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An examination of the role of plasma treatment for lean NO_x reduction over sodium zeolite Y and gamma alumina
Part 2. Formation of nitrogen

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Abstract

NO_x reduction with NO_2 as the NO_x gas in the absence of plasma was compared to plasma treated lean NO_x exhaust where NO is converted to NO_2 in the plasma. Product nitrogen was measured to prove true chemical reduction of NO_x to N_2. With plasma treatment, NO as the NO_x gas, and a NaY catalyst, the maximum conversion to nitrogen was 50% between 180 and 230 °C. The activity decreased at higher and lower temperatures. At 130 °C a complete nitrogen balance could be obtained, however between 164 and 227 °C less than 20% of the NO_x is converted to a nitrogen-containing compound or compounds not readily detected by gas chromatograph (GC) or Fourier transform infrared spectrometer (FT-IR) analysis. With plasma treatment, NO_2 as the NO_x gas, and a NaY catalyst, a complete nitrogen balance is obtained with a maximum conversion to nitrogen of 55% at 225 °C.

For γ-alumina, with plasma treatment and NO_2 as the NO_x gas, 59% of the NO_x is converted to nitrogen at 340 °C. A complete nitrogen balance was obtained at these conditions. As high as 80% NO_x removal over γ-alumina was measured by a chemiluminescent NO_x meter with plasma treatment and NO as the NO_x gas.

When NO is replaced with NO_2 and the simulated exhaust gases are not plasma treated, the maximum NO_x reduction activity of NaY and γ-alumina decreases to 26 and 10%, respectively. This is a large reduction in activity compared to similar conditions where the simulated exhaust was plasma treated. Therefore, in addition to NO_2, other plasma-generated species are required to maximize NO_x reduction. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

In recent years, plasma-assisted catalytic reduction of NO_x in lean and diesel exhaust was extensively studied [1–4]. In the previous paper [5] we discussed the effects of plasma processing on the composition of simulated diesel exhaust. The effect of temperature on the NO_x removal activity of NaY zeolite and γ-alumina was also examined.

It has been reported [1–5] that during plasma treatment of oxygen rich exhaust, NO is oxidized to NO_2. Due to this oxidation step of the plasma, catalysts that utilize NO_2 are being investigated. Some groups have measured the activity of potential plasma-catalysts by simply replacing NO with NO_2 in the feed gas to simulate the plasma effect on the catalyst [6,7]. However, there are differences in activity and storage reported for similar catalysts when tested with NO_2 in simulated exhaust or with plasma treatment of simulated

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exhaust. For example, Lampert showed that with an NO_2 feed and no plasma treatment a γ-alumina catalyst with 200 m^2/g surface area converted less than 40% NO_x to nitrogen at a space velocity of 6000 h^{-1} at 200 °C [6]. They measured up to 15% NO_2 storage and reported that the average conversion efficiency decreased to 20% at 14,400 h^{-1}. Basic zeolites, Na-ZSM-5 and NaY were reported to primarily store NO_2 with only 15% NO_x reduction activity at 200 °C. Conversely, Balmer et al. [8] and Yoon et al. [5] reported that at 200 °C activities as high as 70% can be achieved in plasma treated simulated exhaust streams followed by basic zeolites such as NaY with very little storage. Replacing NO with NO_2 in the simulated lean NO_x exhaust, Penetrante et al. reports that the activity of γ-alumina can be greater than 90% at a temperature range of 300–550 °C [6]. Lastly, Vogtlin et al. [9] show 80% plasma-assisted catalytic reduction of NO_x with γ-Al_2O_3 at 400 °C. The other effect of plasma is to oxidize hydrocarbons present in the exhaust. We found, that about 35% of propylene, used as a hydrocarbon source in the simulated diesel exhaust, is oxidized. Besides CO and CO_2 significant amount of aldehydes are formed [5]. The simultaneous decrease of the aldehydes and NO_x concentrations in the plasma-catalyst treated simulated exhaust suggests that the formation of aldehydes, as well as NO_2, is important for NO_x reduction performance of the plasma-catalyst systems.

The purpose of this study is to examine the significance of plasma, processing on NO_x reduction over γ-alumina and a basic zeolite, NaY. NO_x reduction with NO_2 as the NO_x gas in the absence of plasma is compared to plasma treated lean NO_x exhaust where NO is converted to NO_2 in the plasma. Therefore, the role of NO_2, the input hydrocarbon, and the hydrocarbon byproducts formed in the plasma are elucidated. True chemical NO_x reduction to N_2 is measured for the zeolite and alumina catalyst by conducting nitrogen balance experiments in a helium carrier.

2. Experimental

2.1. Experimental plasma-catalyst apparatus

The experimental plasma-catalyst apparatus has been described earlier [5]. The system consists of a double dielectric-barrier discharge reactor followed by a quartz catalytic reactor tube. The catalytic reactor is capable of testing powders, pellets, and coated monoliths at various temperatures.

The plasma reactor temperature was maintained at 110 °C for all tests to prevent water condensation. The catalyst reactor temperature was separately controlled. Extrudates of NaY (zeolyst) were tested; γ-alumina powder was pressed into pellets and sieved to 10–20 mesh.

Typical gas hourly space velocity (GHSV), calculated by dividing the standard gas flow rate by the catalyst bed volume, was 12,000 h^{-1} in the catalyst reactor. The typical GHSV within the plasma reactor was 30,000–60,000 h^{-1}. The effective operation of the plasma reactor is relatively insensitive to space velocity. The simulated exhaust used in this work was 200 ppm of NO_x, 700 ppm of C_3H_6, 5% of O_2 and 2% of H_2O. The balance gas was helium.

The effluent gas was analyzed by a chemiluminescent NO_x analyzer (CLNA) (Beckman Model 951), an MTI M200 micro gas chromatograph (GC), and a Fourier transform infrared spectrometer (FT-IR) (Nicolet Magna 560) equipped with a heated 2 m gas cell. For each FT-IR spectrum, 50 scans were collected at 0.5 cm^{-1} resolution. Measured absorbencies were converted to concentrations from calibration plots.

2.2. Nitrogen detection

With the typical simulated lean NO_x mix, true chemical reduction to N_2 cannot be measured because the minor amount of N_2 produced from the NO_x reduction cannot be detected above the large nitrogen background. In order to detect N_2 from the reduction reaction, experiments were conducted by replacing the nitrogen bath gas with helium. Previous work reported in Balmer et al. [10,11] has shown that while the energy efficiency is increased, the apparent gas phase chemistry is unchanged with helium. This result is expected since the background nitrogen does not play a role in the gas phase or surface chemistry. In addition, to simplify the GC measurements, CO and CO_2 were removed from the simulated gas mix. Although these constituents will always be present in lean burn exhaust, Tonkyn et al. [12], has previously reported that neither CO nor CO_2 contribute significantly to the observed NO_x reduction chemistry. In

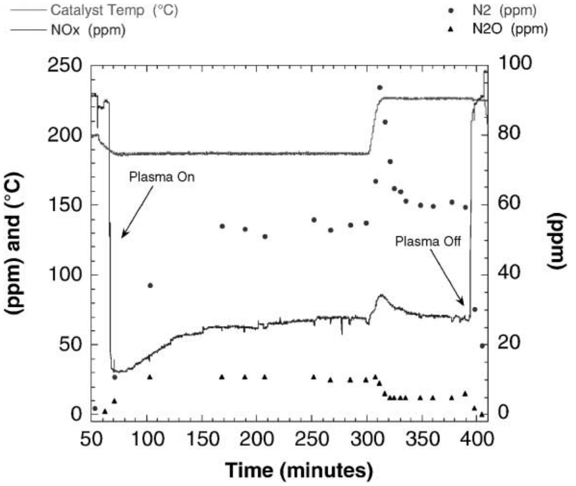

Fig. 1. NO_x concentration (ppm), catalyst temperature (°C), N_2 concentration (ppm), and N_2O concentration (ppm) as a function of time with sodium zeolite Y and simplified lean NO_x exhaust. NO was used as the NO_x input at catalyst temperatures of 180 and 227 °C.

order to elucidate the role of the plasma products in NO_x reduction over the catalyst, nitrogen balance experiments were performed using both NO and NO_2 as the NO_x input with and without plasma treatment of the gas.

2.2.1. NO as NO_x input—Na zeolite Y (180–227 °C)

First, sodium zeolite Y was examined with the simplified lean NO_x mix in helium at temperatures of 180–227 °C where the greatest NO_x conversion is observed [5]. NO was used as the input NO_x to confirm that the previously detected catalytic activity with NaY using a chemiluminescent NO_x meter was true chemical reduction to N_2. As shown in Fig. 1, when the simplified simulated exhaust was passed over the NaY catalyst at a temperature of 180 °C, no significant N_2 formation or NO_x removal is observed until the plasma processing is initiated. An immediate drop in NO_x concentration can be seen at 70 min when the plasma power was initiated and set at a power of 20 J/l.

The initial precipitous drop in NO_x concentration is followed by a slow rise in NO_x concentration until a steady-state value is reached at 250 min. Likewise, when the plasma is initiated, the N_2 and N_2O production increases slowly with time until a steady-state value is reached at 250 min (Fig. 1). All of the NO_x leaving the catalyst is in the form of NO. Since the plasma reactor was operated at powers high enough to convert all of the input NO to NO_2, the catalyst converted a portion of the NO_2 back to NO.

The measured concentrations of N_2 and N_2O out of the catalyst using GC analysis at their steady-state concentrations are shown in Table 1. The large time delay observed to reach a steady-state NO_x concentration is probably due to initial adsorption of NO_x. Due to the large surface area of this catalyst, sufficient time is required until adsorption sites are completely saturated with NO_x. Nitrogen and N_2O production increase slowly over the time frame where NO_x adsorption is occurring, reaching steady-state at about the same time as the NO_x production. This result indicates that nitrogen production is correlated to the surface coverage of adsorbed NO_x. The steady-state N_2 and N_2O ($54+10$ ppm) concentrations account for 81% of the missing nitrogen atoms at 180 °C. Therefore, 19% of the missing nitrogen atoms are neither N_2, N_2O, nor a NO_x.

Using a CLNA a steady-state NO_x reduction efficiency of 69% was measured. Therefore, replacing the N_2 bath gas with helium did not affect the overall activity of NaY. Also, the activity was not negatively

Table 1
Summary of results from nitrogen balance experiments with sodium zeolite Y at various temperatures[a]

Catalyst temperature (°C)	NO_x loss (%)	Nitrogen atoms missing (ppm)	$[N_2]$ (ppm)	$[N_2O]$ (ppm)	Nitrogen recovered (%)	N_2/N_2O
NO as NO_x input—Na zeolite Y						
130	44	107	39	15	100	3
164	55	132	41	8	74	5
180	69	158	54	10	81	5
227	69	158	59	5	81	12

[a] Nitric oxide (NO) was used as the NO_x input.

affected by the lack of CO_2 and CO in the simulated exhaust.

At 300 min, the catalyst temperature was increased from 180 to 227 °C. From Fig. 1, a small NO_x desorption peak can be seen due to the temperature increase. Simultaneously, a burst of N_2 is also observed. Some of the NO_2 initially stored on the NaY at the lower temperature desorbs as N_2 as well as NO at the elevated temperature. At 227 °C the steady-state NO_x efficiency is similar to the efficiency at 180 °C. The 54 ppm of N_2 detected at this temperature is 5 ppm higher than the N_2 concentration detected at 180 °C (Table 1). At the same time the N_2O detected at 227 °C is 5 ppm lower than the N_2O concentration detected at 180 °C (Table 1). At higher temperatures, the reduction chemistry favors the formation of N_2 over N_2O. The ratio of N_2:N_2O increases from 5 to 12 when the temperature is rised from 180 to 227 °C (Table 1). The overall nitrogen atoms accounted for are approximately 81% at both catalyst temperatures. Therefore, the formation of an undetected nitrogen-containing compound occurs at both temperatures. Possible products that could account for the undetected nitrogen include nitric acid (HNO_3), hydrogen cyanide (HCN), or organo-nitrates such as methyl nitrate (CH_3NO_3). The detection and quantification of these species was beyond the scope of this study.

2.2.2. NO as NO_x input gas—Na zeolite Y (130–164 °C)

The nitrogen detection experiment with NaY was repeated at lower catalyst temperatures. A plot of the catalyst temperature, NO_x concentration, N_2 and N_2O concentrations versus time are shown in Fig. 2. The behavior of the NO_x concentration is similar to that at higher temperatures. No initial conversion occurs at 130 °C without plasma treatment. When plasma processing is initiated, a dramatic drop in the measured NO_x concentration is observed. The CLNA determined a steady-state conversion value of 44% at 130 °C (Table 1). The total nitrogen atoms missing as NO_x by the CLNA (107 ppm) and the total nitrogen atoms detected in the form of N_2 and N_2O (39 + 15 ppm) are approximately equivalent after 1 h at this temperature. Therefore 100% nitrogen balance is obtained.

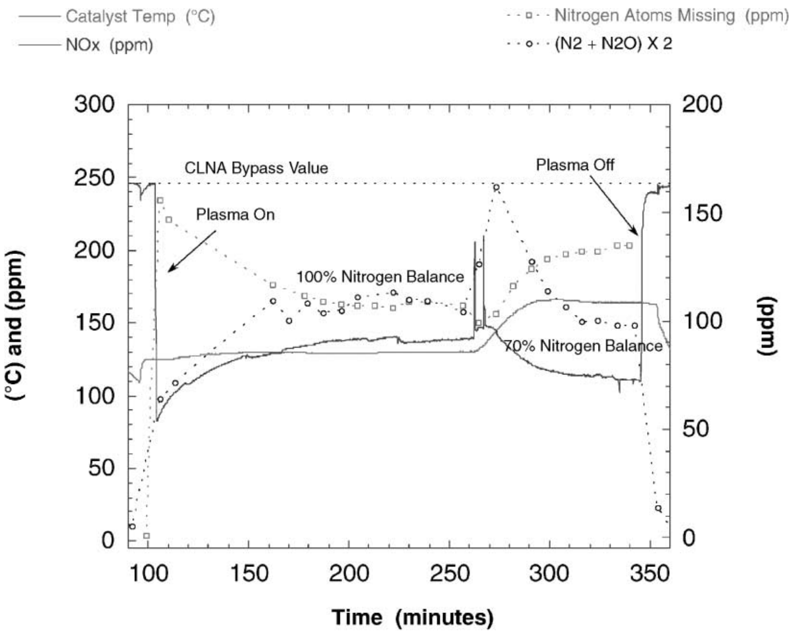

Fig. 2. NO_x concentration (ppm), catalyst temperature (°C), total nitrogen atoms missing (ppm), and total nitrogen atoms recovered in the form of N_2 and N_2O (ppm) as a function of time with sodium zeolite Y and simplified lean NO_x exhaust. NO was used as the NO_x input at catalyst temperatures 130 and 164 °C.

Upon heating the catalyst to 164 °C a burst of NO_x desorbtion was observed. After few minutes NO_x concentration slowly declined to a lower steady-state value. Simultaneously, a burst of N_2 was detected upon heating. At 164 °C, the steady-state NO_x reduction efficiency by CLNA was determined to be 55%. The corresponding nitrogen atoms not detected as NO or NO_2 increased from 107 ppm at 130 °C to 132 ppm at 164 °C (Table 1). However, the amount of product nitrogen atoms detected as N_2 and N_2O slightly decreased, mainly due to a decrease in N_2O concentration. Therefore, there is an incomplete nitrogen balance at 164 °C. It is interesting to note that the decrease in product nitrogen atoms is strictly due to less N_2O formation at the higher temperature. The N_2 concentration increased slightly from 39 ppm at 130 °C to 41 ppm at the higher temperature, while the N_2O concentration decreased from 15 to 8 ppm, respectively. This would suggest that there are competing pathways that lead to either N_2O formation or to the formation of some other nitrogen-containing compound or compounds. From Table 1, it can be seen that the N_2:N_2O formation ratio decreases with increasing temperature.

2.2.3. NO_2 as NO_x input—Na zeolite Y

The nitrogen detection experiment was repeated replacing NO with NO_2 as the NO_x input gas and measuring N_2 formation with and without plasma treatment of the gas. The NO_x concentration by CLNA as well as the N_2 and N_2O concentration by GC analysis as a function of time at 225 °C is shown in Fig. 3. Initially, the simulated lean burn exhaust bypassed the preheated catalyst bed. The catalyst was then exposed to the gas mix at 90 min. At this time, the majority of the NO_2 was adsorbed on NaY. However, over the next hour increasing quantities of NO_2 exited the catalyst bed until steady-state was reached (150 min). At steady-state, a large portion of the NO_x leaving the catalyst is in the form of NO_2 (Fig. 3). The NO concentration increased slowly after the NO_2 was introduced to the catalyst. Even after the apparent steady-state NO_x concentration was reached, the NO concentration continued to rise. The N_2 and N_2O concentrations followed the same trend as the NO_x concentration increasing slowly up to 150 min. The chemiluminescent NO_x meter measured a steady-state NO_x efficiency of 26% or 46 ppm at 225 °C with NO_2 as the NO_x feed gas and no plasma. Addition of N_2 and N_2O concentrations results in 44 ppm of nitrogen atoms or essentially a complete nitrogen balance. A summary of the results and N_2 and N_2O steady-state concentrations are shown in Table 2. The long rise time for N_2 and N_2O concentrations and concurrent NO_x concentration indicates adequate time is required to achieve sufficient surface coverage to allow for reactions on the active sites of the catalyst.

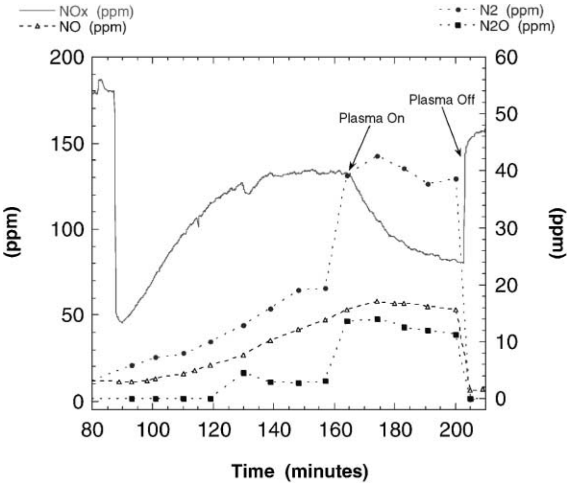

Fig. 3. NO_x concentration (ppm), NO concentration (ppm), N_2 concentration (ppm), and N_2O concentration (ppm) as a function of time with sodium zeolite Y and simplified lean NO_x exhaust. NO was replaced with NO_2 as the NO_x input. The catalyst temperature was set at 225 °C.

Plasma processing was initiated at 160 min (Fig. 3). An immediate jump in the concentrations of N_2 and N_2O were detected. The N_2 concentration increased from 19 to 39 ppm and the N_2O concentration increased from 3 to 11 ppm, respectively (Table 2). In addition, the NO concentration began to level off and the total NO_x concentration slowly declined. After 40 min of plasma processing, the NO_x concentration continued to slowly decrease. At this point, with plasma and the NaY catalyst, the NO_x efficiency had increased to 55%. At 200 min, the N_2 concentration was 39 ppm and the N_2O concentration was 11 ppm. At 55% NO_x efficiency, 100 ppm nitrogen atoms are missing, so a complete nitrogen balance was achieved with NO_2 as the NO_x input combined with plasma processing.

This result shows that NO_2 is required in the reduction mechanism, however, propylene alone is not

Table 2
Summary of results from nitrogen balance experiments with sodium zeolite Y and γ-alumina with nitrogen dioxide (NO_2) as the NO_x input

Catalyst temperature (°C)	NO_x loss (%)	Nitrogen atoms missing (ppm)	$[N_2]$ (ppm)	$[N_2O]$ (ppm)	Nitrogen recovered (%)	N_2/N_2O
NO_2 as NO_x input—Na zeolite Y (no plasma)						
225	26	46	19	3	96	6
NO_2 as NO_x input—Na zeolite Y (with plasma)						
225	55	99	39	11	100	4
NO_2 as NO_x input—γ-alumina (no plasma)						
342	10	21				
NO_2 as NO_x input—γ-alumina (with plasma)						
342	59	128	66	2	106	33

an effective reductant in the reaction. It appears that partially-oxidized hydrocarbons created in the plasma play an essential role in the optimum performance of the catalyst.

2.3. NO_2 as NO_x input—γ-alumina

The nitrogen detection experiment was also performed with the γ-alumina catalyst and NO_2 as the NO_x input. The results are summarized in Table 2. Without plasma, only 10% thermal activity was observed at a catalyst temperature of 342 °C. A large portion of the NO_x exiting the catalyst was reduced to NO without the presence of plasma processing. When the plasma processing was initiated, the N_2 production immediately increased from 20 to 65 ppm. The N_2O production remained low with plasma, similar to the N_2O concentration with thermal activation. The NO_x concentration dropped immediately from 196 to 92 ppm with plasma and a steady-state value was achieved rather rapidly. The chemiluminescent NO_x meter measurements revealed a steady-state NO_x efficiency of 59% at 342 °C with plasma treatment compared to 10% with thermal activation alone (Table 2). At approximately 60% NO_x efficiency, 128 ppm of nitrogen atoms are missing. With plasma processing, 66 ppm of N_2 and 2 ppm of N_2O are detected resulting in a complete nitrogen balance.

The total NO_x concentration leaving the γ-alumina without plasma was 196 ppm and the NO:NO_2 ratio is 1.8:1. So nearly two-thirds of the total NO_x has been reduced to NO and only 10% was reduced to nitrogen. When the plasma treatment was initiated, the total NO_x concentration decreased to 89 ppm and the calculated NO:NO_2 ratio leaving the catalyst decreased to 0.9:1. Without plasma, the majority of the NO_2 is being reduced to NO and a small portion to nitrogen. With plasma processing, and in the presence of other plasma-generated species, a significant portion of the lost NO_2 is reduced to N_2.

In summary, both γ-alumina and NaY catalysts have shown some NO_x reduction with NO_2 as the NO_x input gas. However, the activity is significantly enhanced with the addition of plasma processing. The data imply that species other than NO_2 formed in the plasma are also essential for optimum catalyst performance. It is likely that the important species are plasma-generated partially-oxidized hydrocarbons.

3. Conclusions

Plasma-assisted heterogeneous catalysis has been shown to be an effective process in the remediation of NO_x in synthetic lean burn gasoline and diesel compression ignition exhaust. This study was undertaken to examine the role of plasma processing on lean NO_x reduction over NaY and γ-alumina.

Product nitrogen was measured to prove true chemical reduction of NO_x to N_2. For N_2 detection experiments, the N_2 bath gas of a simplified simulated lean NO_x exhaust was replaced with He to allow for detection of N_2 and N_2O formation after the catalyst. It was shown that true chemical reduction to nitrogen is the dominant reaction over NaY. At 130 °C a complete nitrogen balance can be obtained, however between 164 and 227 °C less than 20% of the reduced NO_x formed on NaY produces a nitrogen-containing compound or compounds not detected by GC or FT-IR analysis.

Nitrogen detection experiments were also conducted replacing the typical NO for the NO_x input with NO_2. This was done to examine the role of NO_2 with and without plasma processing. It was shown that NO_2 is slightly active with propylene as the reductant with NaY and γ-alumina. However, the activity is greatly enhanced with plasma processing, suggesting that in addition to NO_2, other plasma-generated species are important for NO_x reduction. A complete nitrogen balance was obtained for both NaY and γ-alumina with a NO_2 feed.

References

[1] J. Hoard, H. Servati (Eds.), Plasma Exhaust After Treatment, SAE SP-1395, Society of Automotive Engineers, 1998.

[2] M. Lou Balmer, G. Fisher, J. Hoard (Eds.), Non-Thermal Plasma Exhaust Emission Control, SAE SP-1483, Society of Automotive Engineers, 1999.

[3] M. Lou Balmer, G. Fisher, J. Hoard (Eds.), Non-Thermal Plasma, SAE SP-1395, Society of Automotive Engineers, 1999.

[4] B.M. Penetrante, S.E. Schultheis (Eds.), Non-Thermal Plasma Techniques for Pollution Control—Part A: Overview, Fundamentals and Supporting Technologies, Springer, Berlin, 1993.

[5] S. Yoon, R.G. Tonkyn, A.G. Panov, A.C. Ebeling, S.E. Barlow, M.L. Balmer, Topics in Catalysis, submitted for publication.

[6] B.M. Penetrante, R.M. Brusasco, B.T. Merritt, W.J. Pitz, G.E. Vogtlin, M.C. Kung, H.H. Kung, C.Z. Wan, K.E. Voss, Plasma-Assisted Catalytic Reduction of NO_x, SAE 982508, 1998.

[7] Jordan K. Lampert, An Assessment of the Plasma Assisted Catalytic Reactor (PACR) Approach to Lean NO_x Abatement: The Relative Reducibility of NO and NO_2 using #2 Diesel Fuel as the Reductant, SAE 2000-01-2962, 2000.

[8] M.L. Balmer, R.G. Tonkyn, A.Y. Kim, I.S. Yoon, D. Jimenez, T. Orlando, S.E. Barlow, J. Hoard, Diesel NO_x Reduction on Surfaces in Plasma, SAE 982511, 1998.

[9] G.E. Vogtlin, B.T. Merritt, M.C. Hsiao, P.H. Wallman, B.M. Penetrante, Plasma-Assisted Catalytic Reduction System, U.S. Patent 5,711,147 (1998).

[10] M.L. Balmer, R.G. Tonkyn, A.Y. Kim, J. Hoard, I.S. Yoon, D. Jimenez, T. Orlando, S.E. Barlow, Nitrogen measurement from NO_x reduction for a plasma-catalyst system in simulated diesel exhaust, in: Proceedings of the 1998 Diesel Engine Emissions Reduction Workshop in Castine, Maine, July 1998.

[11] M.L. Balmer, R.G. Tonkyn, I.S. Yoon, A. Kolwaite, S.E. Barlow, G. Maupin, J. Hoard NO_x Destruction Behavior of Select Materials When Combined with a Non-Thermal Plasma, SAE 1999-01-3640, October 1999.

[12] R.G. Tonkyn, S.E. Barlow, M.L. Balmer, T. Orlando, J. Hoard, D. Goulette, Vehicle Exhaust Treatment Using Electrical Dishcharge Methods, SAE 971716, May 1997.