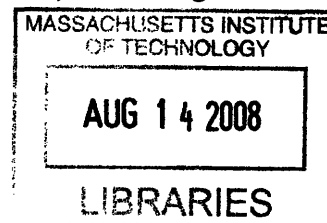Calibration and Performance of a Selective Catalytic Reduction (SCR) Bench Rig for
NO$_x$ Emissions Control

by

Sebastián Castro Galnares

SUBMITTED TO THE DEPARTMENT OF MECHANICAL ENGINEERING IN
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Calibration and Performance of a Selective Catalytic Reduction (SCR) Bench Rig for NO_x Emissions Control

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ABSTRACT

A laboratory test rig was designed and built to easily test SCR (Selective Catalytic Reduction) technology. Equipped with three 6 kW heaters, connections for liquid N_2 and an assortment of test gases, and a connection with an MKS NO_x Analyzer, the rig allows for a vast range of SCR test conditions, and can easily be adapted for degreening, aging, and the implementation of other technologies onto the rig.

To calibrate the test rig, baseline parameterization of a Cu-based zeolite (aluminosilicate) core was performed, including a temperature sweep and an NO/NO_2 concentration sweep, while always maintaining a 1:1 ratio between NO_x and NH_3 reductant. The catalyst was found to have a peak $deNO_x$ efficiency of 99.8% between 250 °C and 300 °C, and maintained 98% efficiency with $NO/NO_2 < 1$, while minimizing pollutant N_2O generation.

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Introduction

As it becomes more apparent that greenhouse gases are contributing to global warming, reducing the emission of gases from vehicle exhaust becomes paramount. In the automotive industry, NO_x gases produced in most combustion processes as a result of elevated temperature have been shown to contribute significantly to the greenhouse effect. Originally designed for use in heavy industry [6], selective catalytic reduction (SCR) provides a means of converting NO_x gases to harmless N_2 and H_2O components through the use of a reductant. In the last decade, adapting SCR technology for use in the diesel automotive industry has been an important topic of research; several technical barriers prohibit the direct transplant of the technology. In industrial SCR applications anhydrous or aqueous NH_3 is used, both of which require large storage vessels that would be difficult to reduce to the appropriate sizes for automotive applications. Additionally, NH_3 or in solution can be extremely toxic and corrosive [4]; therefore, an alternate reductant which can be easily stored on a vehicle platform, can be metered out with relative ease, and most importantly, can be reduced to NH_3 *in situ* to be used as the main reductant of NO_x gases is needed. Most studies focus on the use of urea as this reductant.
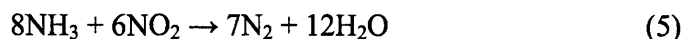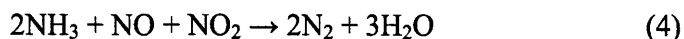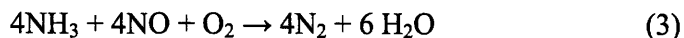
Chemistry of urea decomposition and NO_x reduction

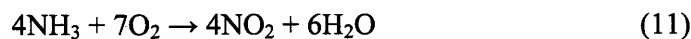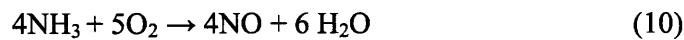To obtain the NH_3 necessary for the catalytic reduction of NO_x, urea decomposes as shown in the following reactions:

$$(NH_2)CO \rightarrow NH_3 + HNCO \tag{1}$$
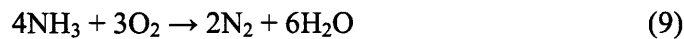
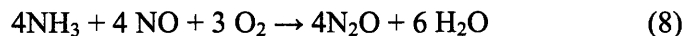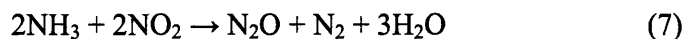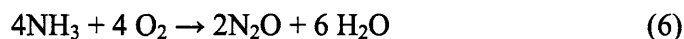$$HNCO + H_2O \rightarrow NH_3 + CO_2 \tag{2}$$
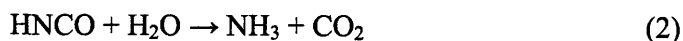
A necessary condition for these reactions to go to completion is a sufficiently elevated temperature of the exhaust gas [3], as inefficiency results in unhydrolized urea depositing itself on the catalyst surface, blocking reaction sites and decreasing the efficiency of the overall catalytic activity. A major part of catalyst design for SCR applications is determining the temperature ranges at which the urea is fully decomposed, and avoiding the passing of excess uncatalyzed reductant, or slip, of both urea and NH_3 through the catalyst.

With this in mind, consider the following reactions of NH_3 and NO_x gases:

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6 H_2O \qquad (3)$$

$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O \qquad (4)$$

$$8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O \qquad (5)$$

The rate of these reactions and their prevalence are determined in large part by the ratio of NO_2/NO gases in the exhaust stream. Reaction (3) dominates when no NO_2 is present. Reaction (4) dominates when $NO_2/NO \leq 1$ and is a fast reaction, while reaction (5) dominates when $NO_2/NO > 1$, and is a slow reaction. Secondary, pollutant-forming reactions (or reactions that prevent NO_x from decomposing to N_2 and H_2O) can also occur:

$$4NH_3 + 4 O_2 \rightarrow 2N_2O + 6 H_2O \qquad (6)$$

$$2NH_3 + 2NO_2 \rightarrow N_2O + N_2 + 3H_2O \qquad (7)$$

$$4NH_3 + 4 NO + 3 O_2 \rightarrow 4N_2O + 6 H_2O \qquad (8)$$

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \qquad (9)$$

$$4NH_3 + 5O_2 \rightarrow 4NO + 6 H_2O \qquad (10)$$

$$4NH_3 + 7O_2 \rightarrow 4NO_2 + 6H_2O \qquad (11)$$

The actual chemistry on the catalytic surface is complex and can involve the evolution of phosphates, sulfates, and other species in the catalyzed exhaust both from the urea itself and from any impurities in the exhaust of a real engine [7]. However, because the metering of urea into an exhaust stream requires bulky, closed loop controlled equipment, simulated exhaust gas is often used and NH_3 is injected into this mixture to establish the baseline behavior of new catalysts. Thus, the above formulae provide a useful theoretical basis for analyzing the baseline behavior of catalysts tested in this manner.

Test Rig Specifications

Much of the work of this thesis focuses on the creation of a practical test rig for the testing of the baseline performance parameters of SCR catalysts. As shown in Figure 1, the developed rig is well suited for this goal, but can also be easily adapted to run different types of catalyst de-greening procedures.
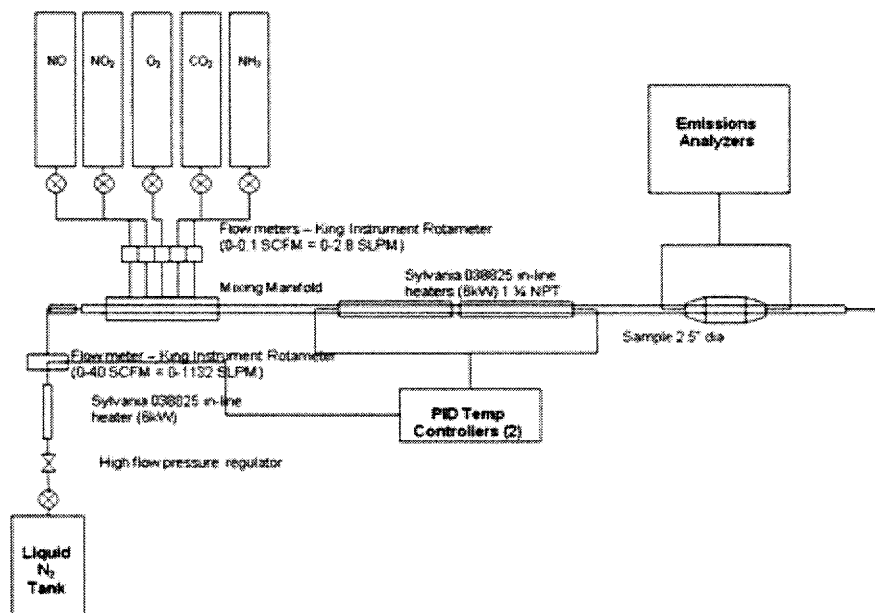
Fig 1. Catalyst bench rig schematic [8]

Because of the high space velocities that many catalyst testing procedures

implement (*i.e.* above 30k hr^{-1}), a dedicated, insulated input line is used to draw nitrogen

gas from a 250 L liquid N_2 dewar pressurized at 230 psig. This input line runs through a 6

kW Sylvania heater, which operates at 208 V and can draw up to 60 amperes of current.

This heater is used to heat the N_2 gas to about room temperature before it enters the

exhaust gas-mixing manifold. Five input ports are used to feed cylinder gases into the

mixing manifold, and both these ports and the insulated line have flow meters used to

control the volume of gas per unit time being mixed into the system. Just downstream of

the mixing manifold are two additional 6 kW Sylvania heaters in series, which are used to

heat the exhaust mixture to the desired testing temperature. An Athena Series 16C and an

Extech 48VTR temperature controller are used in conjunction with a power relay to

control the heaters, with thermocouples placed just downstream of the N_2 input line and

just upstream of the catalyst section. An additional thermocouple was placed just

downstream of the catalyst section, but was not used for temperature control of the

exhaust gas. The catalyst section itself has sampling ports controlled through ball valves just upstream and downstream of the position of the catalyst. These sampling ports lead to an MKS *Multigas 2030* FTIR (Fourier transform infrared spectroscopy) NO_x analyzer capable of discerning all major exhaust gas species (with the exception of diatomic species, although for O_2 there is an built-in dedicated sensor) at a maximum rate of one sample per second. Once exhaust goes through the catalyst section, it is carried through a gate valve that is used to generate a pressure differential to ensure proper gas flow, and subsequently through an exhaust port that removes the gases from the system.

Experimental

Catalyst preparation: For the initial test rig experiment, a proprietary copper-based formulation on a zeolite (hydrated aluminosilicate) matrix was obtained through suppliers at Ford. From the original sample, a 2.5" diameter, 5" long piece was cored with a diamond bit. The catalyst was characterized by 400 cpsi (cells per square inch).

Testing parameters and procedures: The base exhaust mixture used in all experiments was 14% O_2, 1500 ppm NH_3, and the balance in N_2. Before each test procedure, the system was purged with pure N_2 gas at 150° C for 20 minutes. Two distinct experiments were carried out.

To analyze NO_x conversion as a function of catalyst inlet temperature, a temperature sweep scheme was performed. Outlet composition data was taken until the outlet compositions reached a steady state, starting at 150 °C catalyst inlet temperature and increasing the temperature by 50 °C for each data point, up to 500 °C. With each successive temperature increment, data was also taken from the catalyst inlet to ensure

that the desired gas composition of 750 ppm NO and 750 ppm NO_2 was maintained at steady state.

The second procedure focused on the effects of NO_x composition itself. Keeping the catalyst inlet temperature at a nominal 300 °C, 1500 ppm of NO_x was mixed into the exhaust stream at a ratio of 0.5 NO/NO_2. After recording catalyst outlet data at steady state, the ratio of NO/NO_2 was increased with steady state data taken for each additional concentration as shown in Table 1, always maintaining the total NO_x levels at 1500 ppm. As in the first procedure, catalyst inlet data was taken between each data point to ensure that the desired exhaust gas composition was maintained.

NO/NO_2	[NO] ppm	[NO_2] ppm
0.5	500	1000
0.8	670	830
1.0	750	750
1.3	850	650
2.0	1000	500

Table 1. NO/NO_2 ratio sweep procedure exhaust stream composition

Results and Discussion

The results for NO_x conversion efficiency are shown in Figure 2. As the temperature was ramped up from 150 °C, the NO_x conversion efficiency increased and then began dropping at higher temperatures. This kind of behavior is typical for many catalysts [1], and although a peak efficiency of 99.8% is achieved between 250 °C and 350 °C, it should be noted that as a baseline measurement, the catalyst has yet to be degreened or loaded. Under loading, fuel and lubricant pollutants such as sulfates, nitrates, and heavy metals can block catalysis by reacting with the surface copper and deactivating catalyst sites.
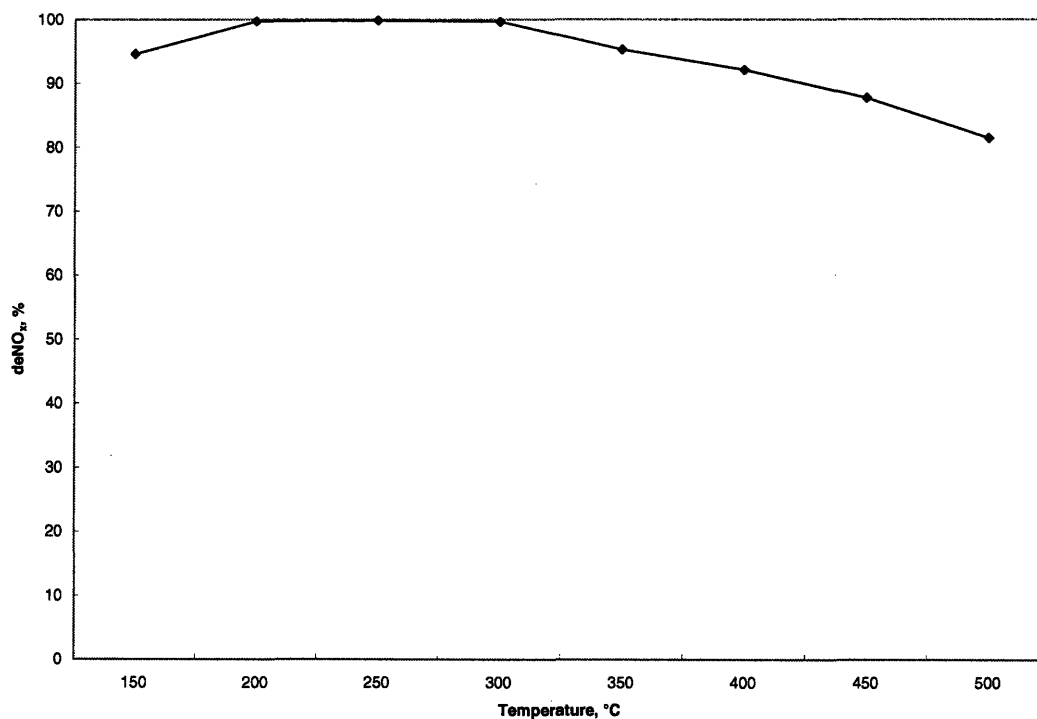
Figure 2. NO$_x$ conversion efficiency as a function of catalyst inlet temperature

To ensure that the reductant is being consumed in its entirety, as given by the

predicted chemistry of reaction based on equation (4), the amount of NH$_3$ going

unreacted through the catalyst, or NH$_3$ slip, is plotted in Figure 3. Slip is highest when the

temperature is lowest, which is expected as there is not enough heat in the exhaust stream

to activate the catalytic reactions and decompose the NO$_x$. This slip, however, continues

to decrease and eventually levels out past the temperatures at which NO$_x$ conversion is at
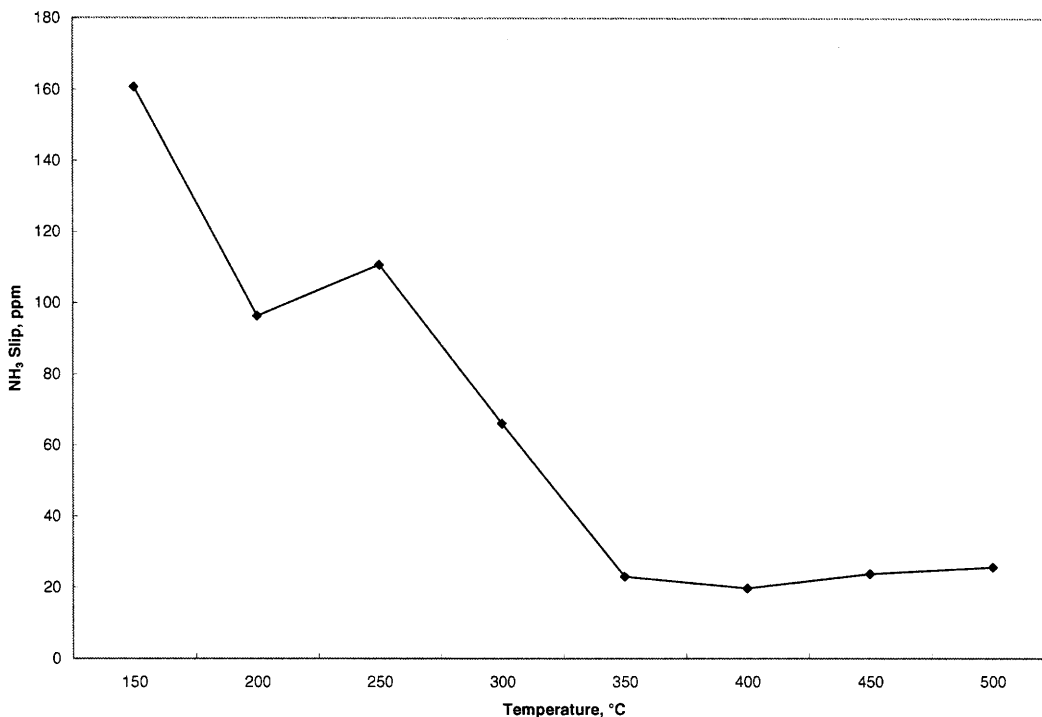
its highest.

Figure 3. NH$_3$ slip as a function of catalyst inlet temperature

It is theorized that the steady state achieved in slip at higher temperatures can be attributed to an adsorption/desorption process in which NH$_3$ adsorbs to the catalyst surface at lower temperatures, and then begins NO and NO$_2$ forming reactions at higher temperatures once desorption begins [5]. The authors of this study suggest that when used with low to medium (200 °C – 350 °C) temperature transients such as those found in heavy duty cycles, this mechanism can be used to improve overall deNO$_x$ efficiency, provided that the temperature is carefully regulated to avoid the formation of additional NO$_x$ as can be seen in reactions (9) – (11).

Pollutant formation is also relevant to the efficiency tradeoffs of any catalyst baseline performance, particularly since the susceptibility to form N$_2$O in the catalyst outlet stream is relatively simple, as seen in reactions (6) – (8). As shown in Figure 4, N$_2$O formation is well matched to increase in deNO$_x$ conversion.
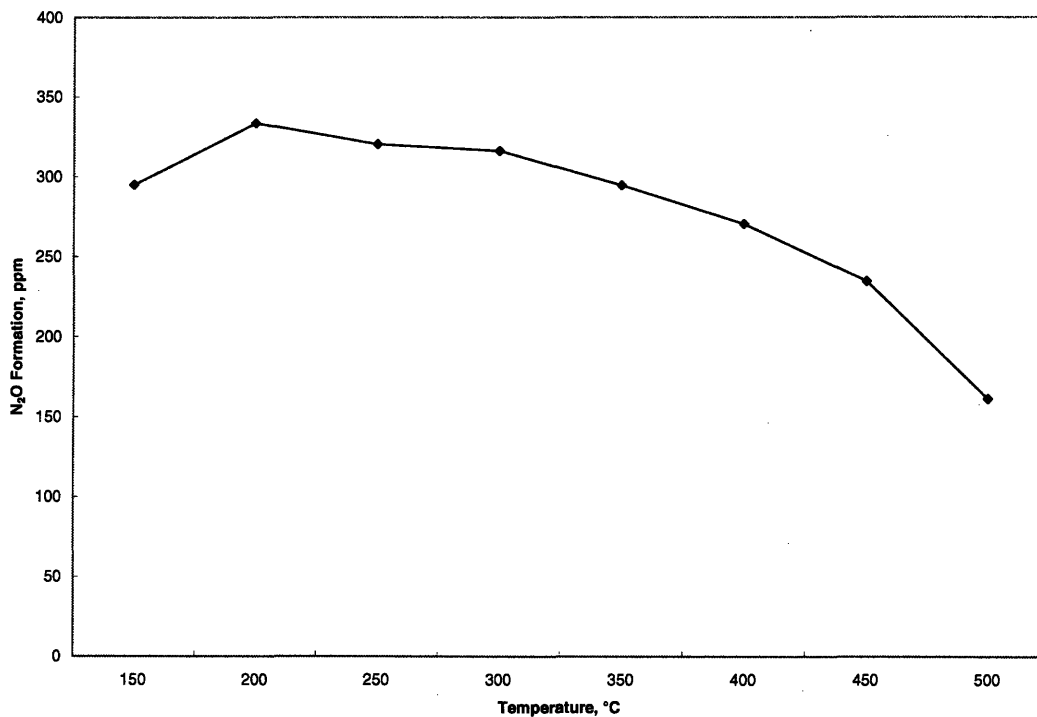
Figure 4. N$_2$O formation as a function of catalyst inlet temperature

Transient imbalances in NO$_2$ concentration, along with elevated temperature, are particularly prone to produce N$_2$O in the catalyzed exhaust stream. However, once the exhaust temperature is sufficiently elevated, NO and NO$_2$ formation is favored, as can be appreciated from the decrease in deNO$_x$ activity.

Varying the NO/NO$_2$ ratio is well established in the literature as a way of testing catalyst behavior when exposed to different types of engine systems, and also when fine tuning other technologies to work in conjunction with SCR, such as LNT (lean NO$_x$ trap) and DPF (diesel particulate filter) [7]. Figure 5 shows deNO$_x$ conversion when exposed to varying levels of NO/NO$_2$ but maintaining both the total NO$_x$ concentration and the amount of reductant in the exhaust stream.
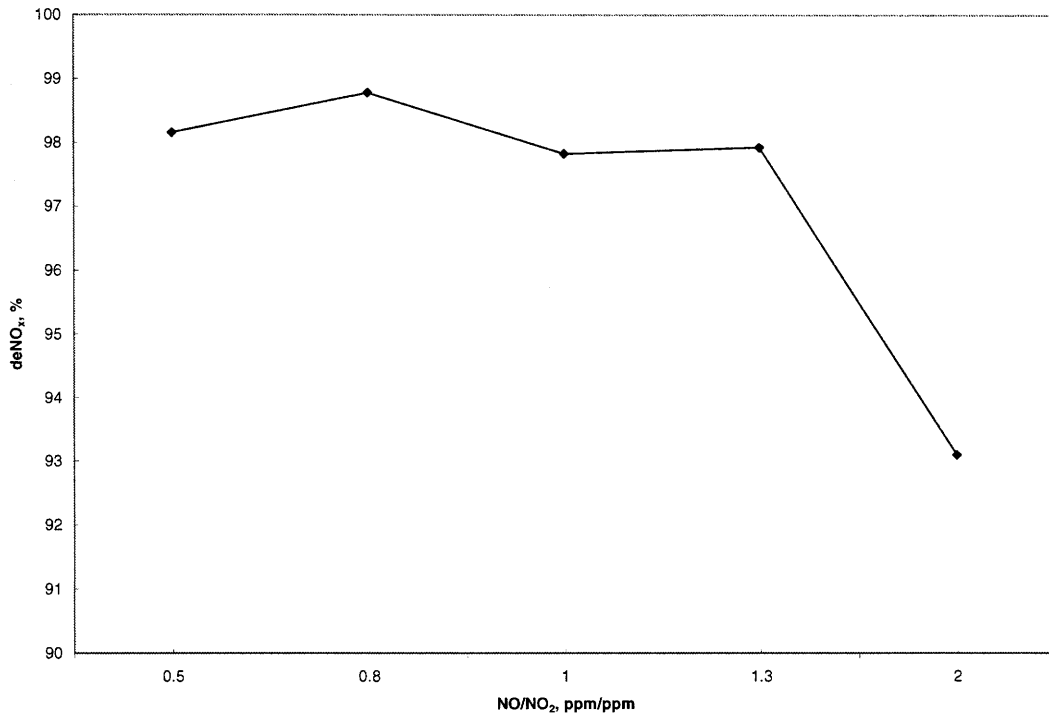
Figure 5. NO$_x$ conversion as a function of NO/NO$_2$ ratio in catalyst inlet

The deNO$_x$ conversion percentage remains relatively constant under low to moderate levels of NO concentration, but begins to fall dramatically once it is predominant in the NO$_x$ stream. Studies show that high concentrations of NO will compete with NH$_3$ for adsorption on copper catalysis sites on the catalyst and will result in decreasing deNO$_x$ capability [2]. However at lower NO/NO$_2$ ratio we incur a penalty in the form of N$_2$O production as shown in Figure 6.
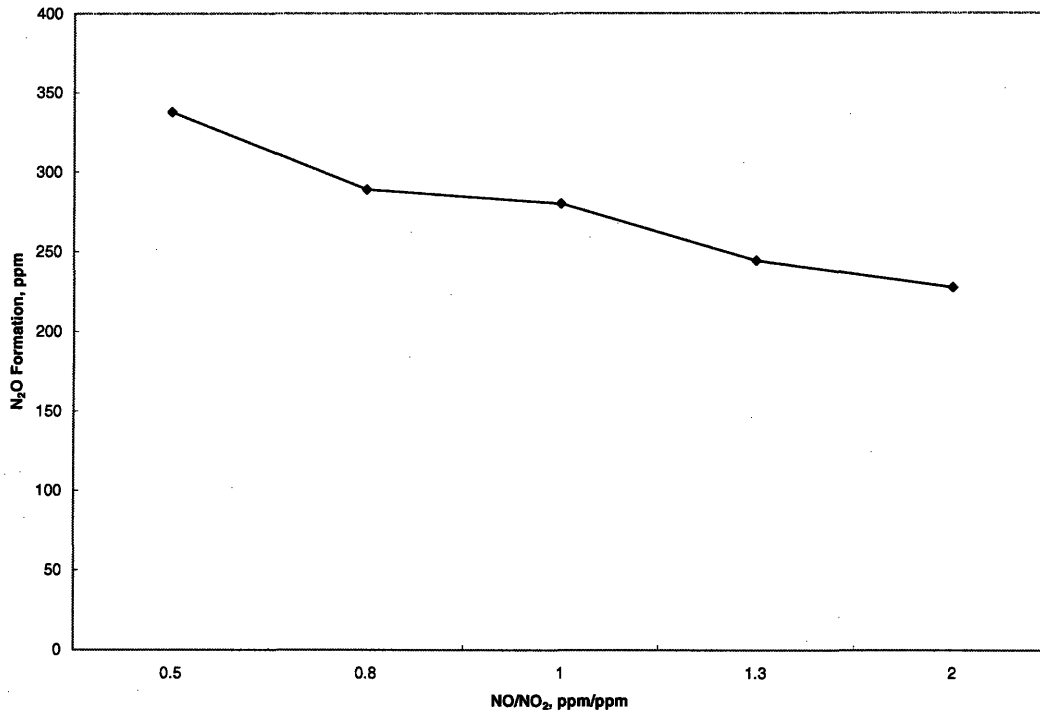
Figure 6. N₂O formation as a function of NO/NO₂ in catalyst inlet

Again, N_2O pollution becomes an issue as the concentration of NO_2 decreases. The problem is simpler to adjust for here as better efficiencies for NO_x reduction are achieved with less NO in the exhaust stream, which also produces fewer pollutants. As mentioned previously, increasing NO_2 concentration in the exhaust stream is beneficial from an outright efficiency standpoint, but also from an adsorption/desorption one [5], as NO_2 that might adsorb to the catalyst is more easily released in a transient cycle and decomposes more readily to N_2; conversely, NO binds more readily to the Cu catalysis sites and is more selective to oxidizing to NO_2.

Conclusions

The tested Cu-based catalyst was found to have an appropriate baseline performance in comparison with other catalyst types [1], and has the advantage of not possessing any vanadium-containing compounds in its structure. Used extensively until recently, studies have shown health risks involved with breathing in released vanadium when the catalyst core's integrity has been compromised [8].

The true test of a catalyst lies in the preservation of its NO_x reduction qualities even after extensive loading. The design of the test rig proves multifaceted in this regard: not only can one establish the baseline performance of the catalyst, but by mixing more demanding mixtures of simulated diesel exhaust and submitting the catalyst to many hours of duty simulating cycles, *in situ* performance can be characterized and compared to the baseline.

The literature has shown that much of the promise in SCR technology is its combination with other mechanisms to further enhance the SCR reactions [7]. An example of this is with DPF technology; when placed upstream of an SCR, it can be a source of NO_2 emissions that in general increase the NO_x reduction efficiency of the SCR reaction, although it should be noted that it can also provide higher temperature gas which can lead to lower efficiencies and durability issues with the catalyst itself. The versatility of the SCR test rig is such that it could be easily adapted to 'piggy back' on a motor with DPF technology, or even adapt a DPF into the test rig itself, making the scope of possible test procedures vast, and the rig itself a valuable tool.

Acknowledgements

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