

CAPoC 9: 9th International Congress on Catalysis and Automotive Pollution Control

Progress in emissions control for diesel and gasoline vehicles

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Introduction

The topical conference series Catalysis and Automotive Pollution Control, generally known by the acronym 'CAPoC', has taken place periodically at the Université Libre de Bruxelles, Belgium, since the first one in 1986. The late Professor Alfred (Freddy) Frennet was central in establishing these conferences and for many years he was their guiding force. The first four Proceedings were published as volumes in the 'Studies in Surface Science and Catalysis' book series (forever associated with Professor Bernard Delmon of the Université Catholique de Louvain, Belgium) (1–4). Later as the organisational helm was increasingly taken over by Professor Norbert Kruse, who is now the Chairman, they were published as special issues of the journal *Topics in Catalysis* (5–9).

Since the first conference there have been many, sometimes dramatic, developments in the catalytic control of emissions from both spark ignition (mainly gasoline) and compression ignition (mainly diesel) internal combustion engines. Platinum group metal (pgm) catalysts have been central to many of these advances and they have been discussed by leading workers at these conferences so the Proceedings provide a valuable and easily accessed record of how the increasingly stringent emissions requirements have been met. A key feature of the conferences has been the wide range of attendees, with a high proportion from light-duty (cars and vans) and heavy-duty vehicle manufacturers as well as catalyst companies, in addition to leading academics from around the world. Indeed the main industrial companies have been instrumental in financially supporting the conferences from the start and have also been represented on the Scientific Advisory Boards that select the content of each conference. Another notable feature of the conferences has been the open discussion periods at the end of each session which allow time for clarification and detailed

discussion about particular points. These also provide an opportunity for industrialists to give updates on what is actually happening in 'the real world'.

The most recent conference, the ninth in the series, took place at the Université Libre de Bruxelles from 29th to 31st August 2012 and was a great success, attracting 240 attendees from 36 different countries and involving almost 30 oral presentations and more than 130 posters. The main current challenges involve control of fine particulate matter (PM) from diesel engines and soon some gasoline engines as well, and the reduction of nitrogen oxides (NO_x) (nitric oxide (NO) and nitrogen dioxide (NO₂)) under lean conditions. Developments and the present understanding of the basic science in these areas were covered during the conference as were fuel alternatives and innovative technologies. The technical lecture programme is reviewed in the order of the final published programme.

Introductory Session

The first session had three presentations that provided a technical context for the conference. They covered legislation, particulate and NO_x control technologies. Nikolaus Steininger (European Commission, Brussels, Belgium) reviewed the successes and failures of European emissions legislation. There are major concerns that many locations in Europe have ambient air quality that is not improving in line with the increasingly stringent emissions standards. It appears that while gasoline cars follow standards in type approval during on road driving, this may not be the case with the increasing number of diesel cars. For instance, the actual emissions for Euro 3 diesel cars on the road may be as much as four or five times higher than they are in the test cycle standards (emissions factors). As a result, and in spite of tightening legislation, there has been relatively little actual change in the total NO_x emissions over the last fifteen years or so. Thus the main problem with real driving emissions (RDE) is high NO_x (and NO₂) emissions outside of the test cycle conditions.

With the introduction of ammonia selective catalytic reduction (SCR) NO_x control systems and especially with Euro 6 certified vehicles that can provide good NO_x control outside of cycle conditions it may be expected that the overall ambient NO_x levels could improve as Euro 6 compliant vehicles are introduced. The European Commission will monitor the situation, and consideration will be given to amending test procedures, using portable emissions measuring

systems (PEMS) and the use of 'not to exceed limits' should this become necessary. The work of the Real-Driving Emissions–Light-Duty Vehicles working group and especially the use of PEMS in random test cycles was discussed and some legal difficulties in adopting such procedures highlighted, as were the concerns associated with NO₂ emission, though as NO_x emissions in test cycle and RDE tend towards very low levels so will the NO₂ emissions.

The amount of research on ultra-fine PM emissions and particularly particle number (PN) measurements of exhaust gas from internal combustion engines has been growing tremendously and it is generally considered that these tiny particles represent a serious health hazard. The Euro 5 PM standard (2 mg km⁻¹) forced fitment of diesel particulate filters (DPFs) on diesel cars in 2009, and with the introduction of Euro 6 legislation in 2014 and 2017 there will also be PN standards. There was discussion about the use of the Particle Measurement Programme (PMP) test procedure, originally developed for use with diesel engines fitted with filters, and its use in the measurement of exhaust PN from gasoline engines that do not have filters. Here there may be huge numbers of solid ultra-fine particles including material derived from lubrication oil and fuel additives that are below the 23 nm cut-off of the PMP procedure, see for example (10). Thus it may be appropriate to use an improved PN measurement procedure, and this is an active area of research. Some form of filtration will have to be used on direct injection (DI) gasoline engines, and it is yet to be confirmed how efficient they will be if the filters remain effectively clean. Special filters may have to be developed for these applications.

The second presentation, by Claus Vogt (NGK Insulators Ltd, Japan), continued the theme of actual ambient pollutant levels being relatively high in many parts of Europe, with the focus being on PM. Ceramic wall-flow filters have been increasingly fitted to European diesel cars since their first introduction on some 2000 model year cars, and to all Euro 5 compliant diesel cars since 2009. At first silicon carbide filters were used and more recently aluminium titanate ones have been introduced. Initially bare filters were used with an inorganic fuel additive (11) that facilitates soot combustion during periodic high-temperature filter regenerations. Then a few years later smaller catalysed filters incorporating platinum and/or palladium catalysts were introduced that did not require a fuel additive and the associated storage tank, dosing pump etc. In some instances not even an additional

oxidation catalyst is needed (12). These cost effective filter units are relatively small since they do not have to accommodate additional 'inorganic ash' from a fuel additive (**Figure 1**).

Now filters incorporating a NOx control functionality are required and this puts an increased emphasis on producing higher porosity filters of sufficient strength that are able to accept within the wall structure an adequate amount of NOx control catalyst and still have a low backpressure and high filtration efficiency. Backpressure affects turbocharger efficiency and the all important fuel economy which must be optimised to meet legislated carbon dioxide emissions standards. New filter designs are able to meet these demanding requirements and some details about them were presented. An example was given of a new filter loaded with a Johnson Matthey SCR catalyst which had 20% lower backpressure than a similarly loaded traditional filter.

As noted earlier, it has become clear that in future filters will be required not only for diesel cars but also for some gasoline cars. The first gasoline engines to have them will be DI downsized engines developed for low carbon dioxide emissions where DI and turbocharging enables power to be available for events such as harsh accelerations when required. It was suggested that these engines will be the predominant Euro 6 technologies, and their filters are referred to as gasoline particulate filters (GPFs) by analogy with the well established DPFs. Filter manufacturers are now providing advanced designs for these applications.

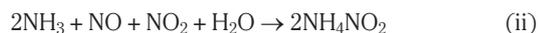
The final presentation in the opening session was a review by the present reviewer on control of NOx emissions from automotive engines. The approach was chronological, starting with the rich NOx reduction catalysts used on mid-1970s gasoline engines, the



Fig. 1. A compact catalysed particulate matter filter mounted directly on the turbocharger of a small diesel engine (Image copyright Martyn V. Twigg)

introduction of three-way catalysts (TWCs) for stoichiometric engines in the early 1980s, and more recently the most challenging NOx control in lean exhausts, first by NOx-trapping catalysts containing platinum and rhodium on lean-burn gasoline engines in the 1990s and now by NOx-trapping and low-temperature ammonia SCR technologies on lower temperature diesel engine cars. The earlier introduction of SCR NOx control on the higher temperature heavy-duty diesel engines was easier because existing vanadium-based SCR catalysts could be used. For use on diesel cars that can have remarkably low-temperature exhaust gas, reflecting their exceptional fuel economy (especially compared to their gasoline counterparts), special new low-temperature zeolite-based ammonia SCR catalysts had to be developed.

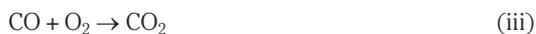
Ammonia is important in several areas of NOx control, and this is because it can react with NOx to form ammonium nitrite which for more than 150 years has been known to readily decompose to nitrogen and water, Equation (i). It was one of the reactions used to produce 'chemical nitrogen' during the discovery of argon in air some hundred and twenty years ago (13). Indeed, even the so called 'fast catalytic SCR' reactions, first reported in the 1980s (14, 15) involving equimolar amounts of NO and NO₂ that are so much a part of modern low-temperature SCR NOx control technology, have long been known as an aqueous solution reaction forming ammonium nitrite. And it has been reported, see for example (16), as a route for producing ammonium nitrite, perhaps according to Equation (ii).



Interestingly ammonia can be formed during the reductive regeneration of NOx-trapping catalysts, and a downstream SCR catalyst can utilise this to convert additional NOx to nitrogen so improving the overall NOx conversion. Already this system has been used on series production diesel cars (17).

Today, pgm-based TWCs are outstandingly efficient at controlling all three pollutants found in gasoline exhaust: carbon monoxide (CO), hydrocarbons (HCs) and NOx, as illustrated in Equations (iii), (iv) and (v). One possibility is that NOx is reduced directly to nitrogen because a clean rhodium surface dissociatively adsorbs NO to adsorbed oxygen and nitrogen atoms. The weakly adsorbed nitrogen atoms combine and are released as dinitrogen into the gas

phase, ultimately leaving a strongly bound oxygenated surface that has to be reductively cleaned for the NO dissociation process to continue.



It was speculated that an alternative process might also take place. With exhaust gas composition oscillating around the stoichiometric point the catalyst surface might be sufficiently rich (i.e. low in oxygen) for short periods of time for surface-bound ammonia to be formed, and there would then be the possibility for NO_x to be reduced to nitrogen during the lean phase *via* ammonia nitrite, as in Equation (i). Although this suggestion is very speculative, ammonia can be formed from NO_x over pgm catalysts, and in fact this often took place in early two stage three-way systems with rich NO_x control. Ammonia that was formed over the rhodium-containing NO_x reduction catalyst was oxidised back to NO_x over the downstream pgm oxidation catalyst thus lowering the overall NO_x conversion. Such speculation is based on insight now available about the mechanisms of various NO_x control reactions (see below).

NO_x Control Technologies

There were six presentations in the initial session concerned with NO_x control, and the first entitled 'DeNO_x Performance and Reaction Mechanism of the DiAir System' was given by Mikio Inoue (Toyota Motor Corp, Japan). This system uses a NO_x-trapping type catalyst with continuous rapid short pulse injections of HCs into the exhaust gas for regeneration. Since this does not depend on the storage of bulk NO_x derived compounds their thermal stability is unimportant. Only surface species are involved, so operation at higher temperatures than with conventional NO_x-trapping is possible. This paper discussed some of the surface reaction mechanisms from the standpoint of the contribution of HC and the reaction intermediates. Good NO_x conversion at 800°C has been demonstrated, performance reminiscent of TWC behaviour, and again the possibility of surface ammonia should not be overlooked. However, direct NO_x dissociation is likely with the short rich pulses keeping the surface free of adsorbed oxygen atoms, in keeping with investigations made several years

ago by Nakatsuji and co-workers when this kind of behaviour was first reported in detail (18–20).

This was followed by a joint contribution by Todd Toops (Oak Ridge National Laboratory, USA) and colleagues from Chalmers University of Technology, Sweden, and Cummins Inc, USA, in which the reactions taking place along the channels of a monolithic SCR catalyst were monitored by taking gas samples at different positions through fine capillary tubes. The ammonia adsorption equilibrium is faster than the SCR reactions, and with increasing temperature the SCR reaction zone, as might be expected, moves closer to the front of the monolith, and rate determining steps may change.

Over recent years there has been a lot of academic interest in the activation of silver/alumina catalyst in HC SCR reactions, and a paper by Sebastian Fogel (Haldor Topsøe A/S, Denmark, and the Technical University of Denmark) and colleagues reported the use of such a silver catalyst in combination with an iron zeolite in a hydrogen-assisted ammonia SCR system. The best combination was to have the silver catalyst upstream of the iron catalyst, and NO₂ formed by oxidation seems to play a role. Of course it would have been interesting to have available the comparison with an upstream platinum oxidation catalyst followed by ammonia injection before the iron SCR catalyst. Robbie Burch's group (Queen's University Belfast, UK) also working with silver catalysts reported that very high HC SCR activity could be obtained at low temperature if the catalyst was prepared by dry ball milling rather than the conventional wet impregnation method. The calcination temperature (650°C) was critical and the final ball milled catalyst had a high silver dispersion. The underlying reasons for the improvement are not completely clear, but a combination of ball milling and the correct calcination temperature was needed to get silver clusters having the right size for optimum NO_x conversion.

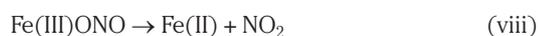
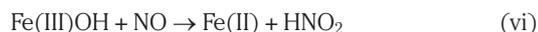
A paper from Hannes Kannisto and Hännä Harelind (Chalmers University of Technology, Sweden) highlighted the practical difficulties associated with marine SCR applications. One of the important factors is the incredibly high sulfur content of most marine diesel fuels that could be described as organic sulfur compounds! There then followed an outstanding contribution presented by Luca Lietti (Politecnico di Milano, Italy) on a study using labelled ¹⁵N with a model platinum barium-based NO_x storing catalyst that provided a real insight into the complex chemistry involved in NO_x storage and reductive regeneration.

Unlabelled NO_x was stored in the catalyst at 150°C and when this was exposed to ¹⁵N₂O there was facile exchange with the stored nitrite and nitrate with the former being easier. This process was inhibited by CO suggesting that platinum is involved in the exchange process. This was confirmed by an experiment with a non-reacting platinum-free formulation. The hydrogen reduction of stored nitrite and nitrate paralleled the NO exchange behaviour indicating that platinum probably has a role. Reaction of unlabelled NH₃ with stored labelled ¹⁵N₂O produced ¹⁴N¹⁵N in agreement with the reaction involving surface NH₄NO₂ species, and nitrous oxide (N₂O) was formed when NO was present at high concentrations. One of the remarkable features of this work was that it demonstrated the ease with which surface NO_x derived species interconvert, and this was later taken up in a subsequent paper from the same institute (see below).

NO_x Control Mechanisms

The next session had five presentations and continued the theme of the mechanisms of NO_x control processes. The first paper was from Mike Harold (University of Houston, USA) and concerned dual layer catalysts in which the lower layer was a NO_x storing formulation and the upper layer a copper- or iron-based zeolite ammonia SCR catalyst. The concept can work well but the two functions must be separated rather than just mixed together, and the addition of ceria has several benefits.

The next paper was from Enrico Troconi (Politecnico di Milano, Italy), and examined the importance of the oxidation of NO to NO₂ in ammonia SCR reactions. It had been proposed that this was the rate limiting step in the NO SCR reaction. It was shown that over copper zeolite NO oxidation is slow, while the activity for the standard SCR reaction is high; over an iron zeolite catalyst there is more NO oxidation although this is still slower than the NO SCR reaction. Moreover water inhibits NO oxidation but not the SCR reaction. Based on the present results and much published information a redox mechanism was proposed in which Fe(III) nitrite decomposes to Fe(II) liberating NO₂, and the resulting Fe(II) is then oxidised back to Fe(III), by oxygen. This is illustrated by Equations (vi)–(ix). Thus NO oxidation and the standard SCR reaction share the same initial reaction, which is not the SCR rate determining step but perhaps a rapidly formed pre-equilibrium. The rate determining step is probably the re-oxidation of iron(II) to iron(III) (Equation (ix)).



HCs are known to ‘inhibit’ NO oxidation over platinum catalyst, and a presentation by William Epling (University of Waterloo, Canada) in collaboration with the University of Houston, USA, provided information to understand more about this phenomenon. The reactivity of surface nitrates in the oxidation of propene was examined, and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments showed that surface nitrate was reduced to linear nitrite by propene. Gas phase NO₂ also reacted with a series of HCs in the reactivity order: dodecane > xylene > propene. Rather surprisingly it was found that over a platinum catalyst propene was oxidised faster by oxygen than by NO₂, although the comparison involved experiments with 6.5% oxygen and with 0.1% NO₂. Perhaps the HC inhibition of NO oxidation can be interpreted by the fact that any NO₂ formed will be consumed oxidising HC and therefore only when there is no reactive HC present will NO₂ be observed.

If there is insufficient reductant available to fully reduce NO_x to N₂ or the temperature is too low for this to take place N₂O may form, and this is undesirable because it is a very powerful greenhouse gas having more than three hundred times the global warming potential of carbon dioxide (by weight over a hundred years). A paper from Šárka Bártová (Institute of Technology, Prague, Czech Republic) and colleagues from Oak Ridge National Laboratory, USA, discussed a model for N₂O formation during regeneration of a NO_x storage catalyst with hydrogen, CO and HCs. Two kinds of N₂O emission were identified. The primary emission takes place before the reductant has broken through the catalyst, and a secondary emission sometimes takes place when conditions return to lean and surface intermediates are oxidised to N₂O. Reforming reactions producing hydrogen and CO can decrease the amount of N₂O released and increase overall NO_x conversion.

The last paper in this session was a joint French contribution given by Arnaud Frobert (IFP Energies nouvelles, France) with PSA Peugeot Citroën, France, on the coupling of the rather unusual ethanol SCR

with ammonia SCR derived from the first stage that had upstream injection of ethanol over a silver on alumina catalyst. The ethanol is oxidised to acetaldehyde by oxygen and NO₂ at quite low temperatures, other products include hydrogen cyanide. The second catalyst was a traditional iron zeolite SCR catalyst. However, this added little to the overall NO_x conversion and had essentially no effect on the hydrogen cyanide content which was found to be particularly detrimental to the NO_x sensor. So for several reasons in the present form this is not the basis of a practical NO_x control system.

Sorption Mechanisms and Ageing

The first paper in this section was by Ines Lezcano-Gonzalez (Materials innovation institute (M2i), Delft, The Netherlands, and Utrecht University, The Netherlands), and resulted from a collaboration between these two institutions plus Ghent University, Belgium. It examined the protonation of zeolites and their copper exchanged counterparts using Fourier transform infrared (FTIR) spectroscopy, temperature programmed desorption (TPD) and theoretical calculations. FTIR and TPD experiments showed that there are three types of surface ammonia species: those coordinated to copper centres, those coordinated to extra framework aluminium atoms, and ammonium cations at Brønsted sites. There was reasonable agreement between calculated and observed infrared absorptions confirming their assignments, and it was concluded that isolated coordinated ammonia at copper sites reacted quickly compared to ammonium ions at Brønsted sites. However, when coordination sites are present the ammonium cations react more quickly, and it is thought that this is where ammonia is stored.

Twenty years or so ago there were in-field problems with some TWCs that were prone to deactivation due to phosphorous poisoning derived from lubrication oil, and this was shown to be due to cerium phosphate formation and hence a decreased oxygen storage capacity (OSC). The next paper, from Angelos Efstathiou (University of Cyprus), returned to this topic. Phosphorous was impregnated into mixed oxides (30 mol%, 50 mol% and 70 mol% cerium) as ammonium dihydrogen phosphate ((NH₄)H₂PO₄) and calcined, which is rather different to what happens in an exhaust, but it enabled interesting information to be obtained. X-Ray photoelectron spectroscopy (XPS) showed a major decrease in surface percentage of Ce(IV) that in itself goes a long way to explain the

reduced activity of phosphate poisoned catalyst, and scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDAX) showed a general depletion of cerium upon phosphation. ¹⁸O exchange experiments showed that for the original mixed oxides the amount of exchangeable oxygen at a particular temperature changed little with composition, and as expected it increased with temperature. For the 'poisoned' samples at a particular temperature composition again had little effect, but there was less than half the amount of exchangeable oxygen. All of these data refer to the mixed oxides themselves, and this reviewer believes that a similar study is needed with materials containing pgms, especially rhodium and palladium.

The oxidation of methane in exhaust gas is becoming increasingly important, and this is usually best done over a palladium-based catalyst. The nobility of palladium is such that it exists under reaction conditions either as oxide or metal depending on the catalyst formulation and the operating temperature, and it is usually considered that the oxide form is more active than is the metallic form. A density functional theory (DFT) and surface X-ray diffraction study from Henrik Grönbeck (Chalmers University of Technology, Sweden) and colleagues at Lund University, Sweden, focused on the dissociation of methane on the surface and concluded that PdO(101) and Pd metal have the highest activities, although there is no immediately obvious way in which this helps with the practical problem of lowering the temperature needed for methane oxidation.

The last paper in this session was from Davide Ferri *et al.* (Swiss Federal Laboratories for Materials Science and Technology (EMPA), Dübendorf, Switzerland) with colleagues from the European Synchrotron Radiation Facility, Grenoble, France, on modulation excitation spectroscopy (MES), an exciting new dynamic X-ray technique enabled by bright cyclotron radiation, that permits detailed monitoring of structural changes in catalysts such as palladium or rhodium on Al₂O₃ or ceria/zirconia mixed oxide. The element specific results are profound and provide time resolved information about parameters such as oxidation state, coordination environments, crystallinity and phase composition under conditions close to real world operating conditions, for instance of TWCs. The results presented included alternate exposure of palladium and rhodium to CO and NO_x. Rhodium remained metallic under CO but was partially oxidised by NO. In contrast when palladium was exposed to CO

there was an expansion of the Pd–Pd bond length, which was very likely due to carbon deposition. This contributes to the debate about palladium surface carbide formation. Another interesting result was that when palladium on ceria/zirconia mixed oxide was pulsed with CO and then oxygen it was the cerium that was first reduced by CO and not the palladium! Clearly these new techniques will provide tremendous insight into pgm-catalysed reactions taking place in automotive pollution control systems in the future.

Fuel Alternatives and Innovation Technologies

In this, the penultimate session, there were three papers of general interest. The first was on the microwave monitoring of the condition of automotive catalysts from Ralf Moos (University of Bayreuth, Germany) and colleagues from Umicore AG & Co KG, Germany. Using a simple robust antenna system it is fairly easy to expose monolith catalysts and filters to microwave radiation and measure the resonance absorption parameters that may be present. This has been done for a variety of catalysts and it has been shown that the resonance frequencies and 'Q' linked half-height absorption widths can be related to meaningful catalyst properties. For instance, the sharp resonance of a fully oxidised TWC were shifted down about 0.5 GHz and dramatically broadened when it was fully reduced, implying that this could be used as an alternative on-board diagnostic (OBD) measurement. Similarly the sharp resonance of an empty soot filter gradually shifted down frequency and broadened as it was loaded with soot, and the amount of ammonia on an SCR catalyst could be monitored. However, the NO_x-trapping catalysts do not appear to be amenable to this technique. Already one instrument is commercially available (from General Electric, USA) and it will be interesting to see if this gains acceptance in the industry.

The second paper was from Akira Obuchi (National Institute of Advanced Industrial Science and Technology (AIST), Japan), and was about the use of a heat exchanger to enhance the operating temperature associated with exothermic reactions. Exhaust gas was heated by effluent evolved from sequential catalytic oxidation, particulate filtration and ammonia SCR after urea solution injection. The design was shown to work well over the Japanese 10-15 mode test driving cycle, providing SCR operating temperatures in the region of 300°C that gave 98% NO_x conversion. The potentially serious problem associated with the development of

very high temperatures during filter regenerations was not discussed.

The last paper in this section was from Djamel Bounechada (Politecnico di Milano, Italy) and Ecocat Oy, Finland, and was concerned with the performance of a rhodium/palladium TWC containing an oxygen storage component for natural gas exhaust, and the effects of lambda oscillations on methane conversion. At 450°C it was shown that during symmetrical lambda oscillations the methane conversion was markedly higher during the rich phases than during the lean phases, and that there was a narrow region where both methane and NO_x conversions were significantly enhanced. These changes were attributed to the oxidation state of the palladium – metal or oxide. At higher temperatures the palladium was not reoxidised to palladium oxide, in keeping with the known thermodynamics of palladium oxide prevailing under such conditions. Lambda scan experiments showed that the effects of increasing the cycle period depended on the available OSC present, and that during long cycle periods there was insufficient OSC to complete the oxidations of HCs and CO to water and carbon dioxide. Hydrogen was then formed from carbon monoxide *via* the water gas shift reaction, Equation (x).

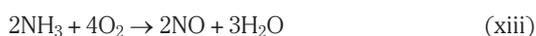
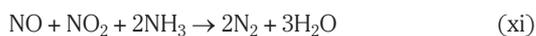


Increasing the water content increased the amount of hydrogen formed under rich conditions, and inhibited methane conversion under lean conditions. The presence of NO_x inhibited methane conversion under lean conditions. Interestingly these experimental results might indicate that a partially reduced palladium oxide surface is a very active phase, as suggested by some surface science studies.

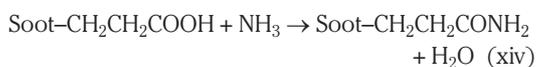
Particulate Matter Control

The final session was on particulate control. The first of six papers was from Alexander Yu. Stakheev (Zelinsky Institute of Organic Chemistry, Moscow, Russia) and colleagues from Haldor Topsøe A/S, Denmark, and was concerned with integration of soot and SCR NO_x removal in a DPF. An iron zeolite SCR catalyst was combined in various ways and locations with a ceria/zirconia mixed oxide to mediate soot combustion. To optimise the carbon oxidation and SCR functions a carbon black was used as a soot substitute in loose contact with ceria/zirconia mixed oxide powder. Thermogravimetric analysis (TGA) experiments showed that this mixture had a significantly lower oxidation temperature (about 420°C) than the same carbon

black mixed with inert alumina (about 600°C). When iron zeolite SCR catalyst was added to the mixture the effect was slightly reduced (488°C). Synergistic effects were found and were attributed to NO oxidation to NO₂ over the ceria/zirconia which optimised the SCR process *via* the fast SCR reaction, Equation (xi). This probably also facilitated low-temperature soot oxidation, as in a Continuously Regenerating Trap (CRT[®]), Equation (xii), although the effect over platinum is more pronounced. Addition of a small amount of manganese to the ceria/zirconia mixed oxide enhanced the NO oxidation capability, and this parameter was optimised as was the positioning of the oxidation catalyst so as to minimise the detrimental oxidation of ammonia to NO_x, Equation (xiii). Base metal systems of this type are usually sensitive to sulfur poisoning but no mention of such sensitivities was mentioned.



There followed a presentation from Oliver Kröcher (Paul Scherrer Institute, Villigen, Switzerland) on ammonia SCR reactions over the same carbon black that was used in the previous study and also actual diesel soot. The results suggested that the NO₂/NH₃ and 'fast' SCR reaction take place on soot, and that the presence of sulfuric acid accelerates NO_x reduction (confirming earlier work by the present reviewer). A particularly interesting feature was the consideration given to the processes taking place on the carbon surface, and how for instance hydrogen cyanide might be formed from surface carboxylic acids *via* the formation and dehydration of surface amides. One possible mechanism is shown in Equations (xiv)–(xvi):



The next contribution, from Kiyoshi Yamazaki (Toyota Central R&D Laboratories, Inc, Japan), provided more details about what appears to be a rather special form of silver/ceria which catalyses the soot combustion reaction. This material, as shown by a transmission electron microscopy (TEM) image (Figure 2), has metallic silver cores surrounded by

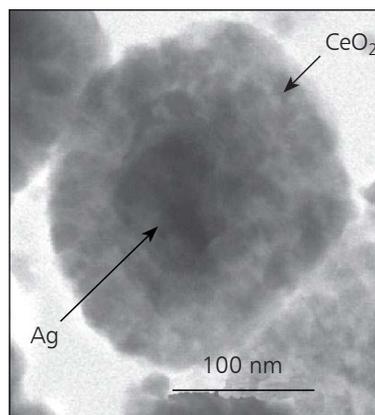
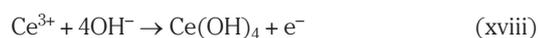
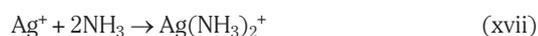


Fig. 2. A TEM image of the cut plane of a single spherical agglomerate of CeO₂-Ag catalyst (reprinted from (21), with permission from Elsevier)

small ceria particles producing an overall spherical particle. The high activity is attributed to the close silver/ceria contacts leading to availability of 'atomic oxygen species'. The preparation of this material involves ammonia coprecipitation of cerium(III) and silver(I) nitrates under neutral conditions in which silver ammine is reduced by cerium(III) to silver metal and ceria, as shown in Equations (xvii)–(xix). An unusual variant on the silver mirror reaction! And of course anyone carrying out this procedure should be aware of the explosive nature of silver nitride that can inadvertently be formed from ammonical silver nitrate.



As discussed previously the PN standards for gasoline DI engines are going to become the same as those for diesel cars fitted with filters within Euro 6 legislation. There will be a transition period starting in 2014, with 6×10^{12} particles km⁻¹, and then in 2017 the limit will be tightened to 6×10^{11} particles km⁻¹. This will force DI gasoline cars to be fitted with some form of filter. At the moment it appears that ceramic filters, perhaps incorporating some TWC functionality, and having at least 75% filtration efficiency will be needed to meet the standard. There is however concern that the additional backpressure caused by a filter will be detrimental to the turbocharger efficiency of the small downsized engines that are capable of providing the fuel economy necessary for the low carbon dioxide emissions requirements. A presentation by Stephanie Spiess *et al.* (Umicore AG & Co KG, Germany) on the emissions performance of a 2 litre turbocharged DI

gasoline engine in a family size car equipped with an under-floor GPF having an equivalent amount of pgm to the current series production vehicle, distributed between a close coupled flow-through TWC and the GPF. The NO_x conversion was improved compared with the series arrangement, and over 160,000 km the PN emissions were better than the required 6×10^{11} particles km⁻¹. Importantly, there was no measurable impact on fuel consumption or carbon dioxide emissions, highlighting the likelihood of this technology being optimised and implemented on European gasoline powered cars in the future.

The penultimate paper from Bengt Andersson (Chalmers University of Technology) was on the reactivity of different soots, especially towards oxidation. Soot from gasoline DI, gasoline port fuelled, ethanol port fuelled and diesel engines were compared with the behaviour of a commonly used synthetic soot. The oxidative reactivity in 2% oxygen increased in the order: synthetic < diesel < gasoline port fuelled, gasoline DI < ethanol port fuelled soot. A number of differences were identified, and particularly interesting was the variation of activation energy with conversion although the range was within that previously reported for diesel soot. It could be worthwhile to compare with the results obtained by Andrea Strzelec (now at Texas A&M University, USA) and her colleagues showing that the rate of oxidation of diesel soot in the presence of 10% oxygen is directly dependent on the available surface area. NO₂ oxidation is different, perhaps because the reaction rate is so rapid that diffusion effects are important.

The final presentation from Marcial Valencia *et al.* (Galician Automotive Technology Centre, Spain) and colleagues at the University of Alicante, Spain, dealt with forming Ce_{0.5}Pr_{0.5}O₂ species within a DPF *via* impregnation of the corresponding nitrates followed by calcinations to catalyse regenerative soot combustion. Both cordierite and silicon carbide filters were used, and data were collected on a commercial 1.6 litre Euro 5 engine. The backpressure of the catalysed filter was consistently higher than that of an uncoated version, and in regeneration experiments only at 550°C did the backpressure of the catalysed filter reduce to match that of the uncatalysed filter. Of course 550°C is the temperature at which soot burns in air, suggesting that the catalyst in the filter is not particularly effective. However, other experiments using pre-sooted filters indicated that the 'balance point' may be around 400°C, although the experiments were only run for a few minutes. Again this work showed that ceria can catalyse the oxidation of NO to NO₂. It is a pity that a

commercial pgm-catalysed DPF was not included in this work to provide a meaningful benchmark.

Conclusions

There are concerns about the lack of significant air quality improvements in parts of Europe over recent years, and increasingly stringent standards and other measures will be introduced to correct this situation. The papers presented at this important conference illustrated that tremendous technical advances are being made especially in the key areas of PM and NO_x emissions control. Developments are being made with filters for PM control, and increasing amounts of catalyst are being incorporated into filters for NO_x control (especially in the form of ammonia SCR for diesels), and TWC for upcoming gasoline applications that will require higher porosity filter materials. In practical systems pgm catalysts provide durable high activity for oxidation of CO and HCs to CO₂ and H₂O, and of NO to NO₂, for 'fast SCR' and passive low-temperature soot oxidation, as well as several functions in NO_x-trapping catalysts.

At present copper and iron are being used in combination with small pore zeolites for low-temperature ammonia SCR NO_x control. Here it appears that an important factor is the elimination of HC species from the active metal sites in zeolite channels, and it would be interesting to know how pgm centres would perform in such situations since in more traditional catalysts they have outstanding low-temperature performance, although their selectivity is less than desired for this application.

Finally, the organising committee, and especially Professor Norbert Kruse (Chairman), Jean-Marie Bastin (Treasurer) and Thierry Visart de Bocarmé (Secretary) are to be congratulated for organising an excellent conference.

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