CAPoC8: 8th International Congress on Catalysis and Automotive Pollution Control

Focus on NOx control and particulate filtration for diesel engines

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The Eighth International Congress on Catalysis and Automotive Pollution Control was held at the Université Libre de Bruxelles (ULB), Belgium, from 15th to 17th April 2009 (1). Some 185 participants attended the congress, which set aside time for discussion of the more than 100 posters submitted, in addition to the normal presentation of papers and keynote speeches. There were displays from several of the sponsors, including a table-top display of emissions control technology from the Association for Emissions Control by Catalyst (AECC), Brussels.

Introductory Session

Following a welcome address from the Baron André Jaumotte (Honorary Rector and Honorary President of ULB), Günter Hörmandinger (Environment Directorate-General, European Commission, Belgium) addressed the congress on the EU's policy for combating threats to health and climate from on-road traffic. Hörmandinger summarised the EU's approach of using air quality legislation in combination with requirements for control of pollution at source, such as vehicle emissions legislation and the integrated pollution prevention and control (IPPC) Directive. He highlighted the importance of air quality and the existence of emissions hotspots, noting that 25% of the EU population lives within 250 m of a main road. Actions to improve air quality and consequently human health include the introduction of an air quality standard for particulate matter of diameter 2.5 μm and smaller ($PM_{2.5}$), the Euro 5 and Euro 6 emissions regulations for light-duty vehicles and the Euro VI emissions regulations for heavy-duty engines. Hörmandinger commented that the emissions regulations now include particle number standards as particulate matter weight limits are no longer seen as being sufficient to force the fitment of closed wall-flow filters.

Vehicle emissions as measured by the new European drive cycle (NEDC) test suggest that vehicle nitrogen oxides (NOx) emissions have successfully

been reduced from Euro 1 to Euro 4 levels but, Hörmandinger said, there is a growing disconnect between these values and real-life NOx emissions as measured on the common Artemis drive cycle (CADC), where Euro 4 vehicles are shown to produce NOx emissions similar to those of Euro 1 vehicles. He noted that the European Commission is to review the carbon dioxide measurement procedure by 2014, and said that he expects the new test procedure to better simulate conditions in the real world, an approach which will also be relevant for pollutant emissions and for emissions control strategies – especially for control of diesel NOx.

The second keynote speech was from Tim Johnson (Corning Environmental Technologies, USA), who addressed the subject of technical achievements and future challenges in automotive pollution control. Johnson said that there are forty types of vehicle available today that will actually clean the ambient air on Los Angeles highways. Future catalysts will have to control methane, nitrous oxide and black carbon as greenhouse gas emissions in addition to the emissions currently treated. Challenges include developing catalysts to work at lower temperatures, reducing petrol engine particle numbers and improving the performance of selective catalytic reduction (SCR) at low temperature and under urban driving conditions. Hydrocarbon deNOx systems are advancing rapidly but need better desulfation and low-temperature NOx storage. For diesel particulate filters (DPFs), oxidation at the soot interface is showing promise for continuous regeneration. Some advanced petrol engine technologies will need particle number control. In the US, the Tier 2 Bin 5 emission standard requires 60% more NOx control than Euro 6, and the super ultra low emission vehicle (SULEV) emission category requires 85% more, according to Johnson (see Figure 1). Future generations of engines are likely to be capable of meeting NOx limits without aftertreatment, but SCR will allow better fuel economy. Johnson concluded by reviewing key aspects of the various emissions treatment technologies.

NOx Control

The remainder of the first day's oral sessions covered NOx control, starting with a paper from Bernd Krutzsch (Daimler AG, Germany), who summarised the options of NOx storage systems and SCR for diesel engines in addition to discussing some of the mechanisms involved. He saw the future challenges for NOx control as being low-temperature operation, catalyst ageing, platinum group metal (pgm) content and compatibility with hybrids and stop-start systems.

The subject of mechanisms for NOx control was followed up by Luca Lietti (Politecnico di Milano, Italy), who considered the detail of NOx reduction by hydrogen under near-isothermal conditions over Pt-K/Al_2O_3 lean NOx traps. It was stated that NOx is stored as nitrites on this material and that ammonia formation is lower than with Pt-Ba/Al_2O_3; there is a lower-temperature onset for consumption of hydrogen than for barium-based material. The two-step process for reduction of stored nitrogen species to molecular nitrogen appears to be similar, however.

Continuing with papers on NOx storage system mechanisms, Do Heui Kim (Pacific Northwest National Laboratory, USA) examined the promotional effects of CO_2 on desulfation of Pt-BaO/Al_2O_3 lean NOx traps, concluding that CO_2 plays an important role in promoting sulfur removal by suppressing the formation of barium sulfide crystals. Robert Büchel (ETH Zurich, Switzerland) considered the effect on NOx storage-reduction performance of the proximity of platinum to the cerium or barium in the CeO_2 or $BaCO_3$ support, concluding that Pt should be close to

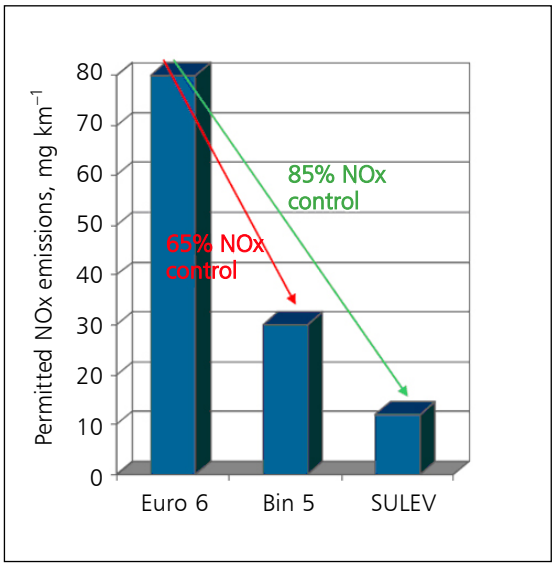

Fig. 1. The US Tier 2 Bin 5 emission standard requires 60% more NOx control than Euro 6, and the super ultra low emission vehicle (SULEV) emission category requires 85% more (Courtesy of Tim Johnson, Corning Environmental Technologies, USA)

Ba sites for the best activity. Anita Kouakou (Renault, France) reported a study of ammonia formation during the purge of a lean NOx trap, showing that a NOx trap without rhodium stored NOx more efficiently, but was limited by the release of nitric oxide during purge due to insufficient reduction of the stored NOx. The amount of NH_3 formed decreases with purge duration.

Three papers in this session covered SCR. Bilge Saruhan (Institute of Materials Research, German Aerospace Centre, Germany) presented a paper on the use of LaFeCoO perovskites with palladium either incorporated in the lattice or deposited after perovskite synthesis for the SCR of NOx with propene. A paper presented by D. Doronkin (N. D. Zelinsky Institute of Organic Chemistry, Russia) concentrated on the nature of the active sites of iron-zeolite SCR catalysts. The authors reported that the activity of Fe-Beta catalysts in ammonia deNOx is determined by isolated tetrahedral Fe^{3+} species in zeolite cationic positions, with activity depending on the localisation of Fe^{3+} in the zeolite structure. In the final paper, from Izabela Czekaj and Oliver Kröcher (Paul Scherrer Institute, Switzerland), theoretical and experimental work was combined to develop an optimised urea hydrolysis catalyst. The most active catalysts were found to be TiO_2 and ZrO_2. The paper concluded that virtual catalyst screening might be feasible for isocyanic acid (HNCO) catalysts.

The session concluded with a discussion on the first thirty-nine posters. It was commented that silver appears to have an advantage as a catalyst for SCR in that N_2O is not produced, although one poster showed N_2O formation over silver-based catalytic material when using dimethyl ether or methanol as the fuel. Only one poster mentioned the use of gold in NOx traps, with work suggesting that it may offer some benefits at low temperature and that it can now be thermally stabilised up to 700ºC. A further poster suggested that Fe disperses nitrates in an Fe-promoted NOx trap.

Mechanisms, Kinetics and Modelling of Catalysts and Sorption Technologies

The focus on NOx storage systems continued with a paper from Henrik Grönbeck (Chalmers University of Technology, Sweden) on NOx adsorption by Al_2O_3 and Ag/Al_2O_3, but much of this session concerned other catalytic systems. Steffen Tischer (University of Karlsruhe, Germany) presented a detailed reaction mechanism for Pt, Pd and Rh surfaces in three-way catalysts, based on the mechanism proposed by Chatterjee *et al*. for Pt/Rh (2), while William S. Epling (University of Waterloo, Canada) evaluated the spatial resolution of reactant species consumption in diesel oxidation catalysts (DOCs). In this work, low-temperature inhibition of NO oxidation was observed, with NO oxidation starting once the carbon monoxide is used up and the hydrocarbon concentration drops. NO oxidation activity increased with distance into the catalytic converter. Another paper, presented by Enrico Tronconi (Politecnico di Milano, Italy), concerned the reactivity, mechanism and kinetic modelling of crushed commercial iron- and copper-promoted zeolite SCR catalysts in a microreactor. This showed that copper zeolites gave a higher activity for both standard SCR and ammonia oxidation at high temperature, although this was accompanied by a small yet significant N_2O formation. It was concluded that the stability of surface nitrates and nitrites is key to both activity and selectivity.

DPF performance was evaluated in a presentation from Johannes Leixnering (ICE Strömungsforschung GmbH, Austria). Simulations were used to assess wall flow, foam and anisotropic filters. Modelling was also the topic of a paper presented by Martin Votsmeier (Umicore, Germany), in collaboration with researchers at Technische Universität Darmstadt, Germany, on the oxidation of NO on platinum. Votsmeier commented that the adsorption of NO on surfaces is neglected by most models – activating this improves kinetic models (see Figure 2). A further simulation paper, from Ai Suzuki and coworkers (Tohoku University, Japan), covered sintering dynamics, showing that simulated thermal sintering of Pt is consistent with experimental results.

Discussion of the twenty-six posters relevant to this session, many of which concerned modelling, led to questions on whether it would be possible for catalytic system suppliers to design formulations using modelling alone. The role of modelling as a tool for original equipment manufacturers was also discussed. It was concluded that the amount of material data required would be too great, but modelling can be used for optimisation and calibration. The issue of N_2O, discussed in the previous poster session, was again picked up in a poster from Georgios Pekridis (University of Western Macedonia, Greece) and coworkers, which suggested that copper zeolites produce a little more N_2O than other types of zeolite.

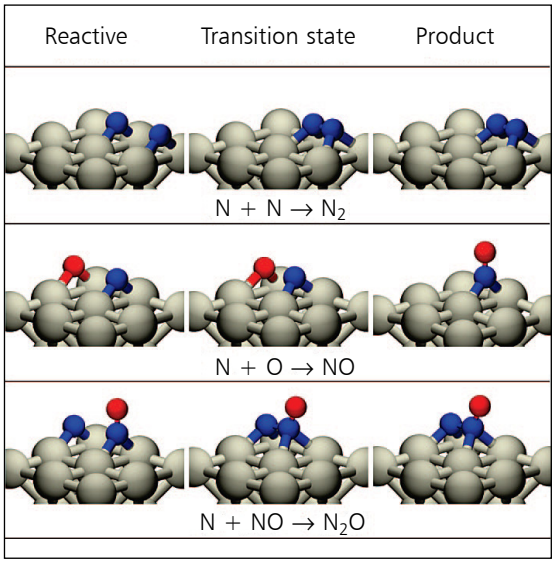

Fig. 2. Representation of the initial, transition and final states for N_2, NO and N_2O formation during the oxidation of ammonia on platinum(100), used in building a kinetic model of NO oxidation (Image reproduced with permission from (3). Copyright 2008 American Chemical Society)

Fuel Alternatives, Ageing and Poisoning

A discussion of methane and natural gas combustion in the poster session was followed by a paper from Per-Anders Carlsson (Chalmers University of Technology) and coworkers on methane oxidation over supported platinum under alternating rich and lean conditions, which suggested that surface coverage of platinum explains product composition and that oxygen 'reservoirs' impact surface coverage. Patrick Da Costa (Université Pierre et Marie Curie, France) examined the enhanced performance at high temperature of a three-way compressed natural gas (CNG) catalyst containing palladium, due to the presence of water leading to *in situ* production of hydrogen.

The statement that a valid method for suppressing noble metal sintering has not yet been established started the presentation by Hirohumi Shinjoh (Toyota Central R&D Labs, Inc, Japan). Platinum on a Ce-based oxide was shown not to sinter after ageing, leading to the conclusion that Pt–O–Ce bonds act as an 'anchor'. To achieve a good balance between this behaviour and catalytic activity, Ce can be used with an additive.

In the discussion of the posters for this session, following a suggestion that the tolerance of silver to high temperatures and impurities such as sulfur found in exhaust gases could be improved by the addition of nickel or cobalt, it was noted that neither of these would be permissible in automotive catalyst formulations. Methane combustion was also discussed, including the potential for oxidation of methane at temperatures below 350ºC.

Particulate Control and Innovative Technologies

Luca Lietti (Politecnico di Milano) presented the results of work on the simultaneous removal of NOx and soot over model Pt-Ba/Al_2O_3 and Pt-K/Al_2O_3 materials using Evonik's Printex® U synthetic soot. With Pt-Ba/Al_2O_3 after four hours under isothermal conditions there was less than 10% oxidation of the soot in oxygen, but soot oxidation started on the introduction of NO. Lean-rich cycles provided evidence that soot is oxidised while NOx is being stored, leading to the conclusion that the presence of soot decreased the stability of surface nitrates. For Pt-K/Al_2O_3, significantly higher reactivity for soot oxidation was observed, with significant soot combustion observed in the lean phase. It was concluded that at 350ºC, soot oxidation occurs mainly in the presence of NO.

Henrik Ström (Chalmers University of Technology) showed a simulation of particulate matter trapping for various filter types, including metallic substrates with protrusions, ceramic monoliths with rotated sections, and partial metallic filters with protrusions and porous walls. Drag force and Brownian motion were shown to be the dominant mechanisms, and result in different-sized particles being collected on different regions of the substrate. Michiel Makkee (Delft University of Technology, The Netherlands) asked whether new fuel regulations will impact DPF regeneration. To investigate this, a fifteen-year-old two-cylinder direct injection engine was used as a soot generator with various fuels. Sulfur and fatty acid methyl ester (FAME) blends each had little effect, but changes in diaromatics led to a difference of over 100ºC in the soot oxidation temperature.

Jens Bernnat (Universität Stuttgart, Germany) presented a proposal for an off-gas heat exchanger and catalytic burner with integrated pgm-containing DOC, NOx storage-reduction catalyst and particulate filter. It is planned to install the system on a CNG engine. Ralf Moos (Bayreuth Engineering Research Centre, Germany) presented a proposal to directly monitor

the electrical properties of catalytic pgm coatings. Two alternatives were discussed: a contact mode impedance measurement and a contactless method using microwaves or radio frequencies. Charles-Henri Nicolas (Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), France) presented a membrane-based process for capturing CO_2 from vehicles which was developed by IRCELYON, the Fraunhofer Institute for Interfacial Engineering and Biotechnology (IGB), Germany, and the Institut National de Recherche sur les Transports et leur Sécurité (INRETS), France. Hollow tube zeolites embedded in a support were used to capture the CO_2.

The final batch of posters, discussed during this session, included differing views on the stability of potassium titanates presented by Qiang Wang (School of Environmental Science and Engineering, POSTECH, Korea) and coworkers, and by Franz Edwin López-Suárez (University of Alicante, Spain) and coworkers. A poster from Henrik Christensen and colleagues (Dinex A/S, Denmark) evaluated base metal oxides for actively regenerating DPFs, and one from José Carlos Caroca and coworkers (Politecnico di Torino, Italy) led to a discussion on possible concerns resulting from the use of DPF coatings incorporating copper.

Concluding Remarks

The Congress closed with the Executive Chairman of the conference organising committee, Professor Norbert Kruse (ULB), noting that the conference had attracted a significant number of representatives from the EU, Japan and Korea and that, although industrial participation was down this year, there was still a good balance between industry and academia. This conference demonstrated that there is still work going on to improve pgm-containing catalysts and to model their performance, but overall the focus of emissions control work appears to have moved towards the improvement of NOx control systems.

A special issue of *Topics in Catalysis* includes a selection of 78 of the original 150 papers and posters from the event (4). The next conference in the series, CAPoC9, will take place in 2012.

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The Reviewer

John May is the Technical Manager of the Association for Emissions Control by Catalyst (AECC), an international scientific association based in Brussels, Belgium. His responsibilities at AECC include the development and control of test programmes and the publication of information on emissions. He represents the Association on a number of EU and UN working groups. Prior to joining AECC in 2003, he spent 30 years in the motor industry as a technical specialist and senior manager where his responsibilities covered vehicle emissions, fuels and lubricants, combustion chemistry and environmental strategy.

