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Development of Improved SCR Catalysts
FY05 Annual Progress Report

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CRADA Partners: Low Emissions Technologies Research and Development Partnership
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Objectives

- Develop new catalyst technology to enable CIDI engines to meet EPA Tier II emission standards with minimal impact on fuel economy.
- Optimize catalyst formulations for activity, stability, and resistance to poisoning.
- Demonstrate feasibility for scale-up of preparation of promising catalysts.
- Transfer technology of most promising formulations to catalyst suppliers via OEMs.

Approach

- Design and develop new non-vanadia, Hydrous Metal Oxide (HMO)-based catalyst materials for reducing NO_x emissions in lean-burn exhaust environments using ammonia as a reductant.
- Test catalyst formulations under realistic laboratory conditions using protocol developed with LEP input.
- Where appropriate, transfer successful powder catalyst formulations to monolith platform and re-evaluate.
- Evaluate short-term durability under hydrothermal conditions and in the presence of SO_2/SO_3.
- Characterize catalysts using a variety of techniques to gain understanding of critical parameters related to activity and aging phenomena.
- Scale-up synthesis and processing of promising catalyst formulations to enable fabrication of prototype catalytic converters for CIDI engine dynamometer testing.
- Technology transfer of the most promising catalyst formulations and processes to

designated catalyst suppliers *via* the LEP.

Accomplishments

- Several new catalyst formulations showed enhanced NO_x conversion performance compared to commercial ZNX material.
- Short-term hydrothermal durability demonstrated for….

Future Directions

- CRADA has ended; no future directions apply for this program.

Introduction

This report covers the end of a multi-partner effort sponsored by OFCVT which involved separate CRADAs between three national laboratories (Los Alamos National Laboratory [LANL], Oak Ridge National Laboratory [ORNL], and Sandia National Laboratories [SNL]) and the Low Emissions Technologies Research and Development Partnership (LEP, composed of DaimlerChrysler Corporation, Ford Motor Company, and General Motors Corporation). The CRADAs with LANL and ORNL ended in FY04 (the FY04 Annual Report was their final contribution) and the SNL CRADA ended April 29th 2005.
The project addressed reduction of CIDI engine NO_x emissions using exhaust aftertreatment – identified as one of the key enabling technologies for CIDI engine success. The overall CRADA efforts were focused on the development of urea/ammonia selective catalytic reduction (SCR) processes for reducing NO_x emissions, specifically targeting the selection of appropriate catalyst materials to meet the exhaust aftertreatment needs of light- and medium-duty diesel engines (SNL and LANL) and understanding the urea-catalyst interaction as well as factors influencing urea decomposition (ORNL). Infrastructure issues notwithstanding, the SCR process has the greatest potential to successfully attain the > 90% NO_x reduction required for CIDI engines to meet the new EPA Tier II emission standards phased in starting in 2004.

Approach

SNL continued to develop catalysts supported on Hydrous Metal Oxides (HMOs). New catalyst formulations were investigated, with emphasis on enhancing low temperature activity. During FY05 we focused on testing catalysts under more stringent testing conditions with particular attention paid to benchmarking of SNL catalysts against a commercial material (ZNX, from Engelhard).

Standard experimental details for catalyst evaluation are summarized in Table 1 together with performance targets under each set of conditions.

Results

Following some extended down-time of the SNL bench test reactor, and extensive troubleshooting and re-calibration of equipment as reported in the FY04 annual report, considerable time was spent evaluating a benchmark catalyst (ZNX monolith core, from Engelhard) on the SNL system in order to establish limits of reproducibility and reliability. Good reproducibility of data was obtained, as shown in Figure 1 for several successive runs using the same monolith core. Note that a small deactivation was noticed after the first run, but NO_x conversion profiles and N_2O selectivity were constant thereafter. Similar results were obtained

for different monolith cores of ZNX, and are not shown. Since the intrinsic performance of a standard catalyst will often vary depending upon the apparatus on which it is evaluated, all data in this report is compared with ZNX measured under equivalent conditions and on the same apparatus. Indeed, the intrinsic ZNX performance measured on the SNL bench test apparatus is typically lower than that measured under comparable conditions on other bench test reactors. The reason for this difference in baseline performance is not known. All NO_x conversion data are compared to ZNX in this report, with the assumption that the relative performances of a new catalyst and ZNX will be similar on a different bench test reactor.

A range of catalyst formulations, based on a previous high-performing catalyst (Catalyst C in previous reports), was prepared and tested under the conditions given in Table 1; these catalysts are designated "Catalyst C*n", where n is an integer. Catalyst C had shown performance satisfying all of the selection criteria for a viable urea-SCR catalyst, viz: NO_x conversion activity and selectivity in the fresh, hydrothermally aged, and sulfur treated forms. Catalysts C* are differentiated from Catalyst C in that they possess metal-oxide components in additions to those of Catalyst C. That is to say, each new catalyst was prepared by adding one or more metal oxide to a common starting material of Catalyst C. Furthermore, the performance of each new catalyst was compared against the commercial benchmark catalyst ZNX (the first data set from Figure 1, i.e., that showing the highest activity for ZNX). The ZNX was tested in monolith core form, while the SNL-developed catalysts were evaluated as powders using the appropriate gas flow conditions given in Table 1. Prior work has shown that comparison of monolith core and powder data is valid provided the gas flow rates for the powder are adjusted to simulate that seen by the catalyst in a monolithic catalyst.[1]

Figure 2 compares the NO_x conversion performance and N_2O selectivity for ZNX, Catalyst C, Catalyst C*1 and Catalyst C*2. It is noteworthy that Catalyst C outperforms ZNX over almost the entire temperature window studied. Each of the C* catalysts in this figure also offer enhanced NO_x conversion relative to ZNX over the majority of the temperature window, but are not as active as Catalyst C.

Two other C* catalysts performed as well as, or better than ZNX over the middle temperature range (250 – 350 °C, Catalysts C*3 and C*4, Figure 3), while the remainder were generally less active than ZNX (Catalysts C*5, C*6 and C*7, Figure 4).

Thus the C* catalysts offered no advantage over Catalyst C in the fresh (un-aged) state, however given the enhanced performance of a few of the new catalysts compared to ZNX, investigation of their hydrothermal durability and sulfur tolerance may reveal advantages over previous catalyst formulations.

Conclusions:

- Benchmarking with ZNX monolith core verified stable operation of SNL bench test reactor system after extended maintenance and troubleshooting.
- New catalyst formulations based on previously-reported Catalyst C were prepared and evaluated.
- Two new formulations out-perform ZNX over majority of temperature window.
- Two new formulations out-perform ZNX over middle-temperature range (250 – 350 °C).
- Catalyst C offers better NO_x conversion performance than new formulations in fresh (un-aged) state.

References:

1 E.N. Coker, J.M. Storey and K.C. Ott, "Development of improved SCR catalysts" *Advanced Combustion Engine Research and Development, 2004 Progress Report*, DOE-OFCVT, pp.166-179.

FY 2005 Publications/Presentations

1. "Development of durable low-temperature urea-SCR catalysts for light-duty mobile CIDI engines" D.A. Peña, J.N. Stuecker, E.N. Coker, J. Cesarano III, J.E. Miller, *29th International Cocoa Beach Conference and Exposition on Advanced Ceramics & Composites*, Cocoa Beach, FL, Jan. 23-28, 2005.

Acronyms

CIDI	Compression Ignition Direct Injection (also known as the diesel engine)
CRADA	Cooperative Research and Development Agreement
DRIFT	Diffuse Reflectance Infrared Fourier Transform
EPA	Environmental Protection Agency
FTIR	Fourier Transform Infra-Red
GHSV	Gas Hourly Space Velocity; a measure of gas flow rate through a reactor in units of liters of gas per liter of catalyst per hour, or L L^{-1} h^{-1}, or h^{-1}.
HMO	Hydrous Metal Oxide, a type of catalyst support.
LANL	Los Alamos National Laboratory
LEP	Low Emissions Technologies Research and Development Partnership (often abbreviated to Low Emissions Partnership); a consortium between Ford, General Motors and DaimlerChrysler.
NO_x	Oxides of nitrogen, defined here as ($NO + NO_2$)
OEM	Original Engine Manufacturer
ORNL	Oak Ridge National Laboratory
ppm	parts per million
SCR	Selective Catalytic Reduction
SNL	Sandia National Laboratories

Table & Figure Captions

Table 1. Standard conditions used in bench reactor evaluation of SCR catalyst performance, and performance targets developed in conjunction with the LEP.

Figure 1. Performance of a ZNX monolith core evaluated in four tests over a two month period after the SNL bench test reactor was re-commissioned. Experimental conditions as in Table 1, with $NO:NO_2 = 4:1$. Solid line = NO_x conversion; dashed line = N_2O selectivity.

Figure 2. Performance of a ZNX monolith core, and three powder catalysts developed at SNL: Catalyst C, Catalyst C*1 and Catalyst C*2. Experimental conditions as in Table 1, with $NO:NO_2 = 4:1$. Solid line = NO_x conversion; dashed line = N_2O selectivity.

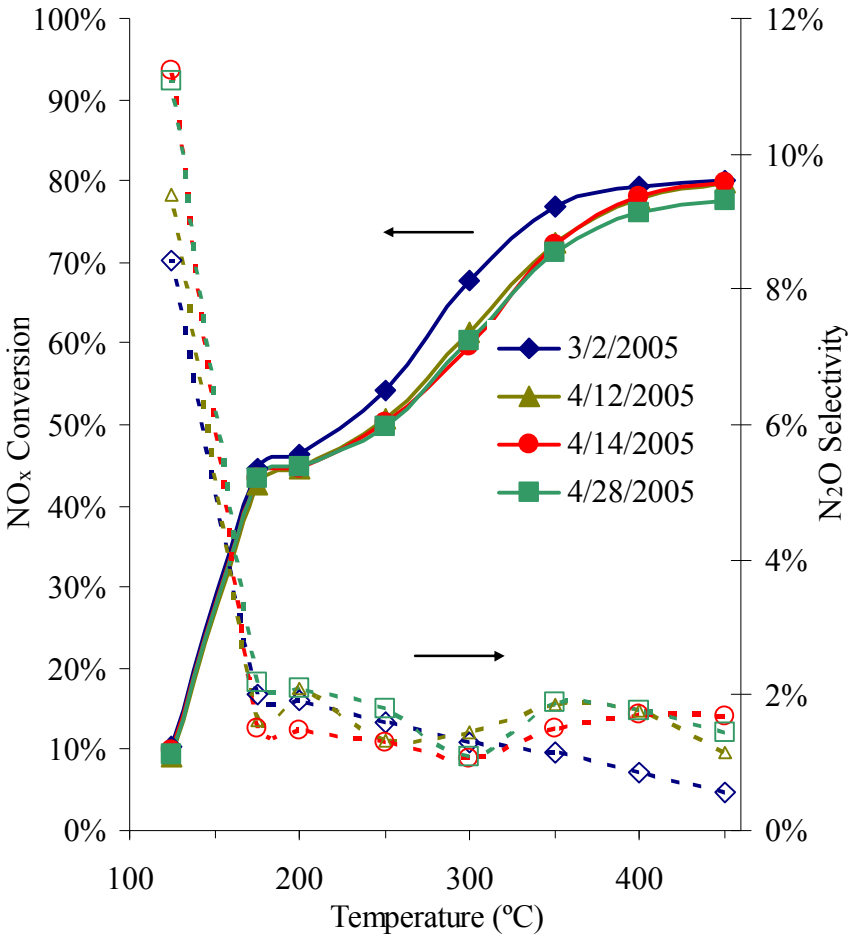
Figure 3. Performance of a ZNX monolith core, and two powder catalysts developed at SNL: Catalyst C*3 and Catalyst C*4. Experimental conditions as in Table 1, with $NO:NO_2 = 4:1$. Solid line = NO_x conversion; dashed line = N_2O selectivity.

Figure 4. Performance of a ZNX monolith core, and three powder catalysts developed at SNL: Catalyst C*5, Catalyst C*6 and Catalyst C*7. Experimental conditions as in Table 1, with $NO:NO_2 = 4:1$. Solid line = NO_x conversion; dashed line = N_2O selectivity.

	Standard Test Conditions I ($NO:NO_2$ = 1:1)	Standard Test Conditions II ($NO:NO_2$ = 4:1)
Temperature	**450 - 125 °C**	**450 - 125 °C**
GHSV (h^{-1}) [monolith]	**30,000**	**30,000**
GHSV (h^{-1}) [powder]*	**120,000 - 140,000**	**120,000 - 140,000**
NO (ppm)	**175**	**280**
NO_2 (ppm)	**175**	**70**
NH_3 (ppm)	**350**	**350**
O_2 (%)	**14**	**14**
CO_2 (%)	**5**	**5**
H_2O (%)	**4.6**	**4.6**
Balance	**N_2**	**N_2**
NO_x conversion target, 200°C (%)	**90**	**50**
NO_x conversion target, 200 – 400°C (%)	**90**	**N/A**

* Powders tested at standard flow rate of 3.125 Liters (g catalyst)$^{-1}$ min^{-1}; GHSV varies depending on catalyst density.

Table 1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Temperature (°C)
NOx Conversion
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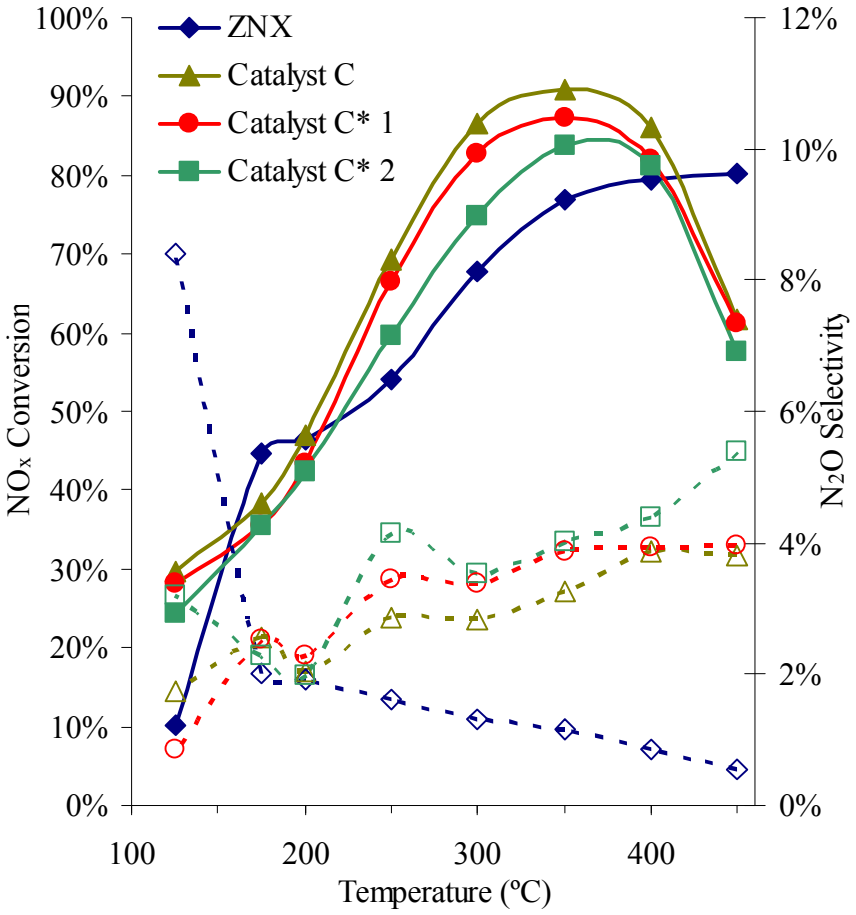
Figure 1


ZNX
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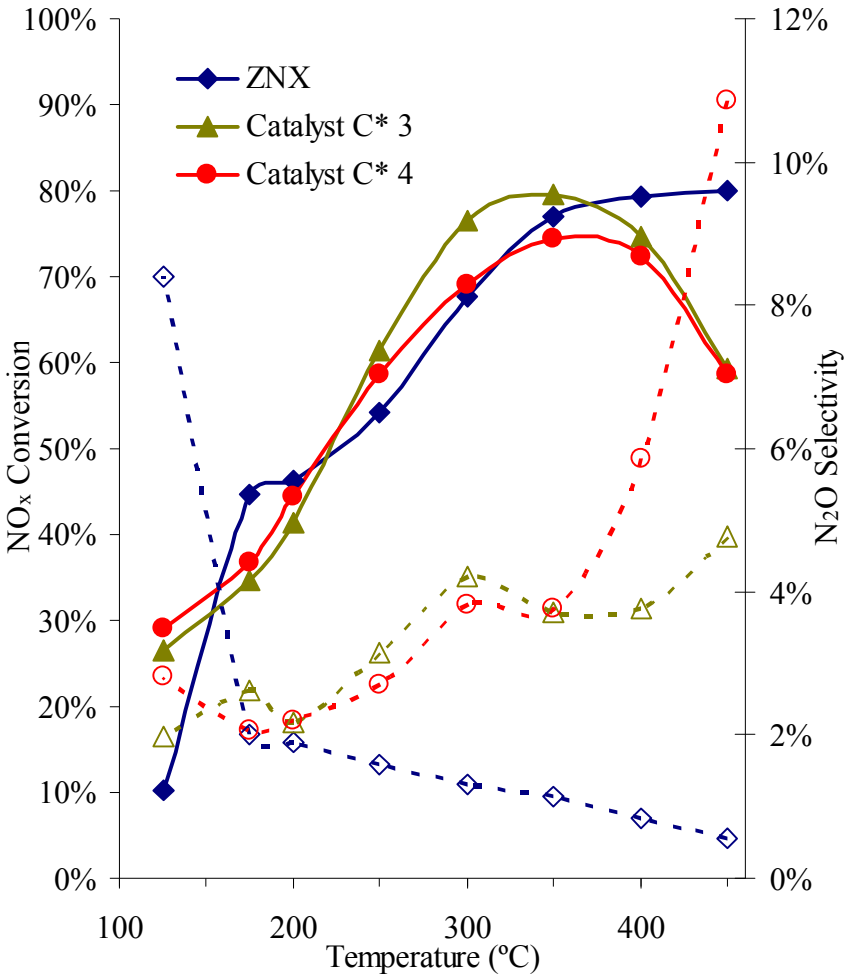
Temperature (ºC)
NOx Conversion
N2O Selectivity

Figure 2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Catalyst C* 4
NOx Conversion
N2O Selectivity
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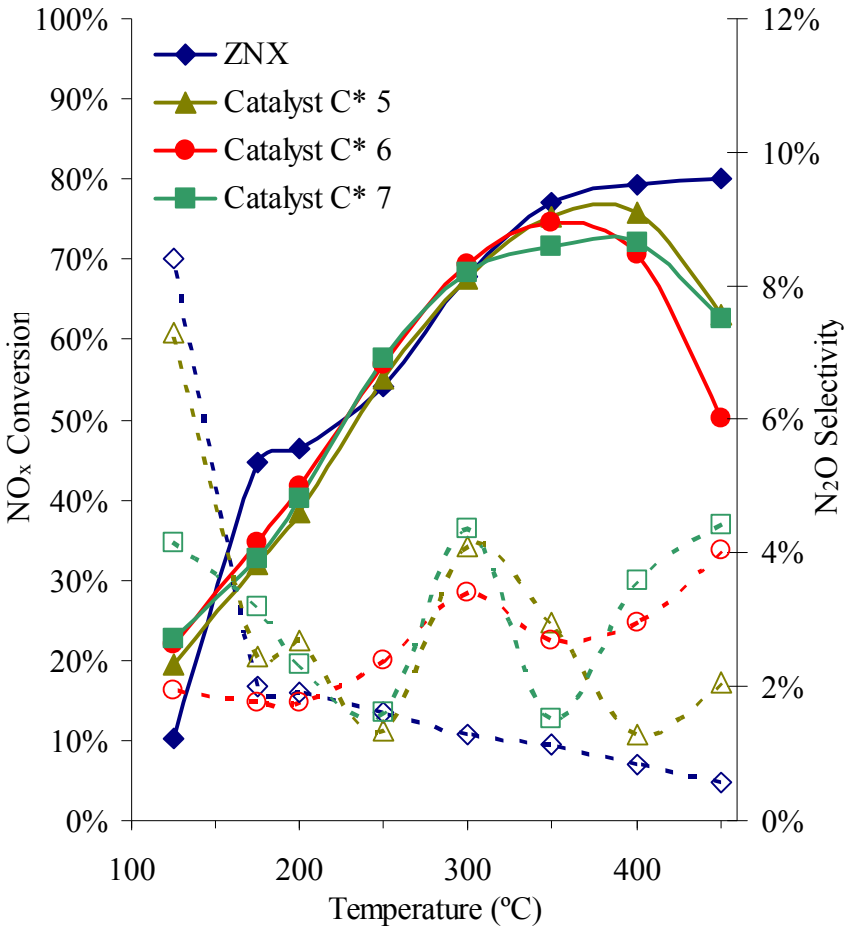
Temperature (ºC)

Figure 3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NOx Conversion
N2O Selectivity
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Figure 4