

Control Strategy for the Removal of NO_x from Diesel Engine Exhaust using Hydrocarbon Selective Catalytic Reduction

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ABSTRACT

A unique catalyst developed using high-throughput discovery techniques in collaboration with BASF Corporation and Accelrys, Inc. was investigated at General Motors under simulated diesel engine exhaust feed conditions for the selective catalytic reduction of NO_x. A hydrocarbon mixture was used as the reductant to model the multi-component nature of diesel fuel and the catalyst was evaluated over a wide range of temperatures (150 – 550°C) relevant to light-duty diesel exhaust. This report investigates the effects of NO_x (as NO or NO₂), hydrocarbon concentration level (HC:NO_x ratio), oxygen concentration, NO concentration, catalyst space velocity, catalyst temperature, and the co-presence of hydrogen on steady-state NO_x reduction activity. Using these results, a control strategy was developed to maximize NO_x conversion over the wide-ranging exhaust conditions likely to be encountered in light-duty diesel applications.

INTRODUCTION

Compression ignition (diesel) and lean-burn spark ignition direct injection engines have the potential to significantly increase vehicle fuel economy and decrease CO₂ emissions. One of the major stumbling blocks in the commercial application of these engines in the United States is the lack of effective methods for the removal of nitrogen oxides (NO_x = NO + NO₂) under the lean-burn conditions. Relative to stoichiometric gasoline engines, when an engine operates with lean (excess oxygen) Air:Fuel ratio, the resultant combustion temperature is lower, leading to lower exhaust gas temperatures and decreased engine-out NO_x emissions. However, it is estimated that compliance with Bin 5 regulations in the United States may still require an aftertreatment system capable of 70% NO_x conversion efficiency on the FTP (Federal Test Procedure) cycle based on Bin 8 (0.2 g/mile) engine-out NO_x levels. Thus, for practical application, high conversion efficiency

of this pollutant must be obtained at the low operating temperature range (e.g., 200 - 350°C) of light-duty diesel exhaust during the FTP cycle and at the higher operating temperature range (e.g., 450 - 550°C) observed over the higher speed US06 test cycle.

Several potential aftertreatment candidates exist for vehicle applications, most notably urea-SCR (selective catalytic reduction) and NO_x storage catalysts; however, each of these methods is not without its own set of technical challenges. Urea-SCR comprises injecting urea as the NO_x reductant upstream of a urea-SCR catalyst to reduce NO_x to N₂. Use of urea as a reductant necessitates a urea distribution infrastructure as well as an on-vehicle storage and monitoring system for this secondary fluid, and may have potential problems in cold weather climates due to the relatively high freezing point (-12°C) of the urea solution. NO_x storage catalysts typically require large catalyst volumes, large amounts of expensive platinum-group metals and low sulfur fuel for efficient storage operation. Such systems require periodic catalyst regeneration involving fuel injection to generate high exhaust gas temperatures and injection of reductants to regenerate the storage material of the catalyst, thus requiring complex engine control.

The SCR of NO using hydrocarbons (HC-SCR) has been studied extensively as a potential alternative method for the removal of NO_x under oxygen-rich conditions [e.g., 1, 2]. Under diesel exhaust conditions ion-exchanged base metal zeolite catalysts (e.g., Cu-ZSM-5) are not active enough and are susceptible to degradation by sulfur dioxide and water exposure, while platinum-group metal catalysts (e.g., Pt/Al₂O₃) operate effectively over only a very narrow temperature window and are highly selective towards N₂O production. Recently, alumina supported silver (Ag/Al₂O₃) has received considerable attention because of its excellent ability to reduce NO_x selectively under lean exhaust conditions with a wide variety of hydrocarbon species. The use of partially oxidized hydrocarbons (e.g., alcohols, aldehydes) over Ag/Al₂O₃ and

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of NO_x at lower temperatures [3-8, 18-19]; however, the unavailability of such reductants on-board the vehicle is problematic. Many of the previous studies on HC-SCR over Ag/Al₂O₃ catalysts utilized light hydrocarbons (e.g., propene, propane) as the reductant [4-5, 9-16, 18-19], but these lighter hydrocarbons present in engine exhaust as combustion products yield NO_x conversion only at higher temperature. Several papers have examined heavier fuel-component hydrocarbons [16-25, 28] and diesel fuel [7-8, 18, 26], with the heavier hydrocarbons (e.g., decane) that are present in diesel fuel providing NO_x conversion at lower temperature. The addition of hydrogen to the feedstream also lowers the light-off temperature further for NO_x conversion over Ag/Al₂O₃ catalysts for both light (propane) [11-14] and heavy (octane, decane) hydrocarbons [20-25, 28]. Therefore, unlike urea-SCR systems, HC-SCR utilizes the fuel on board the vehicle as the NO_x reductant, and does not require the complex engine control and large amounts of expensive platinum-group metal catalysts employed in NO_x storage catalyst systems. In an effort to utilize the inherent advantages of HC-SCR, a Department of Energy (DOE) project was proposed and funded in August, 2002 for General Motors with subcontractors BASF Corporation and Accelrys, Inc. to develop and use high throughput techniques to evaluate a wide range of materials, supports, and preparation techniques to identify high activity HC-SCR catalysts. The catalyst evaluated here is one of the products of the program.

While the conversion efficiencies reported in the literature are commonly > 80% over various temperature ranges [17-18, 22], the adaptability of these results to the reduction of NO_x from light-duty diesel exhaust is difficult. Several factors are responsible for this, including (i) a focus on pure reductants such as lower alkanes, while diesel fuel contains many compounds, most notably aromatic compounds and longer chain alkanes, (ii) the testing utilized conditions not representative of modern light-duty diesel engines, e.g., NO_x levels of 1000 ppm, and (iii) the laboratory micro-reactors frequently employed powder catalysts rather than typical automotive cordierite monolith substrate supported catalysts, thereby making NO_x reduction performance comparisons at realistic space velocity difficult. In order to address many of these shortcomings in the literature, laboratory reactor measurements were performed over one of the discovery catalysts developed in this program supported on a cordierite monolith substrate under conditions of relevance to a modern light-duty diesel engine using an aromatic-containing simulated diesel fuel reductant. The preparation, loading, and coating on monolith cores for this work and the concurrent engine testing were optimized for the maximum NO_x conversion under engine-like conditions using the catalytic materials discovered in the DOE project.

In this paper, we report the NO_x reduction over Ag/Al₂O₃ catalysts in a laboratory flow reactor system using a simulated diesel fuel mixture at the temperatures, flow rates, and inlet NO_x concentrations likely to be

encountered by a HC-SCR catalyst system on a light-duty compression ignition direct injection (diesel) vehicle under the FTP, US06, and highway fuel economy test (HWYFET) schedules. Catalyst temperatures ranging from 150 - 550°C are relevant to this application, as well as the following ranges of gas phase concentrations that the catalyst could potentially be exposed to: O₂ (2 - 20%), NO_x (25 - 250 ppm), and H₂ (up to 8000 ppm supplied by either a partial oxidation fuel reformer or in-cylinder post-injection). In addition, exhaust flow rates ranging from 10 L per second at idle to 75 L per second under acceleration conditions can result in space velocities ranging from ~7,000 h⁻¹ to 54,000 h⁻¹ over a 5 L HC-SCR catalyst volume. The effects of space velocity, NO_x as NO or NO₂, and concentration effects of O₂, NO_x, H₂, and HC were evaluated as a function of catalyst inlet temperature. Based on this laboratory reactor data, general control strategy guidelines were developed that can be used to effectively maintain maximum NO_x reduction levels in a HC-SCR aftertreatment system under the wide-ranging exhaust conditions encountered in a diesel vehicle [30].

EXPERIMENTAL

CATALYST PREPARATION - The catalysts prepared for this project are based on proprietary approaches developed by BASF Corporation under the DOE program [31]. The washcoat containing the catalyst powder was supported on a 400 cell per square inch cordierite monolith substrate and hydro-thermally aged (air and 10% water at 650°C for 16 hours) prior to testing. A catalyst containing 2 wt.% Ag₂O/Al₂O₃ with a washcoat loading of 2.7 g/in³ was selected for the development of the HC-SCR control strategy. This catalyst was used as an example to demonstrate the proof of concept in the development of these general control strategy guidelines, and it is believed that many other Ag based catalysts would benefit from the guidelines developed here.

EXPERIMENTAL SET-UP - Experiments were performed in a laboratory fixed-bed flow reactor system. The catalyst volume was ~14.5 cm³ (sample size ~ 0.75 in. diameter by 2.0 in. length) resulting in a catalyst space velocity (SV) of 12,500 h⁻¹ at 3 L/min (STP) gas flow rate. The higher space velocities of 25,000, 50,000, and 75,000 h⁻¹ were obtained by varying the gas flow rate (3, 6, and 9 L/min), and decreasing the catalyst volume (sample size ~ 0.75 in. diameter by 1.0 in. length ~7.25 cm³). The catalyst was placed inside a 22 mm id quartz tube, and the portion of the tube containing the sample was surrounded by an insulating material and positioned outside the heated zone of the furnace so that catalyst heating occurs through the gas in a manner similar to heat transfer in an automotive catalytic converter. Hollow quartz tubes located inside the heated zone of the furnace facilitates heat transfer to the gas feed stream. The reaction temperature reported here was measured using a chromel-alumel thermocouple located approximately 1 mm upstream of the catalyst bed ("catalyst inlet temperature"). Dependent on the gas

flow rate, the temperature gradient across the catalyst bed ranged from ~4 - 20°C at an inlet temperature of 150°C to ~30 - 100°C at an inlet temperature of 550°C. In general, the lower the gas flow rate, the larger the temperature gradient across the catalyst.

Simulated light-duty diesel exhaust gas was introduced using a series of computer controlled mass flow controllers connected to individual gas cylinders of known composition. Water was introduced using a metering pump, which delivered a constant volume of water to a wick located in a heated (165°C) stainless steel tube. As the reactant feed stream passed over the wick, uniform vaporization of the H₂O occurred. A syringe pump and wick were used to vaporize the liquid hydrocarbons in a similar manner. Heated Teflon tubing (165°C) was used to prevent the condensation of components in the lines prior to analysis. A Nicolet Instruments Nexus 670 Fourier transform infrared spectrometer (FTIR) with a 2 m gas analysis cell heated to 165°C was used for gas-phase analysis. Data was signal averaged using 16 scans at 0.5 cm⁻¹ resolution.

The standard simulated exhaust gas feed stream consisted of 10% O₂, 5% H₂O, 5% CO₂, 750 ppm CO, and 250 ppm H₂, with varying concentrations of NO_x and HC (reported in ppmC₁ or ppm based on atomic mass) in a N₂ background. NO_x conversion is defined as:

$$\text{NO}_x \text{ conversion} = [(^{\text{in}}\text{NO}_x - ^{\text{out}}\text{NO}_x) / ^{\text{in}}\text{NO}_x] \times 100 \quad (1)$$

For a typical measurement, the catalyst was heated to the desired temperature under a flow of 10% O₂, 5% H₂O, 5% CO₂, 750 ppm CO, 250 ppm H₂, and either NO or NO₂. Once the NO_x value stabilized to the desired inlet NO_x concentration, the hydrocarbon was introduced. The temperature of the catalyst was then increased in 50°C increments between 150 and 550°C while measuring the gas-phase species at the reactor exit under steady-state conditions.

Table 1 lists the hydrocarbon compounds used as reductants in this study. Characteristic properties for diesel fuel include a typical formula of C₁₄H₂₅, a carbon range of C9 - C25, and boiling points of ~175 - 350°C. Volumetric mixtures of saturated and aromatic hydrocarbons were evaluated in order to represent the multi-component nature of diesel fuel. The compositions used for the simulated fuels were obtained from the General Motors Global Diesel Database, with the aromatic and poly-aromatic fractions selected based on the maximum volumetric percentages found in the database. Eränen *et al.* [18] show similar NO_x conversions with n-dodecane and Swedish MK1 diesel fuel (low sulfur < 10 ppm, low aromatics < 5 vol.%) over 2 wt.% Ag/Al₂O₃. This is not surprising considering MK1 diesel fuel is predominantly long-chain saturated alkanes with very low aromatic content. However, diesel fuel in the United States may contain a much higher fraction of aromatics; therefore, the simulated diesel fuel #1 prepared here consists of an aromatic component, m-xylene, along with a long-chain saturated alkane, n-

dodecane. Since poly-aromatics can also be present in diesel fuels, simulated diesel fuel #2 was prepared which contains n-dodecane, m-xylene, and naphthalene, a poly-aromatic component.

Table 1. Hydrocarbon reductants used in this study.

Reductant	Composition
n-octane	100 vol.% n-C ₈ H ₁₈
n-dodecane	100 vol.% n-C ₁₂ H ₂₆
sim-diesel #1	67 vol.% n-dodecane 33 vol.% m-xylene
sim-diesel #2	67 vol.% n-dodecane 23 vol.% m-xylene 10 vol.% naphthalene

RESULTS AND DISCUSSION

EFFECT OF HYDROCARBON REDUCTANT TYPE - Figure 1 shows the NO_x conversion as a function of temperature at a fixed HC:NO_x ratio of 8 for four different hydrocarbon reductants: n-octane (n-C₈H₁₈), n-dodecane (n-C₁₂H₂₆), sim-diesel #1, and sim-diesel #2. Previous work [28] has shown that the type of hydrocarbon used as the reductant can strongly influence NO_x reduction performance. In general, increasing the number of C atoms of the long-chain hydrocarbon enhances de-NO_x performance by both improving the light-off temperature (T_{50%}, defined as the temperature at which 50% NO_x conversion occurs) and increasing the maximum NO_x conversion [15-16, 18-19, 28]. In addition, both branching HC's and aromatic HC's are less active reductants for the removal of NO_x [16, 18-19, 28]. The n-dodecane shows very similar performance to n-octane, with only a slightly lower light-off temperature (~10°C) for the dodecane due to the higher carbon number. It has been proposed that hydrocarbon activation is a key step for the NO reduction activity on Ag/Al₂O₃ and that NO_x is reduced by reaction with the partially oxidized HC intermediates that are formed from the reductant [11, 14-17, 20-21, 23-25]. The greater enthalpy of adsorption of the longer chains and the weaker C-H bond strength of their methylene group probably explains their ability to form these reactive intermediates at lower temperatures [2]. This also probably explains why there is very little difference in activity between octane (C₈) and dodecane (C₁₂), as the C-H bond strength becomes indistinguishable at extremely long chain lengths. The simulated diesel fuel #1 shows a higher light-off temperature (~45°C) than n-dodecane, probably due to the higher light-off temperature of the other component, m-xylene [28].

Also, note that the simulated diesel fuel #1 shows lower maximum activity than pure dodecane due to the lower activity of the aromatic component, m-xylene. When a

poly-aromatic compound is added into simulated diesel fuel #2, the light-off temperature is increased even further, suggesting that the fuel composition (i.e., aromatic fraction, HC chain length, other fuel components, etc.) may play an important role in determining overall catalyst performance under actual vehicle conditions. Simulated diesel fuel #1 was selected as the baseline fuel to be used as the reductant for the conversion of NO_x for the control strategy development discussed in the following sections.

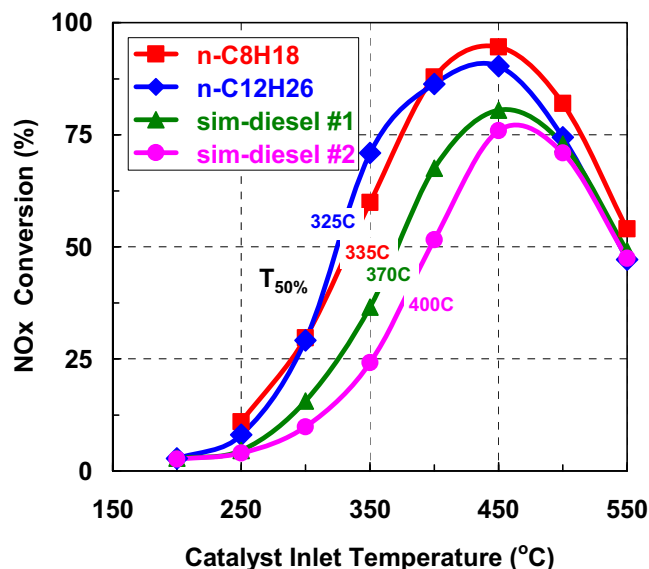


Figure 1. NO_x conversion at 50,000 h⁻¹ using several different HC reductants (HC₁:NO_x ~8). Inlet gas feed stream contains 10% O₂, 5% H₂O, 5% CO₂, 750 ppm CO, 250 ppm H₂, and 250 ppm NO.

INFLUENCE OF CATALYST SPACE VELOCITY - Catalyst performance under the varying flow conditions encountered on the FTP cycle has important automotive packaging implications since it determines the catalyst volume necessary to meet the required emission standards. Figure 2 shows the influence of catalyst space velocity (SV, volumetric gas flow rate in cm³/h divided by catalyst volume in cm³) on NO_x conversion as a function of catalyst temperature for the reaction of NO and sim-diesel #1 (HC₁:NO_x ~8). The catalyst performance is strongly impacted by the catalyst space velocity, with the light-off temperature increasing from 305°C to 435°C and the maximum NO_x conversion decreasing from 98% to 59% as the space velocity increases from 12,500 to 75,000 h⁻¹. The decline in NO_x conversion over Ag/Al₂O₃ with increasing SV has been shown to be much more pronounced at lower temperatures (350°C compared to 450°C) using n-octane as the reductant [16], with propane-SCR [11] and dodecane-SCR [18] showing nearly linear declines in catalyst efficiency as a function of space velocity. The strong space velocity dependence has been proposed to be due to the extremely slow reaction of NO and HC oxidation, considered a key step in the formation of important intermediates, which leads to the long residence time required for efficient NO_x conversion [20]. The SV effect is also observed for NO conversion using

partially oxidized HC's (ethanol, formaldehyde) as reductants [3, 5, 8]. This result using simulated diesel fuel as reductant provides useful guidance in the selection of the "correct" catalyst volume based on the anticipated exhaust flow rate, temperature range, and desired conversion level of a particular vehicle application.

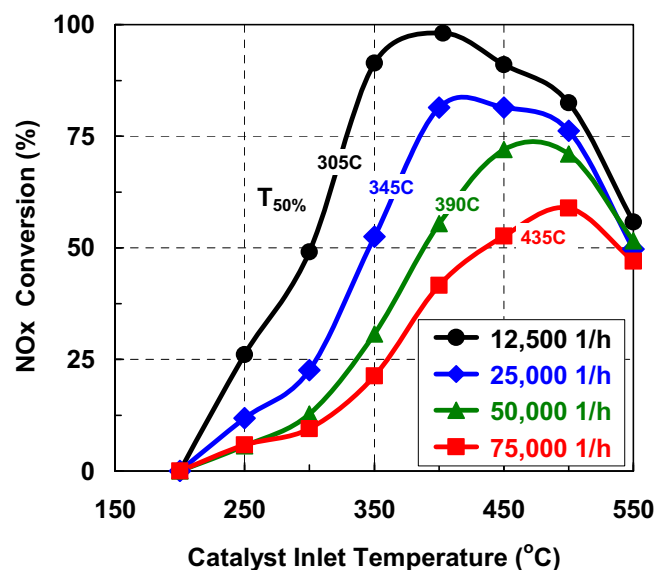


Figure 2. NO_x conversion as a function of space velocity using 187 ppm sim-diesel #1 as reductant (HC₁:NO_x ~8). Inlet gas feed stream contains 10% O₂, 5% H₂O, 5% CO₂, 750 ppm CO, 250 ppm H₂, and 250 ppm NO.

IMPACT OF HC₁:NO_x RATIO, OXYGEN, NO_x AS NO OR NO₂, AND HYDROGEN UNDER HIGH SPACE VELOCITY CONDITIONS - In order to determine the control strategy required for improving NO_x conversion under high space velocity (i.e., high exhaust gas flow rate) conditions, the catalyst was further evaluated at 50,000 h⁻¹. Figure 3 shows the effect of increasing the HC₁:NO_x ratio from 2 to 12 with 250 ppm NO in the feed stream. The peak NO_x conversion becomes higher and shifts to higher temperature as the HC concentration increases; however, there is little effect on the light-off temperature. Note that little benefit is gained at temperatures below 350°C by increasing the HC₁:NO_x ratio above 2 - 4, and doing so can result in lower conversion levels. This decline may be due to competitive adsorption between the HC and the NO_x or to the poisoning effect caused by carbonaceous deposits [16-17] formed by excess amounts of long chain saturated hydrocarbons. In the temperature range between 350 and 450°C, higher HC amounts are required (HC₁:NO_x ~ 6 - 8) to reach peak NO_x conversion. Due to the competing hydrocarbon oxidation reaction, HC₁:NO_x ratios greater than 12 will be required at temperatures above 450°C. The non-selective combustion of the reducing agent with O₂ becomes much faster than the SCR at elevated temperatures [2], leading to the decreasing availability of reductant for the formation of reactive intermediate species, thereby impeding NO_x reduction [15].