families on catalysts and catalytic processes. Martyn has on-going collaborations with universities and holds honorary academic positions, and runs an active consultancy and catalyst development business.

## Erratum

# Computer Simulation of Automotive Emission Control Systems

It has come to our attention that there was a mistake in the published article: M. Ahmadinejad, J. E. Etheridge, T. C. Watling, Å. Johansson and G. John, *Johnson Matthey Technol. Rev.*, 2015, 59, (2), 152

(Equation (xix)):

$$k = \frac{k_{\text{Max}} A}{1 + A x} \quad (\text{xix})$$

The equation should read:

$$k = \frac{k_{\text{Max}} A x}{1 + A x} \quad (\text{xix})$$