

Effects of Fuel Type on Dual SCR Aftertreatment for Lean NO_x Reduction

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ABSTRACT

Global demand for alternative fuels to combat rising energy costs has sparked a renewed interest in catalysts that can effectively remediate NO_x emissions resulting from combustion of a range of HC based fuels. Because many of these new engine technologies rely on lean operating environments to produce efficient power, the resulting emissions are also present in a lean atmosphere. While HCs are easily controlled in such environments, achieving high NO_x conversion to N₂ has continued to elude fully satisfactory solution. Until recently, most approaches have relied on catalysts with precious metals to either store NO_x and subsequently release it as N₂ under rich conditions, or use NH₃ SCR catalysts with urea injection to reduce NO_x under lean conditions. However, new improvements in Ag based technologies also look very promising for NO_x reduction in lean environments. Early in 2009 we proposed "Dual SCR," a further enhancement to Ag HC-SCR, where an NH₃-SCR catalyst follows the HC-SCR catalyst. The second catalyst improves overall efficiency using ammonia formed on the Ag HC-SCR catalyst to further reduce NO_x. This lean NO_x aftertreatment approach, with a catalyst cost at a fraction of precious metal systems, has shown NO_x reduction activity exceeding 90% under a variety of temperature and feed conditions in our bench reactor studies. Here we extend our efforts to an engine test cell and use a range of fossil and biofuels as the reductants for the Ag HC-SCR catalysts and we continue to find excellent NO_x reduction efficiencies. Although relatively low concentrations of H₂ (near 0.1%) are useful for enhancing NO_x activity at low temperatures (below 250 °C), the benefit decreases for exhaust temperatures near and above 400 °C. This technology could be a key enabler for low cost and efficient NO_x reduction to help auto manufacturers meet Tier2/Bin5 and Tier2/Bin2 emissions standards.

INTRODUCTION

Since the pioneering work of Iwamoto et al. (1) and Held et al. (2), extensive research has been conducted on hydrocarbon selective catalytic reduction (HC-SCR) of NO_x to N₂. While the early work focused on a range of metals and washcoat materials, recently the most progress has been made in studies of Ag/Al₂O₃ catalyst systems (3,4). In particular, work done by members of the EU KNOWNOX consortium has led to an advance in understanding of this reaction on silver (5). This research has shown that a wide range of hydrocarbons will react well on silver. Testing has included work with diesel fuel in diesel engine testing (6). However, in much of this work, high activity is often limited to temperatures above 350 °C. These catalysts perform much more poorly in the 150 °C to 300 °C range often found in the lean exhausts of diesel engines.

Studies in 1999 to 2000 have shown that small amounts of hydrogen in the feedstream improve the low temperature performance of silver-based HC-SCR catalysts (7,8). Since that time a great amount of the effort on Ag systems has focused on understanding the role of hydrogen. The enhancement by hydrogen appears to be limited to silver-based catalysts that are also supported on alumina or silica-alumina zeolites. In addition, the effect of hydrogen is reversible. Usually, H₂ impacts the reaction beneficially upon introduction, while under some conditions its benefits decay with a longer time constant upon its removal, indicating the possible storage of a surface species (9).

More recently Ag/Al₂O₃-based catalysts emerged as the most active catalysts in a high throughput study of more than 8,000 catalytic combinations for HC-SCR under diesel conditions (10, 11). Studies of these catalysts on

a bench reactor (10) and on an engine (11) showed the best conditions for their use.

The mechanism of the HC-SCR reaction in general, and the "hydrogen effect" in particular, has also been studied intensively. Many papers have explored the effect of silver particle size and the oxidation state of silver. Recent papers (9) have focused on the role of an NCO intermediate in the pathway of the reaction that leads to N_2 as well as other species, such as ammonia. That same pathway includes the transformation of an Ag^+CN species into the Ag-NCO species.

In actual use it has been noted, as mentioned above, that other nitrogen-containing species are formed over the silver catalyst during HC-SCR, species that may need to be removed from the exhaust. This issue has been addressed by Miyadera and others (12,13), who have used one or more catalysts to remove these species. A later study of a combined catalyst system by Arve et al. (14) also examined the effect of a second catalyst on improving low and high temperature NOx removal. One reaction that can remove ammonia-containing species is the selective catalytic reduction of NOx by ammonia. This is an extremely well studied reaction, particularly when the ammonia results from the thermolysis and hydrolysis of urea in commercial systems, the SCR reaction. This work has been reviewed in many locations and the reactions are well understood (15).

In recent work we have shown a combination of an Ag HC-SCR and an NH_3 -SCR catalyst (Dual SCR) can be controlled to improve on a HC-SCR catalyst alone (16). In bench reactor studies from 150 °C to 500 °C, we reported, for modest C/N ratios, that NOx reacts over the first catalyst to predominantly form nitrogen. In addition, it also forms ammonia in sufficient quantities to react on the second NH_3 -SCR catalyst to improve system performance. In this paper we have extended our work to measure NOx activity in lean exhaust from a single-cylinder engine using a range of possible fuels (diesel, dodecane, California Phase III gasoline, and E85) as reductants for HC-SCR. These test cell studies, supplemented with supporting bench reactor work, show that the Dual SCR approach works well in lean exhaust from an engine run in several operating modes.

REACTOR AND TEST CELL DESCRIPTION

Both a single cylinder diesel engine test cell and a bench reactor were used in our studies of the Dual SCR aftertreatment system. Most of the aspects of the bench gas reactor system employed for this emissions work have been described in earlier papers (16,17). The fuel handling reactor described there controls the quantity, vaporization, and gas phase mixing of the fossil or biofuels injected into the catalyst reactor. For this work, five different fuels were used for HC reduction of NOx over the Ag based catalysts. Four of the fuels were fossil based and included $C_{12}H_{26}$ (dodecane), C_8H_{18} (iso-octane), 2007 diesel cert fuel, and California Phase III gasoline [CAPIII]. The biofuel of interest here was E85

(85% ethanol combined with Howell EEE). With respect to the HC concentration, the objective was to keep constant the C_1 concentration of all the HC fuels so that a comparison of the fuels for supporting NOx reduction could be made. The fuels used as reductants in the testing are shown in Table 1 with several fuel properties.

	Paraf. (%)	Arom. (%)	Olef. (%)	Eth. (%)	S (ppm)
Cert Diesel	67.6	29.6	2.8	0	10
Dodecane	100	0	0	0	0
CA Ph III	62.5	25	5.8	6.7	17
E85	10	4	2	84	4
Iso-octane	100	0	0	0	0

Table 1. Fuels used as Hydrocarbon-SCR Reductants

The performance of the catalyst was examined in a test cell using these fuels (minus iso-octane). Figure 1 shows the apparatus used for this emissions work. Not shown in the schematic is the engine. That engine is a single cylinder diesel Hydra engine. The main function of the engine in this work was to supply the base level combustion products, gas flow, and base gas temperature for the feed to the aftertreatment system. In particular, the engine torque, and EGR were varied to supply catalyst test conditions that included NOx (100-800 ppm), HCs (0 ppm-3000 ppm), space velocity of 25-50 $K h^{-1}$, and supplemental gas temperature (200 - 500 °C). All these variables were controlled upstream of the surge tank. The gas analysis components included a hot FID analyzer, a Fourier Transform infrared spectrometer (FTIR), a H_2 mass spectrometer, and standard bench analyzers. After the surge tank, the combustion exhaust flow passed through a heat exchanger where the gas temperature was quickly stabilized at the value required. The gas then was mixed with the vaporized fuel of choice and injected hydrogen, if any. At this point, all the species of interest were present at the temperature and flow desired and passed through the catalyst system. Temperature and sampling were conducted at ports all along the treatment path so that conversion efficiencies and temperatures could be measured for the individual catalyst components as well as the overall system.

The catalyst samples for this study were proprietary formulations. The HC-SCR catalyst substrate was a silver-based alumina catalyst monolith for nitric oxide (NOx) reduction. In the bench reactor, this catalyst and the following NH_3 -SCR catalyst were separated by approximately 0.5" of quartz wool to physically keep the two catalysts apart. In the test cell, a space of roughly 12 inches separated the catalysts. The second catalyst, as mentioned, was a NH_3 -SCR catalyst using a Cu-zeolite-based monolith. In the test cell, activity data was generally taken as temperatures were raised between 150 °C and 550 °C with steady state data recorded at several temperatures between 200 °C and 500 °C to compare with temperatures found in light-duty lean burn engines. On the bench reactor, typical experiments included slowly ramping the catalyst down in temperature and monitoring its NOx products to obtain the NOx

reduction efficiency of the system under quasi steady state or isothermal conditions. Other experiments involved maintaining the catalyst or catalysts at a predefined temperature and measuring their response to different gas compositions. Catalyst cleaning, after long exposures to inlet gas feeds, was accomplished by heating the dual catalysts to 600 °C in the presence of 10% O₂ and 6% H₂O. The gas analysis components of this system include an FTIR and a chemical ionization

mass spectrometer (CIMS). Together, these analyzers provide quantitative data on a wide range of HC- and N-containing species so that a mass balance can be more accurately estimated. The system is capable of second-by-second analyses of gases both before and after the catalysts to obtain conversion efficiencies.

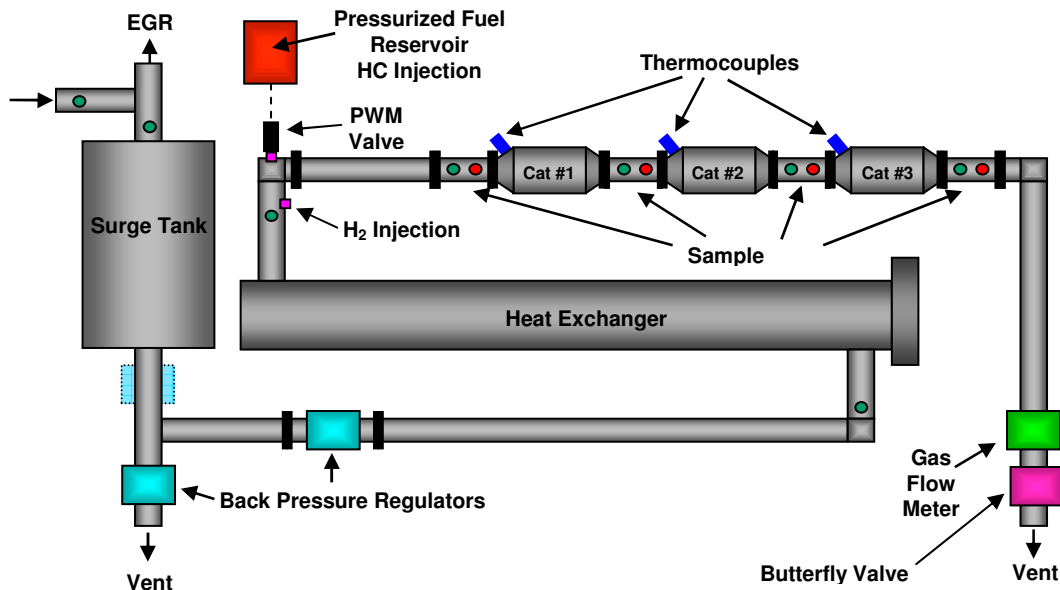


Fig 1. Test Cell Engine Emissions and Catalyst Characterization System

TEST CELL RESULTS: Ag HC SCR & DUAL SCR

A. Fuel Type and NO_x Reduction Activity

In today's vehicle market, tolerance of fuel type is essential for proper modern powertrains. Therefore, catalysts must also be able to respond to a variety of fuels used on vehicles. Ag-based catalysts show this kind of responsiveness. For the results obtained here, several items should be noted. First, all the exhaust species were generated by a single cylinder Hydra engine operated on diesel fuel, except for the injected fuel and H₂. Secondly, conditions here were chosen with 20% EGR to produce about 200 ppm NO and with a space velocity of 25 K h⁻¹. Oxygen and water

concentrations were the result of engine settings, but were nominally 8% O₂ and 8% H₂O. Fuel dosing levels upstream of the HC-SCR catalyst were set to achieve a 4/1 overall C/N ratio. Fuel flow was controlled and measured by an MKS mass flow controller, however, because larger HCs have proportionally more carbon atoms, that translated into fewer fuel molecules injected to achieve the same C/N ratio. For larger molecules, this led to some variability in fuel concentration due to proportionally smaller quantities injected and more error in fuel metering.

Figure 2 shows how effective the different fuel HCs are at reducing NO_x in the exhaust from the single cylinder engine (no injected H₂). As one can see in Figure 2, E85

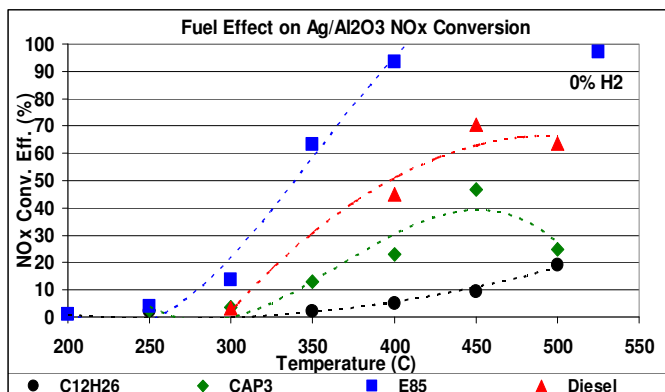


Fig. 2. Ag HC-SCR NO_x Reduction and Fuel Type. 27 K h⁻¹, 8% O₂, 200 ppm NO, 0% H₂, C/N=4/1, engine exhaust, injected fuel (total C₁ = exhaust + inj fuel).

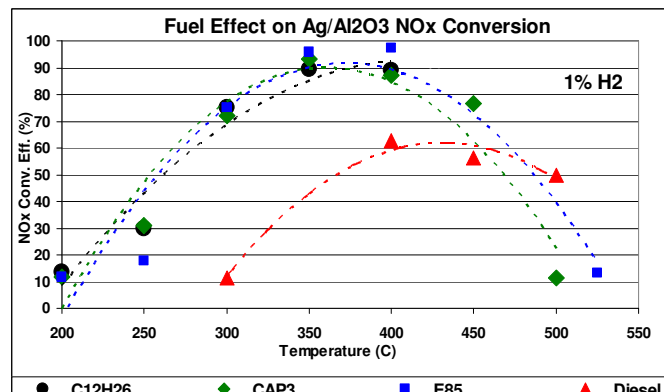


Fig. 3. Ag HC-SCR NO_x Reduction and Fuel Type. 27 K h⁻¹, 8% O₂, 200 ppm NO, 1% H₂, C/N=4/1, engine exhaust, injected fuel (total C₁ = exhaust + inj fuel).