Abstracts

Session 10 – Urea, NOx Adsorber, and Non-Thermal Plasma NOx Reduction

SELECTIVE CATALYTIC REDUCTION SYSTEMS FOR HEAVY-DUTY TRUCKS: PROGRESS TOWARDS MEETING EURO 4 EMISSION STANDARDS IN 2005

Georg Huethwohl

PUREM Abgassysteme GmbH & Co. KG

ABSTRACT

Emissions of diesel engines contain some components that support the generation of smog and are classified as hazardous. Exhaust gas aftertreatment is a powerful tool to reduce NO_x and particulate emissions.

NO_x emissions can be reduced by selective catalytic reduction (SCR) technology. A reduction agent has to be injected into the exhaust upstream of a catalyst. On the catalyst, the NO_x is reduced to N_2 and H_2O. This catalytic process was developed in Japan about 30 years ago to reduce the NO_x emission of coal-fired powerplants. The first reduction agent used was NH_3.

SCR technology was used with diesel engines starting in the mid-1980's. The first applications were stationary operating generator sets. In 1991 a joint development between DaimlerChrysler, MAN, IVECO, and Siemens was started to use SCR technology for the reduction of NO_x in heavy-duty trucks. Several fleet tests demonstrated the durability of the systems. Today, SCR technology is the most promising technology to fulfil the new European Regulations EURO 4 and EURO 5 being effective in October 2005 and October 2008. The efficient NO_x reduction of the catalyst allows an engine calibration for low fuel consumption. DaimlerChrysler decided to use the SCR technology on every heavy-duty truck and bus in Europe, and many other truck manufacturers will introduce SCR technology to fulfil the 2005 emission regulation.

The truck manufacturers in Europe agreed to use aqueous solution of urea as the reducing agent. The product is called "AdBlue," which is a non-toxic, non-smelling liquid. The consumption is about 5 percent of the diesel fuel consumption to reduce the NO_x emissions. A small AdBlue tank has to be installed on the vehicle. With an electronically controlled dosing system, the AdBlue is injected into the exhaust. The dosing system is simple and durable. It has proven its durability during winter and summer testing as well as in fleet tests.

The infrastructure for AdBlue is under evaluation in Europe by urea producers and mineral oil companies to be readily available in time. Urea is one of the most common chemical products in the world, and its production and the distribution are very much known. However, a pure grade is needed for automotive application and requires special attention.

UREA SELECTIVE CATALYTIC REDUCTION AND DIESEL PARTICULATE FILTER SYSTEM FOR DIESEL LIGHT-DUTY TRUCK/SPORT UTILITY VEHICLE MEETING TIER II BIN 5

Robert Hammerle and Christine Lambert

Ford Research & Advanced Engineering

Mike Noorman

ExxonMobil Research & Engineering

ABSTRACT

Ford Motor Company is participating in the U.S. Department of Energy's (DOE) Ultra-Clean Transportation Fuels Program with the goal of developing an innovative emission-control system for diesel sport utility vehicles. This program focuses on diesel vehicles because in Europe they currently offer up to 50-percent better volumetric fuel economy and up to 25-percent lower CO_2 emissions than comparable gasoline vehicles. We are using selective catalytic reduction (SCR) with aqueous urea as the NO_x reductant and a catalyzed diesel particulate filter (DPF) for this program. We plan to demonstrate more than 90-percent reduction in particulate matter (PM) and NO_x emissions on a light-duty truck/sport utility vehicle application. We are using very low sulfur diesel fuel (~15 ppm) to enable low PM emissions, reducing the fuel economy penalty due to the emission control system, and improving long-term durability of the system. The end result will allow vehicles with diesel engines to be Tier II emissions certified at a minimum cost to the consumer.

In the second year of the program, we switched from an ultra low sulfur Swedish-style fuel to a low sulfur fuel developed by ExxonMobil that has properties reflective of those projected for 2007 U.S. diesel fuel. Recalibration of the engine was necessary to compensate for increases in NO_x and hydrocarbon emissions. We continued to separately improve the durability of both the urea SCR and DPF systems. We also have been improving exhaust gas NO_x and ammonia sensors for more accurate control of reductant injection and on-board diagnostics. Finally, we worked with nozzle and dispenser manufacturers to develop durable hardware for delivery of diesel fuel and aqueous urea simultaneously to the vehicle.

ENSURING THE OVERALL SUPPLY OF UREA IN NORTH AMERICA AND THE RELIABILITY OF THE UREA-DOSING UNITS FOR SELECTIVE CATALYTIC REDUCTION SYSTEMS

Glenn Barton

Hilite International

Barry Lonsdale

Terra International

ABSTRACT

Urea is the proven ingredient in the post-combustion treatment of diesel engine exhaust gas for NOx reduction. This paper will discuss the status of urea-dosing units and developments in sensors to insure urea is available and being delivered in the appropriate dose to the post- treatment region and verify that the post-combustion treatment process is effective.

The paper will also address the urea supply infra-structure in North America and how it will insure the proper urea is available for all diesel engine treatment systems, stationary and on-road nationwide.

SELECTIVE REDUCTION OF NO_X IN OXYGEN-RICH ENVIRONMENTS WITH PLASMA-ASSISTED CATALYSIS: CATALYST DEVELOPMENT AND MECHANISTIC STUDIES

C. H. F. Peden, S. E. Barlow, J. H. Kwak, J. Szanyi, and R.G. Tonkyn

Pacific Northwest National Laboratory

M. L. Balmer-Millar and A. G. Panov

Caterpillar, Inc.

J. W. Hoard

Ford Research Laboratory

S. J. Schmieg

General Motors R&D

ABSTRACT

The control of NO_x (NO and NO_2) emissions from so-called 'lean-burn' vehicle en-gines remains a challenge. In recent years, there have been a number of reports that show that a plasma device combined with a catalyst can reduce as high as 90 percent or more of NO_x in simulated diesel and other 'lean-burn' exhaust.

Non-thermal plasma (NTP)-catalysis treatment of a gas stream consists of the sequential (or possibly simultaneous) action of NTP and heterogeneous catalysis. The most common reported strategy for lean NO_x treatment is to separate the plasma from the catalyst, as it is difficult to create robust plasma inside a catalyst bed. In the case of propylene-containing simulated diesel exhaust, the beneficial role of a plasma treatment is now thought to be due to oxidation of NO to NO_2 and the formation of partially oxidized hydrocarbons that are more active for the catalytic reduction of NO_2 than propylene. For plasma-assisted catalysis, both zeolite- and alumina-based materials have shown high activity, albeit in somewhat different temperature ranges, when preceded by an NTP reactor.

This presentation will describe our research efforts aimed at optimizing the catalyst materials for NTP-catalysis devices based, in part, on our continuing studies of the NTP- and catalytic-reaction mechanisms. Various alkali- and alkaline earth-cation-exchanged Y zeolites have been prepared and their material properties characterized. They have been tested as catalytic materials for NO_x reduction in laboratory NTP-catalysis reactors. Interestingly, NO_2 formed in the plasma, and not subsequently removed over these catalysts, will back-convert to NO, albeit to varying extents depending upon the nature of the cation.

Besides this comparative reactivity, we will also discuss selected synthesis strategies for enhancing the performance of these zeolite-based catalyst materials. A particularly important result from our mechanistic studies is the observation that aldehydes, formed during the plasma treatment of simulated diesel exhaust, are the important species for the reduction of NO_x to N_2. Indeed, acetaldehyde has been found to be especially effective in the *thermal* reduction of both NO and NO_2 over Ba- and Na-zeolite-Y catalysts.

Finally, we will discuss experiments aimed at understanding and controlling deactivation of these zeolite-based catalysts due to 'coking.' We believe that this catalyst deactivation mechanism explains a loss of catalyst efficiency with time that is observed in engine dynamometer tests.

HEAVY-DUTY NO_X EMISSIONS CONTROL: REFORMER-ASSISTED VS. PLASMA-FACILITATED LEAN NO_X CATALYSIS

Christopher L. Aardahl

Pacific Northwest National Laboratory

Paul W. Park

Caterpillar, Inc.

ABSTRACT

Recent efforts in plasma-facilitated lean NO_x catalysis and thermal lean NO_x catalysis have shown that hydrocarbon speciation has a dramatic impact on catalyst performance. In particular, use of oxygenated hydrocarbons as reducing agents results in better NO_x efficiency than typical fuel hydrocarbons. In a cooperative research and development agreement between Pacific Northwest National Laboratory and Caterpillar, Inc., reformation of non-oxygenated hydrocarbons to oxygen-containing molecules is being examined as a way to enhance performance in lean NO_x catalyst systems. Recent results for reformer-assisted catalysis are compared to results using traditional plasma-catalysis.

DYNAMOMETER EVALUATION OF PLASMA-CATALYST SYSTEM FOR DIESEL NO_X REDUCTION

John Hoard

Ford Motor Company

Dave Brooks

DaimlerChrysler

Steve Schmieg

General Motors R&D

Charles H. F. Peden, Steve Barlow, and Russ Tonkyn

Pacific Northwest National Laboratory

ABSTRACT

A three-stage plasma-catalyst system was developed and tested on an engine dynamometer. Previous laboratory testing suggested high NO_x efficiency could be obtained. With hexene reductant added to the exhaust, we observed over 90-percent NO_x reduction. However, with diesel or Fischer-Tropsch reductant, the catalyst efficiency rapidly dropped off. Heating the catalyst in air removed brown deposit from the surface and restored conversion efficiency.

Following the engine tests, the used catalysts were evaluated. BET surface area decreased, and temperature-programmed desorption revealed significant storage. This storage appears to be partly unburned diesel fuel that can be removed by heating to around 250-300°C, and partly hydrocarbons bonded to the surface that remain in place until 450-500°C.

Laboratory testing with propene reductant demonstrated that the catalyst regains efficiency slowly even when operating temperature does not exceed 300°C. This suggests that control strategies may be able to regenerate the catalyst by occasional moderate heating.

NOXTECH'S PLASMA-ASSISTED CATALYST SYSTEM DEVELOPMENT AND DEMONSTRATION

Ralph Slone, Victor Puchkarev, and Jeff Marguglio

Noxtech, Inc.

ABSTRACT

The non-thermal plasma-assisted catalyst (NTPAC) technology being developed at Noxtech, Inc., continues to focus on achieving the 2007 and beyond emissions standards for heavy- duty vehicles. Noxtech's NTPAC technology utilizes an efficient non-thermal plasma reactor with a solid-state pulsed power supply to efficiently convert NO to NO_2 in the presence of a suitable hydrocarbon generated on-board from diesel fuel. NO_2 is then converted to N_2 in the presence of a sulfur-tolerant catalyst that contains no precious metals.

Noxtech has made significant progress in the development and enhancement of the NTPAC system under the U.S. Department of Energy-sponsored program. Noxtech has designed, built, and demonstrated an 80-hp NTPAC system with up to 94-percent NO_x reduction from an 80-hp diesel engine generator using diesel fuel as a source of reductant.

Noxtech's emphasis for its 2003 program has been to improve and enhance the performance, reliability, and commercial capability of its NTPAC system. It is working with a commercial partner to reduce the size and cost and improve the efficiency of the pulser for its plasma reactor. Noxtech has also redesigned and improved its diesel fuel converter to produce effective hydrocarbons to act as a catalyst and reductant for the NTPAC system. Several new catalysts have been formulated and evaluated to enhance performance (surface efficiency/availability and selectivity) as well as to improve durability and operating temperature range. The goal is to produce a system that is commercially capable in the near future.

Noxtech has conducted a demonstration of its NTPAC system at a third-party test site for assessment by Government and private industry representatives. The result of this test will be presented at the DEER 2003 Conference.

NO_X ADSORBER REGENERATION PHENOMENA IN HEAVY-DUTY APPLICATIONS

Brian West, John Thomas, Mike Kass, John Storey, and Sam Lewis

Oak Ridge National Laboratory

ABSTRACT

Hydrocarbon species are being measured with a gas chromatograph/mass spectrometer and Fourier transform infrared at NO_x adsorber inlet and outlet locations in the exhaust system of a heavy-duty diesel engine. The engine is equipped with electronic throttle and exhaust gas recirculation, in-pipe fuel injection, and various diesel oxidation catalysts upstream of a catalyzed diesel particle filter (CDPF) and a high-temperature NO_x adsorber catalyst. Raw diesel fuel injected into the exhaust system is readily cracked into lighter compounds over catalysts, and the NO_x adsorber more readily utilizes certain compounds during regeneration. Augmenting the CDPF with oxidation catalysts produces preferred species such that comparable NO_x reduction can be achieved with less supplemental fuel.

COMPARISON OF 4-WAY NO_X ADSORBER CATALYST PERFORMANCE ON FIBROUS AND CONVENTIONAL SUBSTRATES

Neil Currier, Matthew Henrichsen, Bill Epling, and Jim Lucas

Cummins, Inc.

ABSTRACT

Performance of a 4-way NO_x adsorber is dependent on a number of non-operating factors. These include catalyst composition, monolith cell size, monolith aspect ratio, substrate thermal properties, substrate material, and substrate wall morphology. The relative significance of these factors was scouted by comparing a standard cordierite monolith to a fibrous monolith. Flexibility in the choice of catalyst loading and differences in heat distribution were found to play a significant role in determining NO_x performance of these devices.

MEASUREMENT AND CHARACTERIZATION OF NO_X ADSORBER REGENERATION AND DESULFATION

Shean Huff, Stuart Daw, John Storey, Brian West, Bill Partridge, Sam Lewis, Dean Edwards, Katey Lenox, and Jae-Soon Choi

Oak Ridge National Laboratory

ABSTRACT

Experiments at Oak Ridge National Laboratory are being conducted to characterize NO_x adsorber catalysts. Full-size samples are being evaluated on a diesel engine stand with full-pass control of electronic throttle and exhaust gas recirculation (EGR), wastegate, number and timing of fuel injection events, etc. Bench-scale work with powders, wafers, and small monolith cores is being conducted in parallel to the engine work.

The presentation will describe recent measurements of hydrogen and other species inside catalyst channels and in the bulk exhaust using spatially resolved, capillary-inlet mass spectrometry (SpaciMS). Gas chromatography is being used in conjunction with SpaciMS to fully characterize the exhaust hydrocarbons and other species that are formed in-cylinder for various regeneration strategies and the usage of various compounds through the oxidation and NO_x adsorber catalysts downstream.

NO_X ADSORBER CATALYST DURABILITY: LIGHT- AND HEAVY-DUTY PERSPECTIVES

Jim Parks, Bill Epling, Greg Campbell, Michele Sanders, and Aaron Watson

EmeraChem

ABSTRACT

NO_x adsorber catalysts can reduce NO_x from diesel engines by over 90 percent, but to be commercially viable, NO_x adsorbers must demonstrate compliance-range durability. Sulfur masking has traditionally limited NO_x adsorber durability, but sulfur management by a combination of catalyst desulfation and fuel-sulfur reduction is an effective method of controlling degradation from sulfur masking.

Since the control of sulfur masking has been demonstrated, thermal degradation is expected to be the primary degradation mechanism. Thermal degradation rates will great-ly depend on the operation temperatures of the catalyst, and the desulfa-tion process typically results in the highest and most severe temperature exposure. A NO_x adsorber catalyst aging experiment testing repetitive thermal exposure during the desulfation process will be presented. Results will be used to predict catalyst lifetime and compare to compliance mileage requirements. Issues relating to the different requirements for light- and heavy-duty applications will be discussed.

COMPLEMENTARY EXPERIMENTAL TOOLS FOR UNDERSTANDING DIESEL PARTICULATE FILTER BEHAVIOR

Aleksey Yezerets, Neal Currier, Arvind Suresh, and William Epling

Cummins, Inc.

ABSTRACT

During the last 3 years, a set of unique laboratory techniques was developed at Cummins to investigate various aspects of diesel particulate filter (DPF) loading and regeneration processes. A novel rapid protocol for measuring particulate matter oxidation rates under various conditions has been developed using a micro-reactor system. Also, a unique system was designed, which allows us to load soot-filter cores in a diesel exhaust and subsequently study their regeneration and back-pressure behavior under well-controlled conditions in a pilot reactor. The results obtained with these techniques show good correlation with the on-engine testing.