

Catalysts for Lean-Burn Engine Exhaust Aftertreatment Using Hydrocarbon Selective Catalytic Reduction

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ABSTRACT

Unique silver/alumina catalysts developed in collaboration with BASF Corporation were investigated at General Motors under simulated lean-burn engine exhaust feed conditions for the selective catalytic reduction of NO_x using hydrocarbons as reductant (HC-SCR). Catalysts were evaluated using a laboratory fixed-bed flow reactor system over a wide range of temperatures relevant to light-duty and heavy-duty exhaust conditions for CIDI (compression ignition direct injection – diesel) and SIDI (spark ignition direct injection – gasoline) applications. This report investigates the effects of silver content (i.e., wt.% Ag₂O) and reductant composition (i.e., simulated diesel fuel, simulated gasoline, ethanol, and ethanol/simulated gasoline mixtures) on the steady-state NO_x reduction activity. A dual catalyst approach using a HC-SCR catalyst followed by an NH₃-SCR catalyst was also investigated. Stochastic Process Modeling was used to determine the optimum in-exhaust injection strategy using ethanol and simulated gasoline as reductants during the New European Driving Cycle.

INTRODUCTION

Compression ignition direct injection (CIDI – diesel) and lean-burn spark ignition direct injection (SIDI – gasoline) 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 is the lack of effective and affordable methods for the removal of nitrogen oxides (NO_x = NO + NO₂) under the lean-burn conditions. Since lean-burn engines operate with excess oxygen, it

is not possible to sufficiently reduce NO_x in the exhaust with the traditional three-way catalyst (TWC) used for stoichiometric gasoline engines.

Lean-burn exhaust catalyst systems must typically provide extremely high NO_x conversion efficiency (>90%) over a wide temperature window (200-550°C) to be considered as potential aftertreatment candidates for vehicle applications. The reduction of NO_x at low temperature (200°C) is of particular importance for meeting stringent future emission standards. Several technologies already exist, most notably urea-SCR 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, using NH₃ 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 (PGM) 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_x 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., 1-3]. 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 PGM-containing 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 [4]. Many previous studies on HC-SCR over Ag-Al₂O₃ catalysts utilized light hydrocarbons (e.g., propene, propane) as the reductant [5-7], but these lighter hydrocarbons present in engine exhaust as partial combustion products typically only yield conversion at temperatures above 400°C. The large branched-chain alkanes, alkenes, and aromatics found in gasoline also only provide NO_x conversion at higher temperature [7-10]. On the other hand, heavier straight long-chain alkanes (e.g., n-decane) that are present in diesel fuel have been shown to provide NO_x conversion at lower temperatures [10-14]. The addition of hydrogen to the feedstream also lowers the light-off temperature ($T_{50\%}$, defined as the temperature at which 50% NO_x conversion occurs) further for NO_x conversion over Ag-Al₂O₃ catalysts for both light and heavy hydrocarbons [4-6, 8-13]. Other advantages have also been reported for supplemental hydrogen, including improved catalyst tolerance to sulfur in the exhaust feedstream [4, 6, 18] and improved catalyst performance as a function of increased space velocity [6, 12]. However, this method of promoting the low temperature performance would require a means of generating the hydrogen on-board the vehicle (e.g., partial oxidation fuel reformer), thus adding additional cost and complexity to the aftertreatment system. The use of partially oxidized hydrocarbons (e.g., alcohols) over Ag-Al₂O₃ also allows the reduction of NO_x at lower temperatures [7, 15-18]. With the introduction of E85 (70-85% ethanol/gasoline mixture) at the fuel pump for many General Motors (and other automotive manufacturers) gasoline-fueled vehicles, it becomes possible to utilize this fuel as a potential NO_x reductant for lean-burn gasoline-fueled vehicles. Therefore, unlike urea-SCR systems, HC-SCR has the advantage of utilizing the fuel on-board the vehicle as the NO_x reductant, and does not require the complex engine control and large amounts of expensive PGM employed in NO_x storage catalyst systems.

In an effort to utilize the inherent advantages of HC-SCR, a high risk 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 [19] to evaluate a wide range of materials, supports, and preparation techniques to identify high activity HC-SCR catalysts. The catalysts evaluated here are some of the products of the program.

Previous work has shown promising results over 2.0 wt.% Ag₂O-Al₂O₃ catalysts in both laboratory reactor testing using simulated diesel fuel as reductant [11] and dynamometer testing on a light-duty 4.9 L diesel engine using ultra low sulfur diesel fuel as reductant [14]. Based on the 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 light-duty diesel vehicle [20]. Emission tests on the 4.9 L diesel engine employing conventional combustion technology and using 20 L of SCR catalyst volume with no added hydrogen or oxygenated hydrocarbons resulted in 92% NO_x conversion for the highway fuel economy test cycle (HWYFET), 76% conversion for the US06 test cycle, and 60% conversion for a FTP75 test cycle with a rudimentary cold-start heat strategy [14]. Based on these initial promising results of the HC-SCR technology additional testing was planned on both an 2.2 L SIDI lean-burn gasoline engine tested over the New European Driving Cycle (NEDC) and a 6.6 L Duramax diesel engine tested over the United States heavy-duty test cycles (HDFTP and 13-Mode SET). The results from the engine dynamometer evaluations will be published separately. As a prelude to the engine testing, laboratory reactor work was undertaken to determine the optimum catalyst formulations and control strategy guidelines for each of these potential applications. In this paper, we report NO_x reduction over numerous Ag-Al₂O₃ catalysts in a laboratory flow reactor system using simulated fuel mixtures (i.e., diesel fuel, gasoline, ethanol, and ethanol/gasoline) as the reductant, at the temperatures, flow rates, and inlet NO_x concentrations likely to be encountered by a HC-SCR catalyst system on both light-duty and heavy-duty vehicles. While not discussed in this work, future publications will include aspects of thermal durability, sulfur tolerance, and hydrocarbon deactivation.

EXPERIMENTAL

CATALYST PREPARATION - The silver catalysts supported on alumina (Ag₂O-Al₂O₃) prepared for this project are based on proprietary approaches developed by BASF Corporation under the DOE program [21]. 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. The temperature of 650°C correlates to typical diesel particulate filter (DPF) regeneration temperatures on a vehicle. The time of 16 h is based on some internal catalyst aging work conducted at the GM R&D Center. 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, volumetric gas flow rate in cm³/h divided by catalyst volume in cm³) of 12,750 h⁻¹ at 3 L/min (STP) gas flow rate and 25,500 h⁻¹ at 6 L/min (STP) gas flow rate.



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EXPERIMENTAL SET-UP - Experiments were performed in a laboratory fixed-bed flow reactor system described previously [11]. The typical simulated exhaust gas feedstreams are listed in Table 1 and consisted of O₂, H₂O, CO₂, CO, H₂, NO, and hydrocarbon (HC reported in ppmC₁ or ppm based on atomic mass) in a N₂ background. Two different standard feedstreams were used to represent a light-duty (low SV / high %O₂ / low ppm NO) and a heavy-duty (high SV / low %O₂ / high ppm NO) application. Table 2 lists the hydrocarbon compounds used as reductants in this study. Volumetric mixtures of saturated and aromatic hydrocarbons were evaluated in order to represent the multi-component nature of diesel fuel. Volumetric mixtures of branched, saturated, unsaturated, and aromatic hydrocarbons were evaluated in order to represent the multi-component nature of gasoline. The compositions used for the simulated fuels were obtained from the General Motors Global Diesel Database and the General Motors Global Gasoline Database, with the fractions selected based on the maximum volumetric percentages of each hydrocarbon type (i.e., branched, saturated, unsaturated, aromatic) found in the database.

Table 1. Simulated feedstreams used in this study.

Light-Duty Test Conditions	Heavy-Duty Test Conditions
10% O ₂ , 5% H ₂ O, 5% CO ₂ , 750 ppm CO 250 ppm H ₂ , 100 ppm NO HC ₁ :NO _x ratio ~ 8.5 SV ~ 12,750 h ⁻¹	6% O ₂ , 5% H ₂ O, 5% CO ₂ , 750 ppm CO 250 ppm H ₂ , 400 ppm NO HC ₁ :NO _x ratio ~ 8.5 SV ~ 25,500 h ⁻¹

Table 2. Hydrocarbon reductants used in this study.

Reductant	Composition
simulated diesel (sim-diesel)	67 vol.% n-dodecane 33 vol.% m-xylene
simulated gasoline (sim-gasoline)	45 vol.% iso-octane 12 vol.% 1-octene 10 vol.% n-octane 33 vol.% m-xylene
ethanol	100% vol.% ethanol
ethanol / sim-gasoline mixtures	0% vol.% / 100 vol.% 10% vol.% / 90 vol.% 20% vol.% / 80 vol.% 50% vol.% / 50 vol.% 85% vol.% / 15 vol.% 100% vol.% / 0 vol.%

For a typical measurement, the catalyst was heated to the desired temperature under a flow of O₂, H₂O, CO₂, CO, H₂, and NO. Once the NO value stabilized to the desired inlet 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. The NO_x conversion is defined as:

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

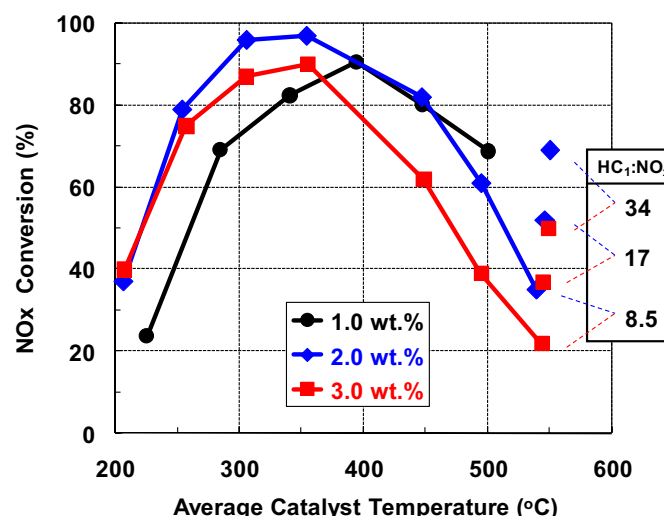


Figure 1. NO_x conversion over 1.0-3.0 wt.% Ag₂O-Al₂O₃ under light-duty test conditions with simulated diesel fuel as reductant (HC₁:NO_x ~ 8.5).

RESULTS AND DISCUSSION

NO_x CONVERSION USING SIMULATED DIESEL FUEL AS REDUCTANT - Supported catalysts ranging from 2-4 wt.% Ag₂O have been shown to be the most effective for low temperature NO_x removal [3, 4]. Using simulated diesel fuel as reductant, Figure 1 demonstrates that Ag loadings around 2 wt.% Ag₂O enhance the low temperature NO_x reduction under conditions representative of a light-duty (low SV / high %O₂ / low ppm NO / HC₁:NO_x ~ 8.5) diesel application. Hence, this catalyst formulation was utilized for the previous laboratory reactor control strategy development and dynamometer emission testing for a light-duty application [11, 14]. Lower Ag loadings are shown to provide greater NO_x reduction at temperatures above 450°C, but lower conversion efficiency below 400°C. Higher Ag loadings show little effect on the low temperature performance, however, above 250°C oxidation of the HC reductant limits the higher temperature conversion. This figure shows the typical volcano-type shape of the NO_x conversion, with the high temperature fall-off in performance attributable to the competitive reactions between NO and O₂ for the reductant [2]. The unselective combustion of the reductant to CO and CO₂ at higher temperatures lowers the amount of reductant molecules available for the SCR reaction. The limitation in the low temperature light-off has been attributed to the activation or partial oxidation of the hydrocarbon reductant, thus the better low temperature performance observed in the literature for oxygenated reductants such as ethanol [4, 7, 15-18]. The deficiency in the high temperature regime can be

overcome by injecting additional HC reductant, however, this results in a greater fuel economy penalty. The NO_x conversion efficiency at 550°C can be improved from 35% to 69% over the 2.0 wt.% Ag catalyst by increasing the $\text{HC}_1:\text{NO}_x$ ratio from 8.5 to 34. Note that the 3.0 wt.% Ag catalyst requires more hydrocarbon than the 2.0 wt.% Ag catalyst to maintain the same NO_x conversion level at high temperature. This is presumably due to the greater ability of the higher loaded Ag catalyst to oxidize the reductant.

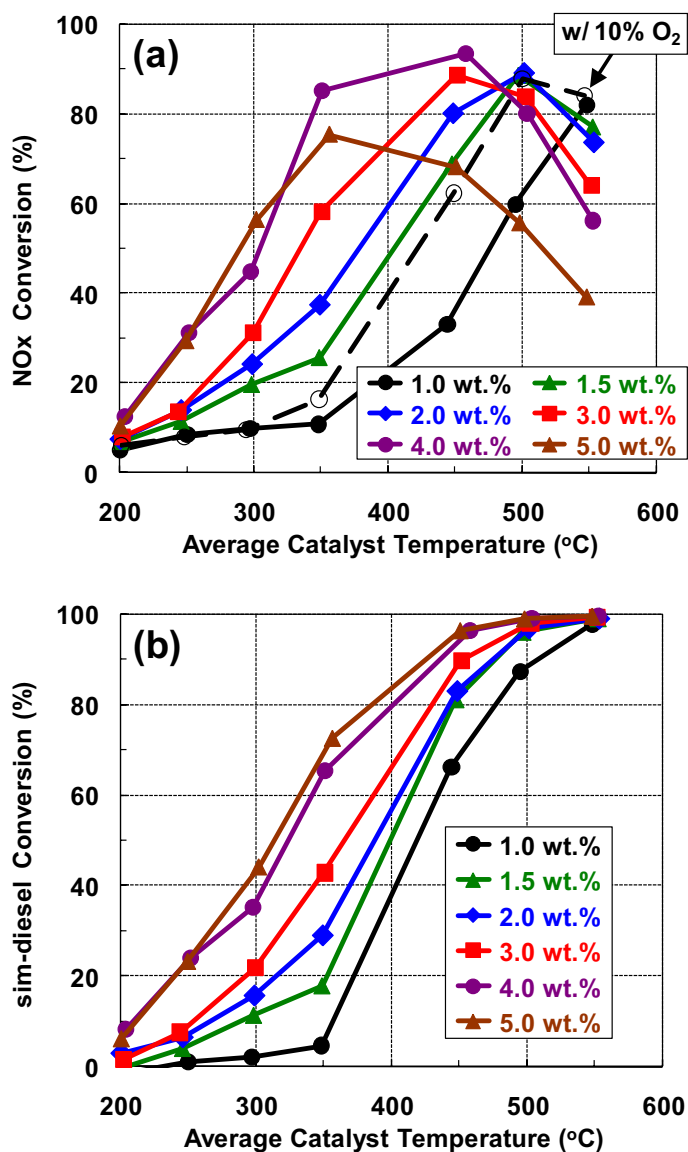


Figure 2. (a) NO_x conversion and (b) simulated diesel fuel conversion over 1.0-5.0 wt.% $\text{Ag}_2\text{O}-\text{Al}_2\text{O}_3$ under heavy-duty test conditions with simulated diesel fuel as reductant ($\text{HC}_1:\text{NO}_x \sim 8.5$).

The optimum Ag loading under heavy-duty (high SV / low $\%\text{O}_2$ / high ppm NO / $\text{HC}_1:\text{NO}_x \sim 8.5$) conditions shown in Figure 2 is quite different than that found under the light-duty conditions. Figure 2a indicates the

light-off temperature decreases substantially from 475°C to 300°C with a peak NO_x conversion of approximately 90% as the loading is increased from 1.0 wt.% to 4.0 wt.% Ag_2O ; however, at the highest loading of 5.0 wt.% Ag_2O the peak NO_x conversion efficiency declines below 80%, thus making the 4.0 wt.% $\text{Ag}_2\text{O}-\text{Al}_2\text{O}_3$ catalyst the optimum selection for heavy-duty diesel applications. Also shown on this graph is the impact of oxygen concentration over the 1.0 wt.% catalyst. As stated previously, it has been proposed that hydrocarbon activation is a key step for the NO reduction activity on $\text{Ag}-\text{Al}_2\text{O}_3$ and that NO_x is reduced by reaction with the partially oxidized HC intermediates that are formed from the reductant [4]. Hence, increasing the O_2 concentration from 6% to 10% presumably increases the formation of the partially oxidized HC intermediates which improves the NO_x conversion efficiency. The conversion of the simulated diesel fuel reductant is shown in Figure 2b. The light-off performance for the HC and the NO_x is similar, with greater than 90% HC conversion at peak NO_x conversion for the 1.0-4.0 wt.% Ag_2O catalysts. However, at temperatures below peak NO_x conversion efficiency HC breakthrough occurs, thereby requiring a downstream diesel oxidation catalyst for hydrocarbon clean-up. Figure 3 shows a direct comparison between the light-duty (with 2.0 wt.% Ag_2O) and the heavy-duty (with 4.0 wt.% Ag_2O) conditions using the optimal Ag loading for each application. It appears that higher loaded Ag catalysts have more capacity to oxidize hydrocarbons [4]. Additionally, higher O_2 concentrations are required to maintain high NO_x conversion levels, particularly as the space velocity increases [11, 14]. Hence, the higher Ag loading of 4.0 wt.% required for a heavy-duty application under higher SV / lower $\%\text{O}_2$ conditions.

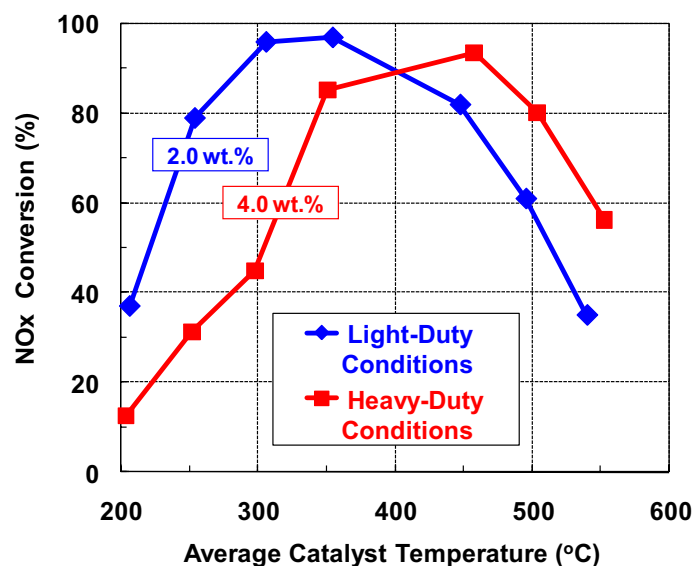


Figure 3. NO_x conversion under light-duty (2.0 wt.% $\text{Ag}_2\text{O}-\text{Al}_2\text{O}_3$) and heavy-duty (4.0 wt.% $\text{Ag}_2\text{O}-\text{Al}_2\text{O}_3$) test conditions with simulated diesel fuel as reductant ($\text{HC}_1:\text{NO}_x \sim 8.5$).

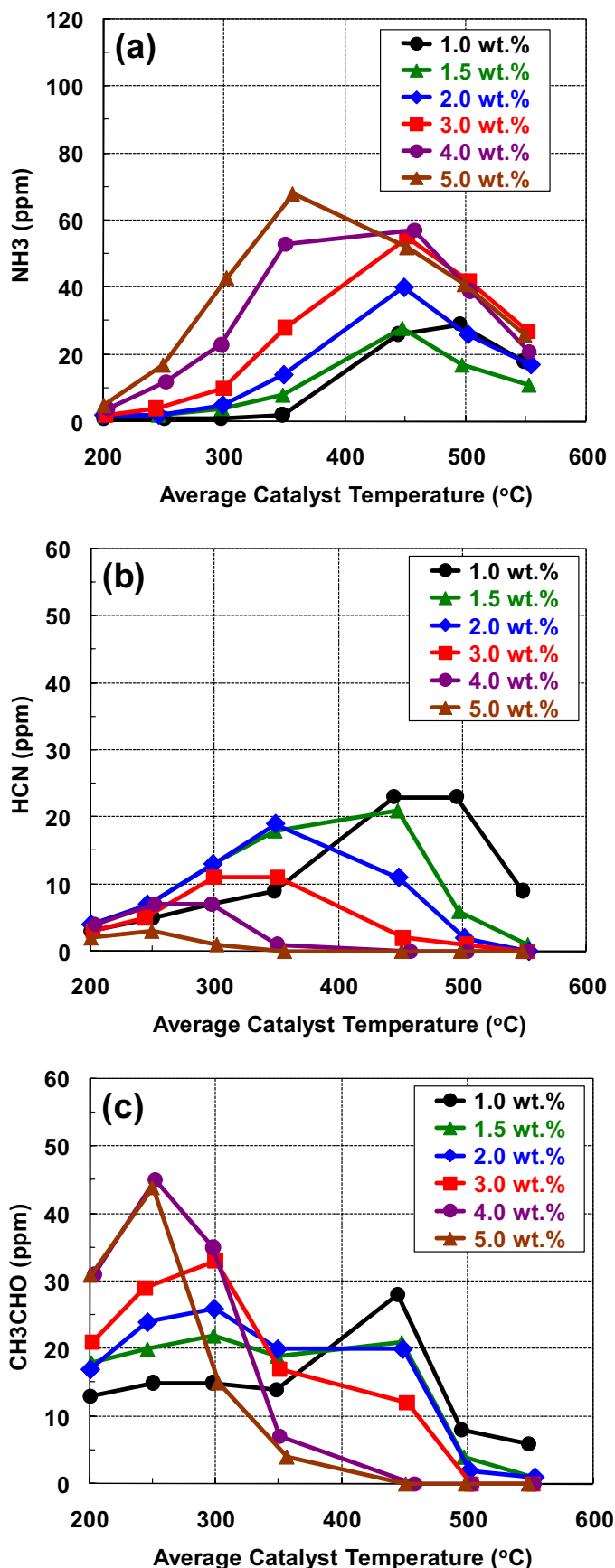


Figure 4. (a) NH₃, (b) HCN, and (c) CH₃CHO produced over 1.0-5.0 wt.% Ag₂O-Al₂O₃ under heavy-duty test conditions with simulated diesel fuel as reductant (HC₁:NO_x ~ 8.5).

While it is extremely important that high NO_x conversion efficiency be maintained over a wide temperature window, it is also equally important that there be limited formation of undesired species during the reaction. Figure 4 shows the formation of ammonia (NH₃, Fig. 4a), hydrogen cyanide (HCN, Fig. 4b), and acetaldehyde (CH₃CHO, Fig. 4c) as a function of Ag loading under the heavy-duty test conditions. As the Ag loading increases the formation of NH₃ increases as well, with approximately 14% of the NO being converted to NH₃ over the optimum 4.0 wt.% Ag₂O-Al₂O₃ catalyst between 350-450°C. On the other hand, less than 2% of the NO is converted to N₂O (data not shown) across the entire temperature window of 200-550°C, and while some HCN is formed at the lower Ag loadings (~5% of NO), virtually none is formed at the optimum 4.0 wt.% loading. At 250°C approximately 45 ppm CH₃CHO (~3% injected HC on C₁ basis) is formed over the 4.0 wt.% Ag₂O-Al₂O₃ catalyst, but this undesired partial oxidation byproduct can be minimized by lowering the HC injection amount from that used here (HC₁:NO_x ~ 8.5). Injection of diesel fuel reductant into an actual exhaust system at temperatures below 300°C is in any event extremely difficult due to the high boiling point (B.P.) of the many constituents in the fuel (e.g., at 300°C about 20% of the average diesel fuel has not evaporated, source = GM Global Diesel Database). Therefore, NO_x conversion below 300°C using diesel fuel as reductant is limited for both light-duty and heavy-duty applications. This major drawback thereby makes HC-SCR using diesel fuel as reductant non-competitive with the urea-SCR aftertreatment system which can provide substantial conversion efficiency at temperatures as low as 200°C.

NO_x CONVERSION USING ETHANOL AS REDUCTANT - The selective catalytic reduction of NO_x using ethanol as the reductant has been shown in the literature to greatly enhance the low temperature NO_x reduction activity [4, 7, 15-18]. Unlike diesel fuel reductant, ethanol can easily be injected into an exhaust system at temperatures below 300°C (B.P. ~ 79°C). However, if utilized as NO_x reductant for a diesel-fueled vehicle, a separate tank would be needed similar to that required for the urea-SCR aftertreatment system. Figure 5 shows the NO_x conversion efficiency under the heavy-duty test conditions at HC₁:NO_x ~ 8.5 as a function of Ag₂O loading. NO_x conversion at 300°C continues to increase to approximately 100% as the Ag₂O loading increases from 1.0 wt.% to 4.0 wt.%, with 5.0 wt.% showing a decline in conversion efficiency to 81%. At temperatures below 300°C only marginal improvement in performance is observed at greater than 3.0 wt. Ag₂O. At 550°C, however, the conversion efficiency continues to decline as the Ag₂O loading increases due to the increased oxidation of the ethanol. Therefore, the optimum loading for ethanol-SCR under the heavy-duty test conditions is 3.0 wt.% Ag₂O-Al₂O₃.