The annual SAE Congress is the vehicle industry's largest conference and covers all aspects of automotive engineering. The latest in the series was held in Detroit, USA, from 13th–15th April, 2010. There were upwards of a dozen sessions focused on vehicle emissions technology, with most of them on diesel emissions. More than 40 papers were presented on the topic. Attendance was up relative to last year, with most sessions having perhaps 100 attendees, but some had more than 200. Of the attendees 86% were from the US, of which 50% were from the Detroit area, with 7% from Europe and 6% from Asia. Original equipment manufacturers (OEMs) represented 23% of attendees and 45% were part of the supply chain, with 50% being involved in the automotive industry and 35% working in the heavy-duty diesel sector.

This review focuses on key developments in diesel emissions control from the conference. Papers can be purchased and downloaded from the SAE website (1). As in previous years, the diesel sessions were opened with a review paper of key developments from 2009 (2).

Selective Catalytic Reduction Technology

Selective catalytic reduction (SCR) is the leading nitrogen oxides (NOx) emission control technology for both heavy-duty and light-duty diesel applications. The field is advancing rapidly with new developments being reported on catalyst enhancements and system improvements.

As engines become more efficient and regulators become more concerned about low-load NOx emissions, better low-temperature SCR system performance will be required. Currently good performance is limited by urea injection issues (evaporation and hydrolysis) at temperatures below 200°C. Reggie Zhan (Southwest Research Institute, USA) reported on a new mixer that allows urea injections at temperatures as low as 180°C and thus lowers NOx by about 30% over the US cold transient cycle, relative to no mixer (3).

Pio Forzatti (Politenica di Milano, Italy) demonstrated that ammonium nitrate (NH$_4$NO$_3$) injections can substitute for nitrogen dioxide (NO$_2$) to enhance
the low-temperature (200ºC) reduction of nitric oxide (NO) (4). Some results are shown in Figure 1 for an iron-ZSM5 zeolite catalyst. The effect was somewhat more pronounced with a vanadia (V₂O₅) catalyst. The reaction mechanisms were described and involve the nitrate oxidising NO to NO₂.

Krishna Kamasamudram (Cummins Inc, USA) explained low-temperature performance differences between copper- and iron-zeolites (5). Ammonia readily adsorbs on the acidic reaction sites of Fe-zeolite, but much less so on the basic Cu-zeolite sites. This can inhibit the low-temperature performance of Fe-zeolites. On the other hand, NO₂ adsorbs on Cu-zeolite reaction sites, inhibiting further NO oxidation. Most interestingly, this behaviour results in better low-temperature transient performance for Fe-zeolites, because the adsorbed ammonia readily reacts with NOx. Conversely, the Cu-zeolite draws ammonia from physical absorption sites instead, and the early reaction can be further inhibited by the suppressed NO oxidation reaction.

Generally, low-temperature SCR reactions are controlled by the rate of chemical reaction mechanisms rather than by mass transfer. In that regard, higher catalyst loadings can enhance low-temperature performance. In addition, Takahiko Ido (Ibiden Co Ltd, Japan) showed in his presentation that a strong relationship exists between ammonia adsorption and deNOx efficiency, which is also tied to zeolite catalyst loading (6). Because most of the stored ammonia resides in the front half of extruded Fe-β zeolite honeycombs, they can be reduced to half the size of typical washcoated catalysts without sacrificing low-temperature performance. However, at higher temperatures, more urea is needed to maintain the performance of the smaller extruded catalyst.

Vanadia SCR catalysts are used in Europe and emerging markets. In the US and Japan diesel particulate filters (DPFs) are fitted on all heavy-duty trucks, and vanadia catalysts have durability issues in these applications caused by high-temperature exposure during DPF regeneration. Advances are now reported by David Monroe Chapman (Cristal Global, Saudi Arabia) (7) on vanadia SCR catalysts that have no volatility up to 750ºC or even higher versus 550–600ºC for some commercial catalysts, giving them similar high-temperature durability to zeolites. DeNOx performance of the new vanadia SCR catalyst at 250ºC and 350ºC is 5–10 points better after high-temperature ageing (>700ºC) than for a benchmarked commercial catalyst, but less severely aged catalysts have lower efficiencies than the base commercial catalyst.

Gang Guo (Ford Motor Co, USA) reported on their leading deNOx approach to bring larger personal vehicles into US Tier 2 Bin 5 compliance (8). Fast SCR catalyst light-off is critical, so the Cu-zeolite SCR catalyst is located upstream of the DPF, and urea storage and dosing strategies are very important. The authors showed that with an exhaust gas recirculation (EGR) strategy the SCR becomes active after about 120 seconds on the US Federal Test Procedure US-FTP75 cycle. In the first 60 seconds or so after light-off, a high dosing rate of urea (urea:NOx ratio of 5:1) provides 30% more deNOx than a stoichiometric injection.

\[
2\text{NH}_3 + 2\text{NO} + \text{NH}_4\text{NO}_3 \rightarrow 3\text{N}_2 + 5\text{H}_2\text{O}
\]

Fast SCR

NH₃ + 340 ppm NH₄NO₃

Standard SCR

$\alpha = 1$

Fe-ZSM5 SCR

Figure 1. Ammonium nitrate can serve as an ‘alternative source’ of NO₂ for the ‘fast SCR reaction’ with the ratio NO: NO₂ = 1:1 to enhance low-temperature performance of selective catalytic reduction (SCR) catalysts (4). Conditions: gas hourly space velocity (GHSV) = 33,000 h⁻¹, NH₃ = 1000 ppm, NOx = 1000 ppm, O₂ = 2%, H₂O = 1%; for fast SCR: NO = NO₂ = 500 ppm.
Ammonia slip can be an issue, so Cu-zeolite SCR catalyst is added to the downstream DPF to capture and utilise the ammonia. Regarding urea storage, injection of 13 equivalents of urea provided 3 equivalents of stored urea as measured by grams stored per litre of catalyst at 100ºC, but this reduces to 1.5 equivalents at 200ºC. Ammonia stored in the entry sections of the SCR catalyst is most critical to performance.

Finally, regulators have a concern about dioxin and furan emissions when using Cu-zeolite catalysts. These extremely toxic components can form if chlorine, polyaromatic hydrocarbons (PAHs) and copper catalyst are present together under exhaust conditions. C. A. Laroo (US Environmental Protection Agency (EPA)) made a presentation (no SAE paper available) updating the industry on the EPA’s test programme to investigate this (9). As shown in Figure 2, there is no evidence that a Cu-zeolite SCR catalyst produces any additional dioxins or furans (expressed in Figure 2 as International Toxic Equivalent (ITEQ) to dioxin). When a pgm catalyst is added to the exhaust system, as is used in practice on the diesel oxidation catalyst (DOC) and catalysed DPF, toxic emissions are expected to be reduced relative to engine-out levels, and the preliminary results show a trend in that direction.

Lean NOx Traps

The lean NOx trap (LNT) is currently the leading deNOx concept for the smaller lean-burn (diesel or direct injection gasoline) passenger cars, and is of interest in applications with limited space or in which urea usage is difficult. The deNOx efficiency is nominally 70%, much lower than that of the next-generation SCR system at ≥90%, and the pgm usage is high (~9–11 g platinum and/or palladium for a 2 litre engine). As a result, efforts are focused on improving efficiency while reducing pgm usage. One of the leading concepts is to use the LNT to generate ammonia during the periodic rich regeneration part of the cycle, and then to store and use this ammonia in a downstream SCR catalyst (2). Papers of note from this SAE Congress extend the understanding of this system, and improve upon the performance.

Yuuichi Kodama (Komatsu Ltd, Japan) and Victor Wong (Massachusetts Institute of Technology (MIT), USA) showed that increasing flow rate (space velocity up to 80,000 h⁻¹ was tested) and hydrogen content (up to 4%) in the feed gas can markedly increase ammonia production in an LNT with 3 g l⁻¹ platinum and or palladium (10). However, increasing the space velocity by decreasing the length gave no benefits.
beyond 50,000 h\(^{-1}\), conversely to results of the flow studies. Further, the total system performance was minimally affected by decreasing LNT length. Hypotheses concerning ammonia and NOx reduction kinetics, rich-lean mixing interfaces, and oxygen storage dynamics with length were proposed but not investigated. Other factors impacting ammonia generation are residual oxygen in the rich gas (strong negative impact), and longer rich times (positive impact). The ratio of NO:NOx in the feed gas had little impact. Water-gas shift reformers result in less ammonia production, but improve system low-temperature deNOx performance.

Lifeng Xu \textit{et al.} (Ford Motor Co, USA) discovered that other non-ammonia species formed in the LNT can contribute to the downstream SCR performance (11). The effect is more pronounced with less aggressive LNT rich purges (less rich, shorter duration). In one case with only two purges over a whole certification test cycle, the system removed \textasciitilde70\% of the NOx with the LNT accounting for most of it (50\%), but >80\% of the SCR performance was attributed to the non-ammonia species. The leading hypothesis is that organo-nitrogen compounds, which may include isocyanic acid (HNCO), form during the rich purge, and are captured and utilised by the downstream SCR catalyst. The researchers showed that a low-pgm LNT + SCR system (3 g l\(^{-1}\) platinum and/or palladium on the LNT) performs as well as a highly-loaded LNT (not quantified, but 3.8 to 4.5 g l\(^{-1}\) platinum and/or palladium is typical), either alone or with an SCR. Cu-zeolite performs better than Fe-zeolite. Interestingly, they looked at a variety of LNT and SCR configurations (in series or alternating), and concluded that the series arrangement is best due to faster LNT light-off. On a vehicle, the system achieves \textasciitilde97\% deNOx efficiency for a system roughly the same size as an SCR-only system.

In another paper Joseph R. Theis (Ford Motor Co, USA) investigated the ageing properties of the LNT + SCR system (12). With constant LNT management, the SCR advantage decreases if the LNT is aged for 4.5 hours at 700ºC versus the baseline of 600ºC ageing. The effect is attributed to pgm ageing on the LNT and less efficient ammonia production. Longer rich periods as the system ages can counteract these impacts. During LNT desulfation, the SCR effectively oxidises hydrogen sulfide (H\(_2\)S) and carbonyl sulfide (COS) to sulfur dioxide (SO\(_2\)).

Hai-Ying Chen (Johnson Matthey Inc, USA) reported on further optimisation of both the LNT and the SCR using NOx adsorber catalysts (NACs) (13). The LNT was improved by decreasing the oxygen storage capacity (OSC) and replacing 20\% of the platinum in the NAC with palladium. The results are shown in Figure 3. The lower OSC allows more ammonia to be produced at higher temperatures without as much oxidation. The palladium promotes the NOx reduction function. The Cu-zeolite in the SCR catalyst was improved by adjusting the support material. It better withstands rich-lean cycling, wherein hydrocarbons are adsorbed in the rich period and then oxidise in the lean period, creating damaging exotherms.

Finally, Tetsuya Murayama (New ACE Institute Co, Ltd, Japan) reported on the CO\(_2\) and N\(_2\)O emissions coming from a heavy-duty LNT system (14) com-

\[\text{Fig. 3. The ammonia producing capability of a lean NOx trap (LNT) was improved by optimising the oxygen storage capacity (OSC) and pgm content. 5.0:1/120 refers to 120 g ft}^{-3}\text{ of pgm containing 5 parts platinum, 0 parts palladium, and 1 part rhodium (13)}.\]
bined with an advanced engine with low NOx emissions. About 3% of the global warming potential of the exhaust comes from the N₂O emitted by the LNT during the rich period. Another 2.4% is attributed to the fuel that is dosed to make a rich purge gas. The balance, 94.6%, comes from the engine.

Diesel Particulate Filters

Although DPFs have been in commercial production for original equipment manufacturer (OEM) application for more than ten years, there is still much optimisation activity in the field. Papers on DPF regeneration dominated this part of the SAE Congress, with new understanding on current and new regeneration methods being gained.

James R. Warner (Ford Motor Co, USA) investigated current DPF regeneration dynamics (15). Active regeneration efficiency, wherein exhaust temperature is increased to ~600°C and the soot is burned by oxygen, is not strongly dependent on oxygen content at levels >2%, nor on whether the filter contains pgm, although the pgm does oxidise the resultant CO to form CO₂. However, the efficiency is strongly dependent on soot loading due to the build up of heat. Passive regeneration, wherein the soot is oxidised by NO₂, is more than three times more effective at 370°C than at 485°C, as the decomposition of NO₂ back to NO at the higher temperatures overwhelms the faster soot oxidation rate at these temperatures. A DPF with Cu-zeolite behaves similarly to the uncoated filter, and has minimal impact on DPF regeneration. Isocyanic acid (HNCO) is a byproduct of active regeneration without catalyst, and needs to be taken into account in the mass balance when examining regeneration effectiveness. Active regeneration ‘costs’ about 0.5 miles per gallon (mpg) in terms of fuel economy (2–3% fuel consumption), and passive regeneration strategies can lower this penalty by about 20%.

Direct oxidation catalysts have been of interest in the field for more than five years (16, 17). These catalysts use oxygen conducting materials (such as ceria, zirconia or manganate) to burn the soot at the soot–catalyst interface, rather than using oxygen in the gas phase. Barry W. L. Southward (Umicore, Germany) showed that a complex ceria material can begin oxidising soot with model gas at 160°C with completion at 220°C using no or very little pgm (18). Once started, the exotherm causes soot not in contact with the catalyst to oxidise via the gas phase oxygen. When tested using vehicle exhaust, the balance point temperature (BPT, at which soot accumulation rate is the same as the oxidation rate) is 20°C lower than with a commercial filter coated with 0.2 g l⁻¹ of 1:1 platinum and palladium (BPT = 420°C). The regeneration efficiency, shown in Figure 4, is much better than for a lightly catalysed filter at 550°C, but similar at 620°C. In another paper, by Svetlana Iretskaya (Catalytic Solutions Inc, USA), a base metal mixed oxide catalyst supported on a rare earth mixed oxide has a BPT of 350°C in the absence of NO₂ (19).

Soot can also be burned by adsorbed oxygen on the surface of a SiC fine particle membrane. Preechar Karin (Tokyo Institute of Technology, Japan) (20) showed much lower activation energy for a DPF with a SiC membrane compared to one without (80 kJ mol⁻¹ versus 130 kJ mol⁻¹), indicating a shift in reaction mechanism. In the paper the authors show anecdotal

![Figure 4. A diesel particulate filter (DPF) with direct oxidation catalyst ("OS3") regenerates much better at 550°C than either an uncoated DPF or one with light pgm catalyst loading (green bars). Red bars indicate performance at 620°C (18)](image)
evidence of the surface oxidation phenomenon, but the presentation had new data confirming this mechanism using thermal desorption spectroscopy. In another study, Takashi Mizutani (NGK Insulators Inc, Japan) showed that ceramic membranes cause the soot to deposit as a layer rather than being dispersed throughout the porous wall of the DPF (21). This creates a more localized exotherm that improves regeneration efficiency by 10–15%.

In other developments worth noting, Gregory Austin (Michigan Technological University, USA) showed that soot formed from fuel containing 20% biodiesel burns three times faster than soot from regular diesel (22). Also, Shohji Tsushima (Tokyo Institute of Technology, Japan) demonstrated that very small nanoparticles (1 nm), acting under Brownian diffusion effects, are nearly all trapped in the surface porosity of DPFs, while larger particles (>10 nm) are trapped throughout the filter wall and may break through (23).

Conclusions

High-efficiency deNOx systems are and will continue to be a key area of development as regulations tighten and engine fuel efficiency demands increase. Cost reduction, primarily through better utilisation of pgm, will also become important in future systems. Addressing low-temperature NOx emissions is emerging as a future need. Low-temperature performance of deNOx systems is enhanced by the presence of NO2, but excessive amounts can result in higher emissions. The design and management of pgm-containing systems can play a major role in this regard. In a similar context, LNT systems seem to be yielding to LNT + SCR systems, wherein pgm is removed from the LNT to facilitate ammonia production for a downstream SCR unit, in combination with a pgm-containing DOC and DPF.

On DPFs, most work is being done on optimising regeneration strategies to reduce fuel consumption and cost. Most impactful to pgm use is the use of direct oxidation catalysts based on ionic conducting materials. Membranes are also evolving to improve performance.

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