

Aspects of HC-SCR Catalyst Durability for Lean-Burn Engine Exhaust Aftertreatment

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ABSTRACT

Unique silver/alumina ($\text{Ag-Al}_2\text{O}_3$) catalysts developed using high-throughput discovery techniques 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 (HC-SCR). Hydrocarbon mixtures were used as the reductant to model the multi-component nature of diesel fuel and gasoline. Previous work has shown promising HC-SCR results in both laboratory reactor and engine dynamometer testing. This report investigates several aspects of HC-SCR catalyst durability, including thermal durability, sulfur tolerance, and hydrocarbon deactivation. Results from this laboratory reactor work provide the basis for the development of general guidelines that can be used to maintain maximum NO_x reduction by controlling the maximum catalyst thermal exposure, providing suitable sulfur regeneration conditions, and determining the appropriate catalyst formulation to mitigate low temperature hydrocarbon poisoning.

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. However, commercial application of these engines requires effective and affordable methods for the removal of nitrogen oxides (NO_x, comprising NO and NO₂) under the lean-burn conditions. 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. In addition, for an emission control

system to be commercially viable, the fuel economy penalty for the system must be low enough (< 2-3%) not to compromise the fuel economy benefit gained using the lean-burn engine technology. 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. Several technologies already exist, most notably urea-SCR and NO_x storage catalysts; yet 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, liberating NH₃ to reduce NO_x to N₂. Use of urea as a reductant necessitates urea distribution infrastructure as well as on-vehicle storage and monitoring of this secondary fluid, and may have potential problems in cold weather climates due to freezing 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 catalyst storage material, 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, 2, 3]. 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. Recently, alumina supported silver ($\text{Ag-Al}_2\text{O}_3$) 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]. In an effort to utilize the inherent advantages of HC-SCR, a high risk Department of Energy (DOE) project was funded for

General Motors with subcontractors BASF Corporation and Accelrys, Inc. to develop and use high-throughput techniques [5] 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 HC-SCR results in both laboratory reactor [6, 7] and engine dynamometer testing [8, 9]. Laboratory reactor findings have been utilized to determine the optimum catalyst formulations and the HC injection control strategies necessary for various applications. Results show that NO_x conversion is significantly reduced under high space velocity conditions, with key enablers for maintaining high conversion levels involving sustaining high inlet oxygen concentration, low inlet NO_x concentration, optimal fuel dosing, and the addition of supplemental hydrogen. Sufficient catalyst volume lessens the low temperature requirement of supplemental H₂ injection and sustaining high O₂ concentration levels. When using simulated diesel fuel as the reductant, heavy-duty CIDI applications with higher exhaust gas flow rates and lower O₂ concentrations require higher Ag loadings (4.0 wt.% Ag₂O-Al₂O₃), while light-duty CIDI applications with lower exhaust gas flow rates and higher O₂ concentrations require lower Ag loadings (2.0 wt.% Ag₂O-Al₂O₃). Heavy-duty CIDI applications using ethanol as the reductant and SIDI applications using simulated gasoline as reductant require intermediate Ag loadings (3.0 wt.% Ag₂O-Al₂O₃). NO_x conversion efficiency over the 3.0 wt.% Ag₂O-Al₂O₃ catalyst shows substantial improvement with as little as 10-20 vol.% ethanol in the simulated gasoline mixture, with 50-100 vol.% ethanol showing near 100% NO_x conversion between 300-500°C.

However, the HC-SCR lean-burn engine exhaust aftertreatment system is not without its own set of technical challenges. Based on engine test results it is clear that HC-SCR using diesel fuel as the reductant can significantly reduce NO_x emissions, but catalyst temperatures need to be relatively high, greater than 300°C, in order to obtain good NO_x efficiency [9]. The NO_x efficiency over 20 L of SCR catalyst volume with diesel fuel as the reductant is not good enough to meet the 2010 heavy-duty NO_x emission standard. HC slip past the SCR catalyst requires a downstream diesel oxidation catalyst for HC clean-up. In addition, low temperature (330°C) catalyst deactivation can occur when diesel fuel is used as the reductant, yet this poisoning is reversible either by raising the catalyst temperature higher than 440°C or by simply stopping the dosing of the reductant [10]. The decrease in activity due to diesel fuel poisoning on multiple highway fuel economy tests has also been shown [11]. On the other hand, with ethanol as the reductant a significant improvement in NO_x efficiency is achieved with

15 L catalyst volume, resulting in this system meeting the heavy-duty NO_x emission target. Low temperature deactivation does not occur with ethanol as the reductant [12]. Using ethanol-SCR as an aftertreatment technology for lean-burn SIDI gasoline vehicles or CIDI applications would require a secondary tank containing the ethanol or ethanol/gasoline fluid and also results in significant NH₃ production over the HC-SCR catalyst [7, 9]. Additionally, catalyst exposure to high temperatures and sulfur present in the fuel also provide potential means for catalyst deactivation.

Little work has been published in the literature regarding low temperature hydrocarbon poisoning or thermal durability of Ag-Al₂O₃ catalysts. Breen et al. [13] found that catalyst temperature and composition of the gas mixture were important in determining the change in activity upon thermal aging. They reported that 2 wt.% Ag catalysts deactivated at 800°C regardless of the reaction mix due to Ag particles becoming more ordered. They also showed that the reductant mix with the highest aromatic content yields the lowest activity and also results in the greatest deposition of coke. However, the addition of small amounts of noble metal (Pt, Pd, Rh) has been shown to improve the low temperature performance [24, 25, 26, 27]. On the other hand, the effect of SO₂ on the performance of Ag-Al₂O₃ catalysts for the HC-SCR reaction has been well documented [13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23]. SO₂ accumulation as sulfates is worse with HC/NO in the feedstream [15, 16]. Catalyst activity has been shown to degrade by varying amounts with differing amounts of SO₂ exposure when using a number of hydrocarbon reductants, including diesel fuel [14, 15], n-octane/toluene [13, 15], propane [16, 17, 18], propene [19], and ethanol [20, 21, 22, 23]. Breen et al. [13] demonstrated that with 1 ppm SO₂ in the feedstream severe deactivation can occur at intermediate temperatures (305-400°C), with little deactivation occurring at low temperatures (<235°C) and catalyst activation occurring at high temperatures (>500°C). This behavior was attributed to the activity of the catalyst for SO₂ to SO₃ oxidation. They also showed that the catalyst activity could be regenerated by heating the catalyst in a H₂-containing (7200 ppm) lean gas mixture, with regeneration considerably faster at 650°C in a rich gas mixture. Other researchers have also noted the positive attributes of H₂ for both improving the SO₂ tolerance and regenerating an SO₂-deactivated catalyst [16, 17, 18, 22]. Still others have shown that hydrocarbons improve the ability to appreciably regenerate the catalyst activity after sulfur poisoning [14, 15]. Sulfur removal as SO₂ during temperature programmed desorption (TPD) occurs between 400-800°C from Ag and from 800-1000°C from Al₂O₃ [15]. In only one study was H₂S measured, and it was not observed during sulfur regeneration [17]. As part of the effort at General Motors to understand and improve the limitations of this technology, several aspects of HC-SCR catalyst durability



Documents

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Table 1. Catalyst aging conditions used in this study.

Hydro-Thermal Aging Cycle (HT)	Air / 10% H ₂ O 16h/650°C, 50h/650°C, 16h/750°C, 16h/850°C
Reduction / Oxidation Aging Cycle (REDOX)	40 s 0.5% O ₂ / 1.0% CO / 10% H ₂ O (stoichiometric) 6 s 0.5% O ₂ / 3.0% CO / 10% H ₂ O (rich) 10 s 3.0% O ₂ / 3.0% CO / 10% H ₂ O (lean) 4 s 3.0% O ₂ / 1.0% CO / 10% H ₂ O (lean) 16h/650°C, 50h/650°C, 16h/750°C, 16h/850°C

Table 2. Simulated exhaust feedstreams used in this study.

Light-Duty Application	Heavy-Duty Application
10% O ₂ , 5% H ₂ O, 5% CO ₂ , 750 ppm CO 250 ppm H ₂ , 100 ppm NO HC (reported in ppm based on atomic mass) HC1:NOx ratio ~ 8 / 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 (reported in ppm based on atomic mass) HC1:NOx ratio ~ 8 / SV ~ 25,500 h ⁻¹

Table 3. 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 / 33 vol.% m-xylene 12 vol.% 1-octene / 10 vol.% n-octane

were examined, including 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. These preparation techniques have been filed for protection with the United States patent office [28]. Silver loading (wt. %) is indicated on an Ag₂O-basis since it is common practice in elemental analysis data of elements in an oxide matrix to be reported as metal oxides. The wt.% Ag₂O can readily be converted to wt.% Ag by multiplying by the ratio of the atomic weight of Ag and the molecular weight of Ag₂O (e.g., 3 wt.% Ag₂O is equal to 2.72 wt.% Ag). The catalyst comprises well-dispersed silver on surface hydroxylated alumina particles that are substantially free of silver metal and silver aluminate. The washcoat containing the catalyst powder was supported on 400 cell per square inch cordierite monolith substrates and exposed to hydro-thermal aging for 16h at 650°C prior to testing. Table 1 lists the two types of

aging conditions used in this study. The HT aging conditions are meant to simulate exhaust exposure from a diesel engine while the REDOX aging conditions are meant to simulate exhaust exposure from a lean-burn spark ignition direct injection gasoline engine. The catalyst volume for this study 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.

EXPERIMENTAL SET-UP

Experiments were performed in a laboratory fixed-bed flow reactor system. The catalyst was placed inside a 22 mm ID quartz tube and located in a position inside the heated zone of the furnace such that the catalyst temperature was approximately isothermal. The reaction temperature reported here ("average catalyst temperature") was measured using chromel-alumel thermocouples located approximately 1 mm upstream and downstream of the catalyst bed. Hollow quartz tubes located inside the heated zone of the furnace and upstream of the catalyst sample facilitate heat transfer to the gas feedstream. Simulated 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 feedstream 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 6 scans at a resolution of 0.5 cm⁻¹. For the sulfur poisoning and regeneration experiments a Picarro, Inc. Model ESP-1000 H₂S analyzer was used. It was connected to the outlet of the FTIR instrument in a bypass mode and sampled 200 cc/min of the exhaust gas feedstream. Since the H₂S analyzer and the FTIR analyzer both measure CO₂ the delay time was measured between the instruments in order to time align the SO₂ and H₂S measurements.

The typical simulated exhaust gas feedstreams are listed in [Table 2](#) and consisted of O₂, H₂O, CO₂, CO, H₂, NO, and hydrocarbon (HC) in a N₂ background. Two different standard feedstreams were used to represent a light-duty (low SV / high %O₂ / low ppmNO) and a heavy-duty (high SV / low %O₂ / high ppmNO) application. [Table 3](#) lists the hydrocarbon compounds used as reductants in this study. Volumetric mixtures of hydrocarbons were evaluated in order to represent the multi-component nature of diesel fuel and 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.

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 NO concentration, the HC 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:

$$\text{NO}_x \text{ conversion} = \left[\frac{\text{in}_{\text{NO}_x} - \text{out}_{\text{NO}_x}}{\text{in}_{\text{NO}_x}} \right] \times 100$$

RESULTS AND DISCUSSION

THERMAL DURABILITY

Supported catalysts ranging from 2-4 wt.% Ag 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 ppmNO) 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 [6, 8]. 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 [3, 4]. 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]. 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.% Ag₂O catalyst by increasing the HC1:NO_x ratio from 8.5 to 34. If one assumes a light-duty vehicle with a fuel economy of 18 miles/gallon and an engine out NO_x level of 0.50 g/mile on the FTP test cycle, then the fuel penalty for providing diesel fuel for HC-SCR at a HC1:NO_x ratio of 8 would be approximately 1.0%. The 2.0 wt.% Ag₂O-Al₂O₃ catalyst formulation was utilized for the following thermal durability measurements.

Thermal durability of the catalyst is important since the catalyst may be exposed to very different temperatures and gas feedstreams depending on the vehicle application and the exhaust system architecture. Both the temperature and the composition of the gas mixture have been shown to be important in determining the change in activity upon thermal aging of the catalyst [13]. The temperature that the catalyst is exposed to is dependent on the engine displacement and the catalyst location relative to the engine. For example, smaller displacement engines and catalysts located closer to the engine typically expose the catalyst to hotter exhaust gas temperatures. While both diesel and lean-burn gasoline applications operate with excess oxygen in the exhaust

feedstream, only the gasoline application routinely exposes the catalyst to stoichiometric and rich conditions. For this reason two aging cycles shown in Table 1 were utilized, hydro-thermal (HT) aging to simulate exhaust from a diesel engine and reduction/oxidation (REDOX) aging to simulate exhaust from a lean-burn gasoline engine. However, diesel catalysts can also be exposed to rich conditions, for example during a diesel particulate filter regeneration utilizing in-cylinder fuel post-injection. In this case the excess fuel reacts with the oxygen in the exhaust over a diesel oxidation catalyst, producing heat and rich conditions over the downstream HC-SCR catalyst. Additionally, lean-burn gasoline catalysts are typically exposed to much higher oxygen concentrations than occurs in the REDOX aging cycle. In an effort to examine the thermal durability of HC-SCR catalysts, individual 2.0 wt.% $\text{Ag}_2\text{O}-\text{Al}_2\text{O}_3$ catalyst core samples were exposed to both aging cycles in Table 1 and evaluated for NOx conversion performance using the light-duty test conditions in Table 2 with both reductants listed in Table 3.

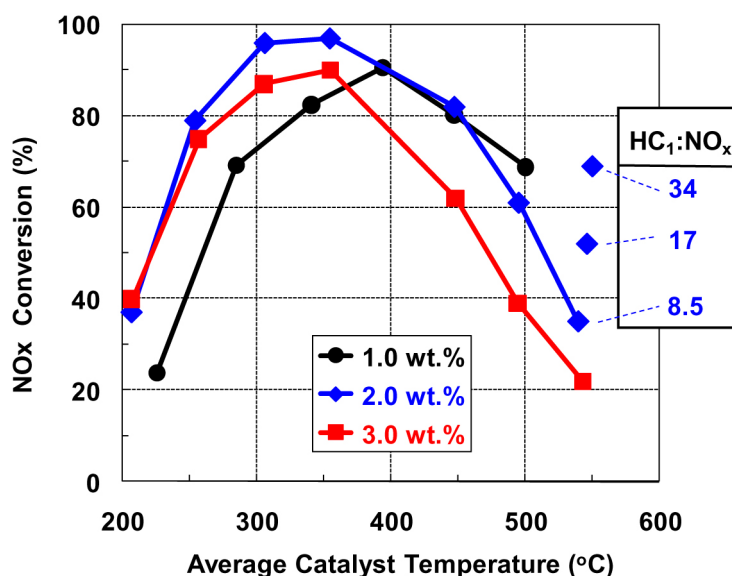


Figure 1. NOx conversion over 1.0-3.0 wt.% $\text{Ag}_2\text{O}-\text{Al}_2\text{O}_3$ using the light-duty simulated exhaust gas feedstream (Table 2) with sim-diesel reductant at $\text{HC}_1:\text{NO}_x \sim 8.5$. Additional data is also shown over 2.0 wt.% $\text{Ag}_2\text{O}-\text{Al}_2\text{O}_3$ at 550°C with $\text{HC}_1:\text{NO}_x \sim 17$ and 34.

Figure 2 shows the NOx conversion as a function of average catalyst temperature for catalysts aged 16h at 650°C, 750°C, and 850°C under the following aging temperature / reductant conditions: (a) HT / sim-diesel, (b) REDOX / sim-diesel, (c) HT / sim-gasoline, and (d) REDOX / sim-gasoline. As shown in Figure 2a for a HT aged catalyst using sim-diesel as reductant, the conversion efficiency at 350°C decreases from 96% to 86% as the aging temperature increases from 650°C to 750°C. Upon aging at 850°C the conversion at 350°C falls

even further to 48%. On the other hand, for REDOX aged catalysts utilizing diesel fuel as the reductant (Figure 2b) the NOx conversion at 350°C falls substantially from 87% to 23% as the aging temperature increases from 650°C to 750°C. Also note that the entire NOx conversion curve shifts to lower temperature when comparing HT and REDOX aging at 650°C (NOx conversion at 250°C: HT = 69% vs. REDOX = 82%, NOx conversion at 450°C: HT = 75% vs. REDOX = 43%). This may be due to the formation of metallic silver (Ag^0) during the reducing conditions present in REDOX aging, which has been shown to have a greater capability to partially oxidize the hydrocarbon to form key reactive intermediates at lower temperatures [4]. When sim-gasoline is used as the reductant (Figure 2c) the light-off temperature (temperature at which 50% NOx conversion occurs) is higher and the peak conversion efficiency is lower than when sim-diesel is used as the reductant (Figure 2a). The large branched-chain alkanes, alkenes, and aromatics found in gasoline provide NOx conversion only at higher temperatures [4]. On the other hand, heavier straight long-chain alkanes (e.g., n-dodecane) that are present in diesel fuel have been shown to provide NOx conversion at lower temperatures. Figure 2c indicates that a peak conversion efficiency of 66% occurs at 400°C after 650°C HT aging, with a subsequent decline to 49% and 27% as the aging temperature increases to 750°C and 850°C, respectively. After REDOX aging, the conversion efficiency at 400°C falls from 38% to 5% as the aging temperature increases from 650°C to 750°C. There is also a shift of the entire NOx conversion curve to lower temperature when comparing HT and REDOX aging, similar to the case utilizing sim-diesel as the reductant.

While it is extremely important that high NOx conversion efficiency be maintained over a wide temperature window, it is also equally important that there be limited formation of undesired byproducts during the reaction, including NH_3 , HCN, and N_2O . No other nitrogen-containing products (e.g., methyl nitrate) were observed in this study. For this work it was not possible to measure the desired product, nitrogen, since the background gas was N_2 ; however, it was calculated from the following equation:

$$\text{N}_2 \text{ (ppm)} = \frac{\text{in}[\text{NO} + \text{NO}_2] - \text{out}[\text{NO} + \text{NO}_2 + \text{N}_2\text{O} \times 2 + \text{NH}_3 + \text{HCN}]}{2}$$

Product selectivity toward N_2 was then calculated from the following equation:

$$\text{N}_2 \text{ selectivity} = \left[\frac{\text{N}_2 \times 2}{\text{N}_2 \times 2 + \text{N}_2\text{O} \times 2 + \text{NH}_3 + \text{HCN}} \right] \times 100$$

Figure 3 shows the NH_3 formation and the calculated N_2 selectivity at 350°C after HT aging using (a) sim-diesel

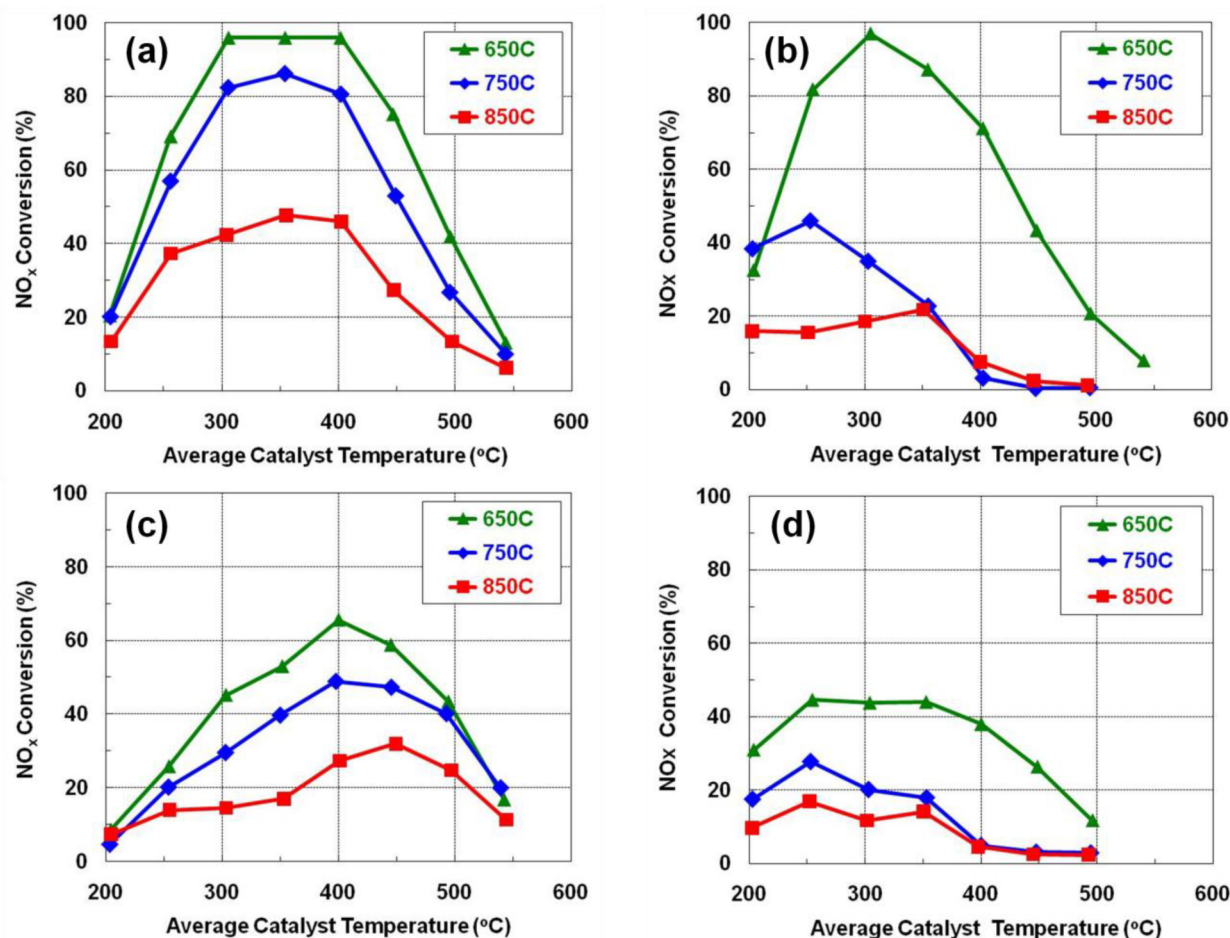


Figure 2. NO_x conversion over 2.0 wt.% Ag₂O-Al₂O₃ using the light-duty simulated exhaust gas feedstream (Table 2) under the following conditions: (a) HT aged / sim-diesel reductant, (b) REDOX aged / sim-diesel reductant, (c) HT aged / sim-gasoline reductant, and (d) REDOX aged / sim-gasoline reductant.

(corresponds to Figure 2a) and (b) sim-gasoline (corresponds to Figure 2c) as reductants. In this work there was virtually no HCN or N₂O formed over these catalysts (< 2 ppm). After aging at 650°C the selectivity toward the desired nitrogen product was over 90% with less than 8 ppm NH₃ formed from either reductant. As the aging temperature increased so did the NH₃ formation, thereby decreasing the N₂ selectivity to near 60% after aging at 850°C when using either HC reductant. In general, lower amounts of NH₃ were formed using sim-gasoline relative to sim-diesel due to the lower overall NO_x conversion efficiencies for sim-gasoline. There are similar amounts of NH₃ formed after HT and REDOX aging at 650°C using sim-diesel as the reductant, however, significantly less NH₃ (< 3 ppm) is formed after higher temperature REDOX aging (data not shown).

Results shown in Figure 1, Figure 2, and Figure 3 involve aging for only 16h; however, typical aging times for both diesel and lean-burn gasoline applications are 50h. Therefore, additional catalyst samples were aged for 50h at 650°C and

then compared to those aged for 16h at 650°C for both HT and REDOX aging. Figure 4 shows the NO_x conversion after 16h and 50h of HT or REDOX aging using sim-diesel as reductant under the light-duty test conditions. There is virtually no loss in NO_x conversion with additional time spent under the HT aging conditions. Therefore, the not-to-exceed (NTE) temperature for HT aged HC-SCR catalysts utilizing diesel fuel as the reductant is 650°C. However, further degradation does occur with additional time spent under the REDOX aging conditions, with ~10-15% loss of conversion efficiency across the entire temperature window. This is consistent with the much more severe deterioration observed in Figure 2 for the REDOX aged samples. This may be due to the agglomeration/sintering of the active component and will be discussed later. Thus, a NTE temperature below 650°C is required for REDOX aged catalysts.