

Low Temperature Urea Decomposition and SCR Performance

C. Scott Sluder, John M. E. Storey, Samuel A. Lewis, Linda A. Lewis

Oak Ridge National Laboratory

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ABSTRACT

Urea-SCR systems are potentially a highly-effective means of NO_x reduction for light-duty diesel vehicles. However, use of urea-SCR technologies at low temperatures presents unique technical challenges. This study was undertaken to provide more knowledge about low temperature urea decomposition and the resulting effects on SCR performance. Data are presented for experiments using two SCR catalysts of differing size with a light-duty diesel engine. Analyses of the NO_x reduction efficiency, NH₃ storage phenomena, and unregulated emissions are shown. Over production of NO₂ by the oxidation catalyst is demonstrated to be problematic at 25,000 hr⁻¹ space velocity for a range of temperatures. This leads to production of N₂O by both SCR catalysts that is higher when urea is injected than when NH₃ is injected.

INTRODUCTION

Compression-ignition (CI), or diesel, engines have been recognized for many years as a highly-efficient powerplant for both mobile and stationary applications. Oxides-of-nitrogen (NO_x) and particulate matter (PM) emissions have historically been problematic for diesel engines. However, improvements in engine design have reduced engine-out NO_x and PM emissions considerably. Nevertheless, increasingly stringent emissions regulations have resulted in the need for highly efficient emissions control technologies that can be used with diesel exhaust streams. Continuing and increasing the utilization of this powerplant requires meeting these stringent regulations while maintaining high fuel efficiency. Urea selective catalytic reduction (SCR) has received considerable attention in the past several years as a NO_x control technology for compression-ignition (CI) engines.

Diesel engines utilize varying air/fuel ratio for control of the engine's brake power output. Fuel-lean operation is typical for most, if not all, conditions. This results in an exhaust stream that contains a large and variable amount of oxygen. This net-oxidizing chemical environment presents difficulty in accomplishing chemical reduction reactions, such as reduction of NO_x. For this reason, NO_x reduction requires the addition of a

reductant to the exhaust stream. Earlier attempts at lean NO_x catalysis utilized added hydrocarbons as a reductant, but typically did not accomplish high levels of NO_x reduction. Lean-NO_x traps (LNTs), or NO_x adsorbers, also require reductant addition, but in a different way. These devices require a periodic fuel-rich (hydrocarbon rich, or oxygen deprived) exhaust stream to reduce NO_x stored within the device. NO_x traps, then, require periodic reductant addition, rather than a continuous flow as SCR and Lean-NO_x catalysts do.

Stationary engines and other NO_x sources have been using ammonia and urea based SCR systems for many years (1). Urea SCR utilizes added urea in combination with a specifically-formulated catalyst to accomplish NO_x reduction. The urea ideally breaks down to form ammonia, NH₃, the reductant utilized in reactions with NO_x (2, 3, 4, 5, 6). Handling anhydrous NH₃ requires extreme caution, and would not be practical for automotive applications, although it is used in some stationary applications. Urea is a crystalline powder that is usually introduced to the exhaust stream as a solution 32.5% by weight with water. Since this technology only requires enough reductant to treat the amount of NO_x being produced, the amount of urea injected into the exhaust stream is very small. Injecting a solution of urea in water is, at present, more convenient than metering the solid form.

The complete decomposition of urea takes place in three steps. The water in the solution is first evaporated releasing the urea. The urea then decomposes to release one NH₃ molecule plus one isocyanic acid (HNCO) molecule. The next step is for the HNCO to decompose to release a second NH₃ molecule and one CO₂ molecule (2, 3, 4, 5, 6). The two NH₃ molecules are then available for NO_x reduction. There are ample opportunities in this process for non-ideal behavior, such as the incomplete decomposition of HNCO, trimerization of the HNCO to form cyanuric acid as well as other reactions that sequester the NH₃ as undesirable compounds (2, 3, 5, 7).

Urea decomposition does not reach completion in the gas phase at temperatures that are typical for light-duty diesel exhaust (below 300 °C). In fact, only about 20% or less of the urea decomposes to HNCO and NH₃ in the gas phase at 330 °C, and only about 50% decomposes

at 400 °C (2, 3). HNCO has been shown to be very stable in the gas phase, requiring an oxide surface to catalyze its decomposition to NH₃ (9). Since the HNCO is half of the initial decomposition of urea, only about 25% of the desired NH₃ is available at the catalyst inlet at 400 °C. Very nearly all of the urea decomposition for low-temperature conditions will occur on the surfaces of the SCR catalyst. It is unclear how much impact these competing reactions have on the performance of the SCR catalyst under these conditions. A much better understanding of these effects is needed for identifying potential SCR catalyst improvements and for improving model-based controls for automotive SCR systems.

Several reaction pathways have been offered to explain the function of SCR systems. These have been well-explored in the literature (2, 3, 5, 6, 7) and are repeated here for use in discussion of the results. The first pathway, hereafter referred to as “standard-SCR” occurs according to equation 1 for NO.



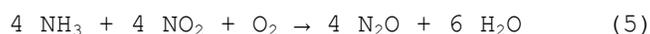
This process has been characterized as a relatively slow pathway. The more desired pathway is the “fast-SCR” reaction, shown in equation 2. This pathway is much faster, but requires equal amounts of NO and NO₂ in the feedgas.



A third pathway is slower than either standard- or fast-SCR reduces NO₂, and is shown in equation 3.



In cases where the NO₂ content exceeds the NO content in the feed gas, N₂O formation pathways have also been reported (7). These pathways are particularly important at intermediate temperatures that are common for light-duty applications. These pathways are shown in equations 4 and 5.



Thus, when the NO₂/NO ratio is higher than unity, N₂O can be produced at or near stoichiometric equivalence to NO₂.

The urea SCR process is a complex one involving the deposition of gaseous and aerosol reactants on the surface of the catalyst. Decomposition of urea occurs in multiple steps, most of which not be completed prior to deposition on the catalyst surface. Reduction of NO_x on the SCR surface can also take several paths, depending upon temperature and NO₂/NO ratio. The complexities of this system point to the need for development of models and model-based controls that will increase the likelihood of successful deployment of this technology in light-duty vehicles (5, 10, 11).

EXPERIMENTAL SETUP

ENGINE AND CATALYSTS

This study was performed using a modified Mercedes-Benz 1.7 L turbocharged, direct-injection compression ignition engine (OM668). The factory engine control unit (ECU) was replaced with a rapid prototype control system to allow departures from the factory engine calibration. The engine was installed on an eddy-current dynamometer. For the purposes of this study, the engine acted as an exhaust gas generator. The flexibility of the engine control system allowed variation of the SCR inlet temperature while holding both exhaust gas flow rate and NO_x concentration very nearly constant. The fuel used in all of the experiments presented in this paper was BP-15 diesel fuel. Some of the characteristics of the fuel are shown in Table 1.

Table 1. Characteristics of BP-15 diesel fuel.

Characteristic	Result
Cetane Number	49.7
Total Aromatics	27.2 %
Sulfur	15 ppm-wt
Specific Gravity	0.8374
Heat of Combustion	19,644 BTU/Lb

An oxidation catalyst was mounted downstream of the turbocharger. The urea injection port was located approximately 1 meter downstream of the oxidation catalyst. The SCR catalyst(s) were then mounted approximately 2 meters downstream of the urea injection port. The entire exhaust system was insulated to reduce the heat lost to the environment from the exhaust gases. The oxidation catalyst was a 144-millimeter (mm) diameter x 152-mm long cylindrical monolith with 46.5 cells per square centimeter (cm). The SCR catalysts were also 144 mm in diameter, but with two lengths; one monolith was 76 mm long and the other 152 mm long. Four 0.5-mm diameter thermocouples were inserted to various lengths in each SCR catalyst to monitor the temperature of the monolith.

The urea injection system metered and introduced urea solution into the exhaust stream. It utilized an automotive fuel injector to meter the urea based on a pulse-width modulated driver signal. The urea was conveyed to the injection nozzle and atomized by compressed air. The urea flow rate was calibrated prior to installation of the system using a catch-and-weigh procedure. The injection nozzle was instrumented with a thermocouple to determine the internal tube wall

temperature as the exhaust temperature and flow rate varied.

INSTRUMENTATION

Standard automotive exhaust gas instrumentation was utilized to provide a basic knowledge of the exhaust makeup as it entered the SCR catalyst. Exhaust oxygen (O_2) content was monitored using paramagnetic detectors (PMDs), carbon monoxide (CO) and carbon dioxide (CO_2) were measured by non-dispersive infrared instruments (NDIRs), hydrocarbons (THC) were measured using heated flame ionization detectors (HFIDs), and oxides of nitrogen (NO_x) were measured using heated photochemiluminescence detectors (HCLDs). A Fourier transform infrared (FTIR) spectrometer (Thermo Nicolet Nexus 670) was utilized for species measurements downstream of the SCR catalyst. This avoided problematic interferences in the HCLDs arising from NH_3 and other SCR byproducts. The various temperatures and pressures were monitored using thermocouples and pressure transducers. Fuel consumption was measured by utilizing a Max Machinery 710-213 positive displacement volumetric flow measurement system. Air consumption was measured using a laminar flow element and intake mass-airflow sensors.

A microdiluter device was configured to provide a dilute (non-condensing) exhaust stream for analyzing exhaust chemistry based on a design by Abdul-Khalek and Kittleson (12). The raw exhaust sample was routed to the microdiluter through a heated stainless steel sample line maintained at 190 °C. The microdiluter device was heated and insulated to maintain a sample temperature of 50 °C within the device itself. Various samples were extracted from the diluted sample stream and trapped for off-line analysis. Dilution ratio was monitored by observing gas concentrations in the raw exhaust stream and the dilute sample and was confirmed by periodic volume flow measurements. Aldehyde emissions were measured using di-nitro phenylhydrazine (DNPH) cartridges to trap the sample. The analytes were later eluted with acetonitrile and analyzed using a high pressure liquid chromatograph equipped with a mass selective detector (LC/MS). Nitroxyalkanes were trapped using a Florisil™ cartridge, eluted with acetone, and analyzed using a gas chromatograph equipped with a chemiluminescence detector. Nitrates were trapped with a teflo filter (particulate-phase nitrates) and backup nylasorb filter (gas-phase nitrates). The filters were later extracted and the extract analyzed by ion chromatography to quantify the nitrate emissions.

An impinger apparatus was configured to sample the raw exhaust downstream of the SCR catalyst. The impinger was a Greenburg-Smith high-velocity impinger that is frequently used in stack-sampling applications. The impinger solution was a specially-formulated buffer solution developed at ORNL for sampling urea and related chemical species. The buffer solution was necessary to prevent NO_x in the sample stream from

forming an acidic environment in the impinger that might result in reactions among the species of interest. 300 ml of the buffer solution was placed in the impinger and the impinger placed in an ice-water bath. A pump pulled sample from the exhaust and through the impinger. The flow was metered using a rotameter. After collection, the samples were concentrated and analyzed by capillary electrophoresis.

EXPERIMENTAL APPROACH

A number of both steady-state and transient measurements were conducted to determine the effects caused by urea decomposition on the SCR catalyst. Engine conditions were determined that provided appropriate conditions at the SCR catalyst inlet. NO_x concentration was held at 200 +/- 20 ppm for all but the lowest temperature conditions. The exhaust gas flow rates were held at approximately 1.1 standard cubic meters per minute (SCMM). This flow rate results in an SCR catalyst space velocity of approximately 25,000 hr⁻¹ for the 152-mm long monolith and approximately 50,000 hr⁻¹ for the 76-mm long monolith. It is important to note that in both cases the gas velocities were the same for all of the data points; only the catalyst length was changed. The catalyst inlet temperature was varied between approximately 160 °C and 250 °C for data collection while maintaining the NO_x concentration and gas velocity setpoints.

STEADY-STATE DATA

After warming the engine and catalysts initially, the engine was operated at a point that resulted in the SCR catalysts experiencing exhaust gases at approximately 300 °C. This condition was maintained until no NO_x conversion was observed in order to clean the catalyst of reductant prior to data collection. The engine condition was then changed to provide the desired SCR catalyst temperature condition. The temperatures were then allowed to stabilize. Data were then taken to characterize the exhaust makeup prior to injection of reductant. Injection of a stoichiometric ratio of reductant to NO_x was then initiated. The injection was allowed to continue for either 20 minutes (76-mm long monolith) or 40 minutes (152-mm long monolith) prior to the start of collection of impinger samples. FTIR and other data were collected at 10 minute increments before and during the impinger sample collection. Following collection of the necessary data at a given point the reductant injection was turned off and the engine was returned to a condition that resulted in the SCR experiencing exhaust gas temperatures of approximately 300 °C until no NO_x conversion was observed. The process was repeated for each data point.

TRANSIENT DATA

The transient data did not involve collection of samples, only FTIR and standard gas measurements. The engine and catalyst were conditioned as outlined for the steady-state data, the condition of interest set, and the temperatures allowed to stabilize. Collection of FTIR and other data were begun, then reductant injection was started. The injection was allowed to continue for various lengths, some as long as 1 hour. After data collection, the reductant injection was turned off and the engine and catalyst were again conditioned before proceeding to the next data point. Some transient experiments were carried out using a gas mixture of 1% NH₃ in N₂ instead of urea. In these cases, the injection was still carried out at stoichiometric NH₃ to NO_x ratios. The NH₃ injection was introduced at the same point in the exhaust as the urea by switching from the urea nozzle to a simple gas injection setup.

RESULTS

OXIDATION CATALYST PERFORMANCE Several studies have reported that urea-SCR systems are most effective when coupled with an oxidation catalyst upstream to convert some of the NO to NO₂. This promotes NO_x reduction through the fast-SCR reaction path on the SCR catalyst. The NO₂/NO ratios produced by the oxidation catalyst are shown in Figure 1. The NO₂/NO ratio is plotted as a function of the SCR inlet temperature. The oxidation catalyst monolith temperature was approximately 40 °C hotter than the SCR inlet temperatures shown for each case. As shown, the oxidation catalyst produced more NO₂ than desired for SCR-inlet temperatures above 200 °C. The horizontal line on the figure at a value of 1 denotes the optimal NO₂/NO ratio. All data shown are for a space velocity of 25,000 hr⁻¹, which was characteristic for the exhaust flow rate at which most experiments were conducted. Limited data showed that the NO₂/NO ratio was approximately unity at a space velocity of 50,000 hr⁻¹ at 250 °C.

APPARENT NO_x REDUCTION The apparent conversion efficiency for this study is defined as the conversion efficiency for a given species without regard to the formation of undesirable intermediate products such as N₂O. The apparent conversion efficiency for both NO and NO₂ was strongly impacted by the overall NO₂/NO ratio. This dependence was observed with both the 76-mm long and 152-mm long monoliths. The conversion efficiencies for NO and NO₂ are shown in Figure 2 for the 76-mm long monolith and in Figure 3 for the 152-mm long monolith.

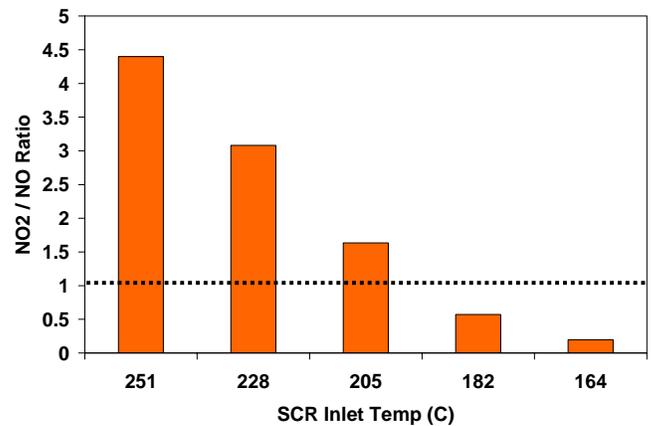


Figure 1. NO₂/NO Ratios produced by the oxidation catalyst.

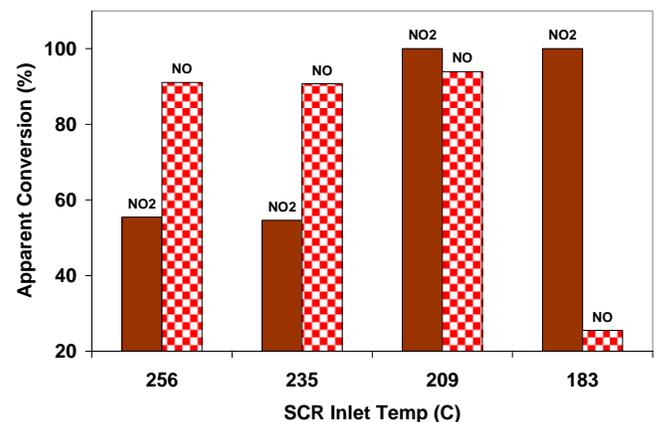


Figure 2. NO and NO₂ conversion results for the 76-mm long SCR monolith.

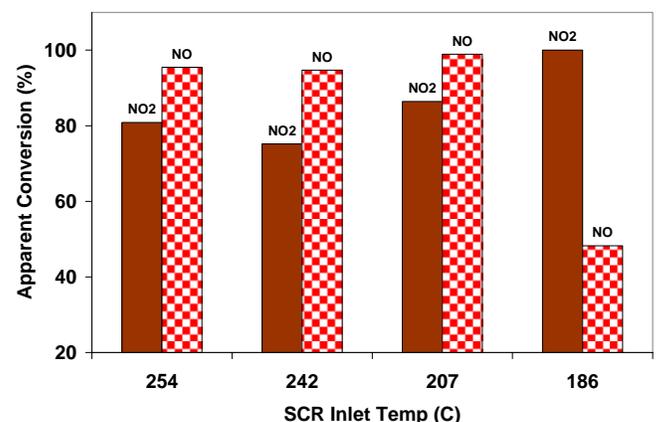


Figure 3. NO and NO₂ conversion results for the 152-mm long SCR monolith.

The data show that NO conversion is preferred over NO₂ conversion at higher temperatures, with this preference reversed at temperatures below 200 °C. This indicates relatively higher conversion efficiency for the species that is of lower concentration at a given temperature and indicates the fast-SCR reaction is dominant. The apparent conversion efficiency for both NO and NO₂ was higher when the 152-mm long monolith was used than with the 76-mm long monolith, with the exception of the results at ~210 °C. The difference in conversion efficiency between the 76-mm and 152-mm monoliths at this point is small and the error is believed to be caused by an inlet NO_x excursion caused by the engine controls during the data collection. The data in all cases is encouraging given the small size of the monoliths.

Figure 4 shows an example of one of the transient experiments.

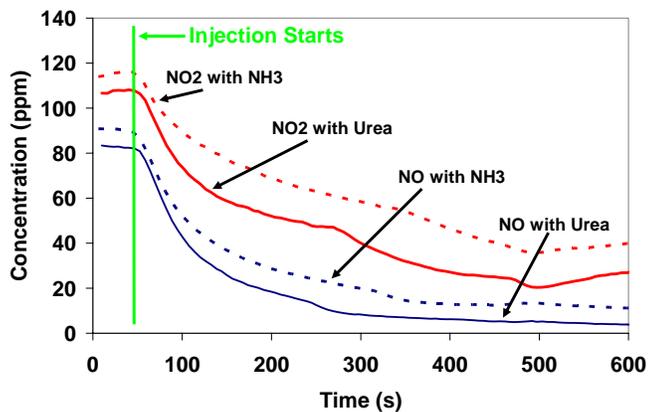


Figure 4. Transient experiment showing post-SCR NO and NO₂ emissions profiles.

The data shown in Figure 4 were taken using the 76-mm long SCR monolith at an inlet temperature of 205 °C. Urea and NH₃ were both injected at stoichiometric rates. The two curves with NH₃ injection are very similar to their counterparts with urea injection. The small offset in both NO and NO₂ prior to injection accounts for much of the difference between the two curves. A non-uniform urea spray or other anomaly with the urea delivery system would likely have caused a detriment in the apparent conversion of NO and NO₂ compared with injection of gaseous NH₃. The similarity (up to 600 seconds) of these curves shows that the urea injection system was introducing a spray that was well-mixed and distributed, even at this relatively low temperature. The 205 °C condition is characterized by a near 1:1 ratio of NO₂ to NO; hence, the fast-SCR reaction is dominant for this condition. This reaction reduces an equal amount of NO and NO₂ simultaneously. This is the reason for the similarity in the rates of conversion of NO and NO₂ for both the NH₃ and urea injection cases. The apparent NO_x conversion is highest when the NO₂/NO ratio is nearly 1, without regard for the catalyst temperature (at least in the range from 180 – 250 °C).

NH₃ EMISSIONS NH₃ emission (slip) from the rear of the SCR catalyst was observed using the FTIR during steady-state experiments. This was expected, since the catalysts were intentionally undersized. The NH₃ slip was observed to be nearly zero for both the 76-mm and 152-mm long monoliths at the 205 °C point, where conversion efficiency was at a maximum. Other conditions were observed to exhibit considerable slip, with the 76-mm monolith always exhibiting a higher concentration of NH₃ slip than the 152-mm monolith. The presence of NH₃ slip at these other conditions confirmed that reduction reactions at the various conditions were not reductant-limited. The amount of NH₃ slip was generally indicative of nearly-stoichiometric injection of urea. NH₃ first escapes the 76-mm monolith at less than 10 minutes, while for the 152-mm monolith an equivalent slip is observed at between 30 and 40 minutes after the start of injection. These times were the basis for selecting 20 and 40 minutes of operation prior to data collection for the two catalysts. The time-to-slip for the 152-mm monolith was always much more than double the time-to-slip for the 76-mm monolith.

VOLATILE NITRO-ORGANIC EMISSIONS

Measurements of volatile nitro-organics were conducted both upstream and downstream of the 76-mm SCR monolith. A small amount of nitromethane was detected upstream of the SCR monolith at 250 °C. A similar amount was detected downstream of the SCR monolith at the same temperature, suggesting that there is little, if any, formation of nitromethane by the SCR catalyst. At 180 °C, a number of volatile nitro-organic compounds were formed. Nitromethane, nitroethane, and nitropropane were detected and identified. At least one other compound was present, but was not identifiable based on retention time comparison with available standards for the instrument. The levels of the volatile nitro-organics were never higher than 200 – 300 ppb, indicating that they do not represent a significant sink for NH₃. It appears that these compounds are formed at these low levels in the gas phase upstream of the SCR monolith and pass through the monolith untreated. An oxidation catalyst downstream of the SCR monolith would most likely treat these compounds successfully. The low concentration of these compounds suggests that they are not likely to be of concern. Their formation at 180 °C suggests that more compounds are available to react with NH₃ as the oxidation catalyst cools and becomes slightly less effective.

UREA DECOMPOSITION PRODUCTS

Impinger sample analyses to date have not detected the presence of urea decomposition products other than NH₃ downstream of either SCR monolith. Previous studies have reported the presence of HNCO downstream of undersized SCR catalysts at low concentration using Vanadia-based catalysts (2). FTIR data collected during this study have not shown the presence of HNCO downstream of the SCR monolith. FTIR analysis of urea decomposition upstream of the SCR catalyst required reducing the filter temperature at the sample point from 100 °C to 60 °C. This was necessary to reduce the amount of urea

decomposition on the filter that resulted in NH_3 formation other than in the exhaust stream. This technique was generally successful, although hot gas impingement on the filter still caused some urea decomposition at high exhaust temperatures upstream of the SCR catalyst. Sample analysis for direct measurement of urea downstream of the catalysts is ongoing.

N_2O EMISSIONS N_2O is an undesirable intermediate product in the reduction of NO_x to N_2 . The formation of N_2O on precious-metal catalysts has been well-documented in previous studies of NO_x -reduction technologies. Studies of urea-SCR systems to date have demonstrated that N_2O production is likely if the NO_2/NO ratio is too high, as detailed previously. In this case, the standard SCR reaction thermodynamically favors production of N_2O from NO_2 over the complete reduction to N_2 (7). Figure 5 shows steady-state N_2O production data for both monoliths.

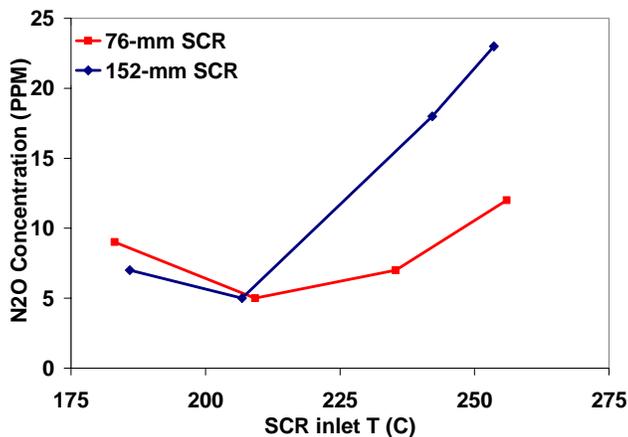


Figure 5. N_2O production for both SCR monoliths.

N_2O is produced in significant quantities at temperatures above 200 °C. As shown previously, too much NO_2 is present at these conditions for complete reduction by the fast-SCR pathway. The excess NO_2 is reduced according to reactions 3, 4, and 5. The longer SCR catalyst produces very nearly double the amount of N_2O that is produced by the 76-mm long monolith under these conditions, but does not consume double the amount of NO_2 . N_2O levels at SCR temperatures lower than 200 °C closely approximate N_2O levels that are produced by the oxidation catalyst alone. Varying the amount of urea injected from 85% to 115% of the stoichiometric rate increased the amount of N_2O produced by 3 ppm at 250 °C. Most of this increase in N_2O formation occurred when the urea injection rate was increased from 85% of stoichiometry to stoichiometry.

HCN FORMATION Interestingly, both monoliths produced a small amount of HCN. The concentrations of HCN downstream of the SCR monoliths are shown in Figure 6. The concentration in both cases remains small, but is measurable. The identification and

quantification of HCN by the FTIR was verified at the 250 °C point by comparative analysis using a gas chromatograph equipped with a mass-selective detector (GC/MS). The emission profile of HCN is virtually identical to that of NH_3 . The steady-state NH_3/HCN ratio appears to more or less constant for each catalyst. For the 76-mm monolith the ratio is approximately 16 regardless of temperature, while it is approximately 10 for the 152-mm monolith.

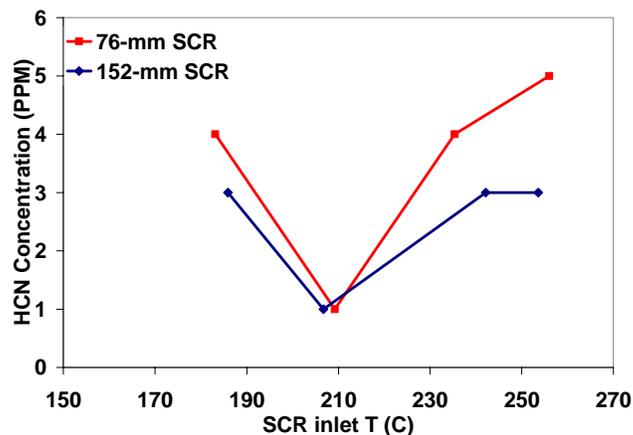


Figure 6. HCN emissions profiles for both SCR monoliths.

This behavior suggests that HCN is formed in a reaction relating to gas-phase NH_3 . Though the concentrations are small, the differences between the 76-mm and 152-mm profiles appear to be significant. The difference in the ratios appears to be both a function of decreased NH_3 slip and decreased HCN formation for the 152-mm monolith compared with the 76-mm monolith. Other conditions where HCN and NH_3 were observed together never exhibited an HCN concentration higher than 6 PPM, though the NH_3 exceeded 100 ppm. This suggests that reactions leading to the formation of HCN may be limited by some other reactant so that large amounts of HCN production are not possible.

TRANSIENT EXPERIMENTS Additional transient experiments were conducted with both the 76-mm long and the 152-mm long SCR monoliths to further investigate the effects (if any) that urea decomposition on the catalyst surface had upon performance. Experiments were conducted with both monoliths at the same temperature and flow conditions as the steady-state experiments. The decline in post-SCR NO and NO_2 typically required minutes, rather than seconds, to equilibrate. Figure 4 showed a typical plot of the NO and NO_2 disappearance at 205 °C. The profiles of NO_x disappearance at other temperatures and with the 152-mm long monolith were very similar, though cases with NO_2/NO ratios greater than unity required much longer to achieve equilibrium concentrations. Figure 7 shows an example of the behavior of N_2O and NH_3 at 235 °C for the 76-mm monolith.

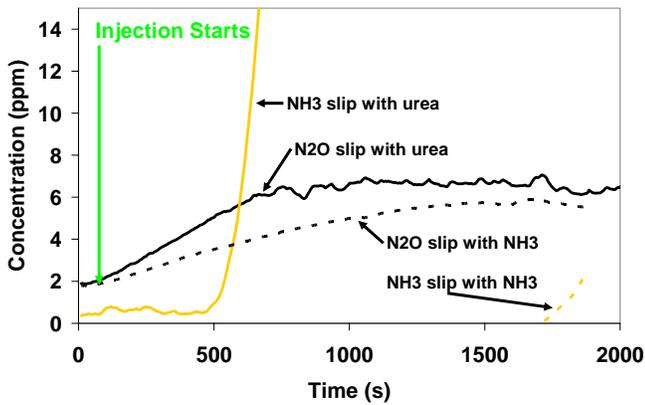


Figure 7. N_2O and NH_3 profiles for the 76-mm monolith at 235 °C.

The data shown in Figure 7 are typical of other experiments. In most cases the experiment was not run long enough to observe NH_3 slip using NH_3 as an injected reductant, but all experiments observed NH_3 slip using urea as an injected reductant. Simple comparisons of the 76-mm results to the 152-mm results showed that the time-to-slip for NH_3 for the 152-mm catalyst was, as indicated previously, always more than a factor of 2 longer than for the 76-mm monolith at the same temperature when using urea as an injected reductant. NH_3 slip when using NH_3 as an injected reductant was longer still. Both reductants exhibited very similar NO_x reduction profiles. These data show that the 76-mm monolith has a smaller apparent storage capacity of NH_3 per unit volume than the 152-mm long monolith. This is almost certainly related to the delivery and decomposition of urea. It is unclear whether this is because a urea layer is formed that impedes NH_3 storage or because urea is deposited sufficiently far along the monolith that a relatively smaller volume of the catalyst is available for storage, or both.

N_2O production for both monoliths at 250 °C is shown on Figure 8 for both urea and NH_3 reductant injection. NH_3 slip when injecting urea is shown. NH_3 slip was not detected when using NH_3 as an injected reductant. The two curves using NH_3 as an injected reductant should, therefore, be identical. The difference between the two curves seems to suggest a difference in activity between the two monoliths with regard to N_2O production. This cause of this difference is unclear. Similarly, the two curves using urea as an injected reductant should agree up to the point where NH_3 slips from the 76-mm monolith. This does in fact seem to be the case if the postulated difference in activity is applied. Beyond the NH_3 slip point, the curves diverge more sharply, showing that the 152-mm monolith produces even more N_2O as NH_3 begins to reach the rear half of the monolith. A similar trend was observed at an SCR inlet temperature of 235 °C, but at lower overall concentrations. At an SCR temperature of 205 °C, the N_2O does not rise above the level prior to reductant injection with either

urea or NH_3 for either monolith. This is likely due to higher NO_x reduction via the fast-SCR reaction since the NO_2/NO ratio is near unity. Any excess NO_2 at this point may also be sequestered as ammonium nitrate, NH_4NO_3 , rather than forming N_2O (7, 13). Figure 8 also shows that there is a significant increase in the N_2O production when urea is injected compared with NH_3 injection. This suggests that the delivery and decomposition of urea on the 76-mm monolith and the front 76mm of the 152-mm monolith impedes NO_x reduction to N_2 and forming an increased amount of N_2O . A similar, but smaller difference is also evident at the 235 °C condition.

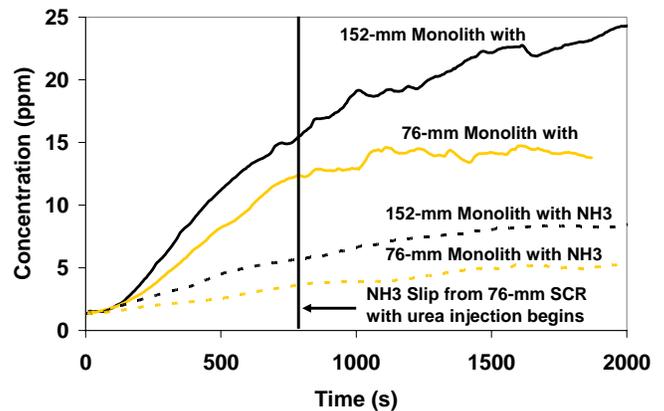


Figure 8. N_2O production for the 76-mm and 152-mm monoliths at 250 °C.

HCN emissions were found to precede NH_3 emissions slightly, but did not appear in cases where NH_3 slip never occurred. Figure 9 shows the NH_3 and HCN profiles for the 76-mm and 152-mm monoliths at 235 °C.

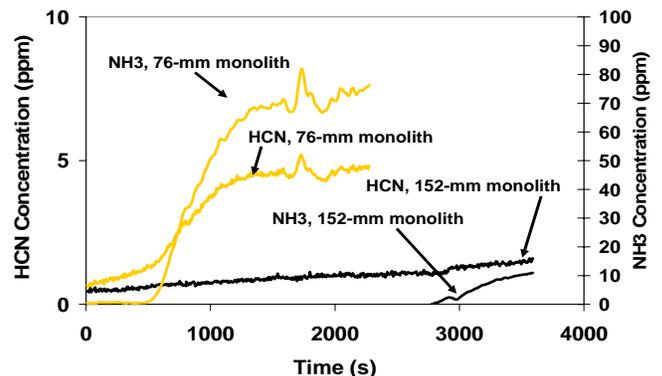


Figure 9. HCN production for the 76-mm and 152-mm monolith at 235 °C.

HCN escapes the 76-mm monolith just prior to NH_3 . The same tendency is observed with the 152-mm monolith, but the profile is not as steep. Similar profiles are observed when near-stoichiometric urea injection is

used. A transient comparison of both monoliths was not conducted at 180 °C, but multiple steady-state readings of HCN suggest that it follows a steep emissions profile at 180 for both the 76-mm and 152-mm monolith. The NH₃ slip at these conditions is very high, since stoichiometric injection is used but only a small amount of NO₂ is reduced. This results in a relatively high NH₃ slip for both the 76-mm and 152-mm monoliths. These data underscore a strong dependence of the HCN emissions on the concentration of NH₃ at the slip condition. This dependence seems to dominate over catalyst temperature, since higher HCN emissions are observed any time that higher NH₃ emissions are observed. Figure 9 also shows that HCN slip only occurs when NH₃ slip is imminent. This suggests that NH₃ storage and NO_x reduction take precedence over HCN formation. HCN seems to be formed only at the time when there is no other process for NH₃ sequestration. Some HCN production was observed when NH₃ was used as an injected reductant, but was considerably lower than when urea was injected.

CONCLUSIONS

- NH₃ storage on the first 76-mm of SCR catalyst is reduced significantly compared with the second 76-mm when urea is injected as a reductant compared with NH₃ injection.
- More N₂O is formed for over-oxidized cases when urea is injected compared with NH₃ injection.
- HCN formation and emission is observed just prior to NH₃ slip. HCN concentration is generally proportional to NH₃ concentration, but remains below 10 ppm. HCN emissions are higher when urea is injected compared with NH₃ injection.
- Volatile nitro-organic compounds appear to be formed in the gas phase upstream of the SCR catalyst, but only in quantities of 200-300 ppb. There are no indications of significant additional nitro-organic compound formation on the SCR catalyst.
- Formation of urea-related decomposition products (other than NH₃) and by-products has not been observed downstream of the SCR catalyst to date.

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