NO_X REDUCTION BEHAVIOR OF ALUMINA AND ZEOLITE CATALYSTS IN COMBINATION WITH NON-THERMAL PLASMA

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ABSTRACT

NO_x reduction under simulated lean burn conditions was studied using a non-thermal plasma in combination with zeolite and alumina catalysts. The influence of temperature and plasma treatment on the catalytic performance was investigated.

Zeolite catalyst B showed high activity in the 150-300^oC temperature region. Alumina Catalyst D was most active at temperatures higher than 250^oC. In addition, the alumina catalyst was effective in oxidation of aldehydes formed during plasma treatment of the reaction mixture.

Effect of formaldehyde on NO_2 reduction over both catalysts was investigated. Formaldehyde is one of the major products of partial oxidation of propylene in plasma, but it was found that it is not the key component responsible for NO_2 reduction.

When the reaction was carried out over a catalyst bed consisting of separate layers of the zeolite and alumina catalysts, the catalyst temperature range for significant NO_x reduction was expanded to 150-500^oC.

INTRODUCTION

Lean burn gasoline and diesel engines provide improved fuel economy when compared to engines operating under stoichiometric fuel/air conditions. At the same time, lean burn and diesel engines present a problem for emission control. Because they operate under oxidizing conditions, the conventional three-way catalyst is not effective in NO_x reduction [1,2]. In addition, the wide temperature range of automobile exhaust gases present a challenge for catalyst design. The temperature of exhaust gases from a light duty diesel engine can vary from 150 to 500^oC, depending on the operating conditions. To date, a catalyst that operates with high NO_x conversion efficiency over the entire operating range has not been found. Non-thermal plasma assisted catalysis has been shown to be a promising technology for NO_x reduction in lean-burn and diesel exhaust gases [3,4]. The approach exploited in this paper is to use a plasma in combination with several catalysts, each of which are active over unique temperature ranges.

It was reported in the literature, that the one of the essential roles of plasma treatment is to oxidize NO to easier reducible NO_2 [7]. In this contribution, the other important function of plasma treatment, namely partial oxidation of propylene, will be demonstrated.

EXPERIMENTAL

Catalysts were tested in the two-stage plasma-catalyst reactor described earlier [2]. The power deposited in the plasma reactor was measured with a capacitive circuit, and the energy density of the discharge was typically 35-40 J/l.

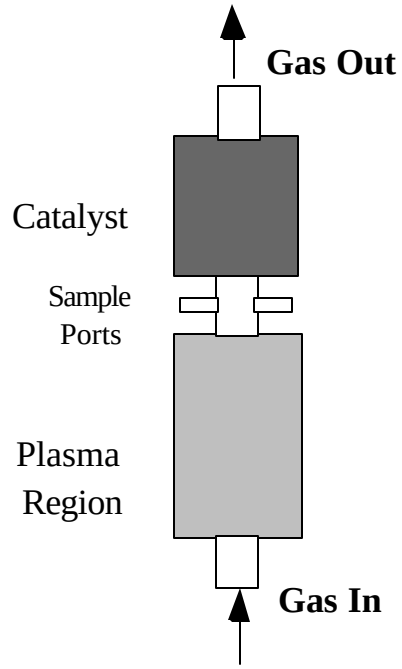

Figure 1. Schematic of the two-stage, plasma-catalyst reactor.

The space velocity in the plasma region was 60,000 h^{-1} and over the catalyst was 12,000 h^{-1}. All catalysts were in the form of extrudates.The temperature of the catalyst was measured with a thermocouple located in the catalyst bed close to the gas inlet. The composition of the simulated exhaust gas mixture is given in Table 1.

Table 1: Concentrations of components in simulated exhaust gas mixture.

Component	Concentration
NO*	200ppm
C_3H_6	715ppm
CO	400ppm
CO_2	7%
O_2	8%
H_2O	2%
N_2*	Balance

*As specified in the text NO and N_2 were replaced with NO_2 and He respectively for selected experiments.

The product gases were analyzed with a chemiluminecent NO_x analyzer, a MTI M200 micro gas chromatograph (GC), and a Fourier transform infrared spectrometer (FTIR) (Nicolet Magna 560) equipped with a heated 2 m gas cell. For FTIR analysis 50 scans were collected for each spectrum at the 0.5 cm^{-1} resolution. Absorbencies were converted to concentrations using calibration plots.

Temperature decomposition of $Al(NO_3)_3$ was performed with the ASDI RXM-100 catalyst testing instrument.

To determine the role of plasma treatment, some experiments were done using NO_2 instead of NO.

Experiments when formaldehyde was injected were performed with the same catalytic system with NO_2 as NOx source. Formaldehyde was injected before plasma reactor with a syringe pump. 10% formaldehyde solution in water-methanol mixture (10% methanol) obtained from VWR scientific was used.

RESULTS AND DISCUSSION

Plasma treatment converted NO to NO_2, so NOx coming out of plasma is ~98% NO_2. About 30% of propylene is oxidized to CO, CO_2 and partially oxidized products. In NO experiments passing the plasma treated mixture over the catalysts does not significantly change C_3H_6 concentration. During NO_2 experiments about 10% of propylene is oxidized thermally over zeolite catalysts at 300^{o}C and over alumina catalyst at 340^{o}C.

ZEOLITE CATALYST B

Previously, we reported that zeolite catalyst B reduces 70% of NO_x in a plasma-catalyst system [5]. The temperature dependence of the conversion for catalyst B at a constant power of 41 J/l is shown in Fig 2. As seen from the figure, this catalyst is active in the 150-300^{o}C temperature range, but at higher temperatures the conversion decreases.

<u>NO_2 experiments</u>

It is commonly accepted that non-thermal plasma treatment of exhaust gases oxidizes NO to NO_2 [6, 7]. In order to determine if oxidation of NO to NO_2 was sufficient to promote catalytic reduction to N_2 over catalyst

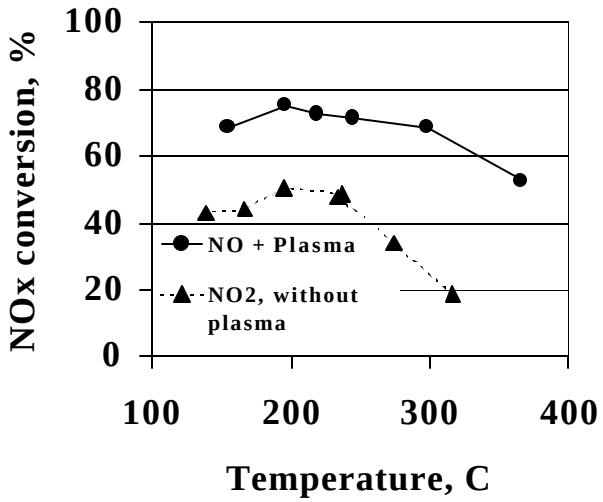

Figure 2. Temperature dependence of NOx conversion over zeolite catalyst B (NO 200ppm, CO 400ppm, C_3H_6 715ppm, O_2 8%, CO_2 7%, H_2O 2%, N_2-balance).

B, NO was replaced with NO_2 and the gases were not treated with plasma. For zeolite catalyst B, the NOx reducing behavior as a function of temperature is similar to that observed with an NO feed and plasma. However the overall NO_x conversion is lower (50% conversion at 230°C). Application of plasma on the reaction mixture containing NO_2 improved catalytic performance of the system (During the NO_2-plasma experiment at 230°C, the conversion reached 60% after 50 min of the plasma exposure. At this point, the NOx concentration did not reach the equilibrium value and was still dropping.)

ALUMINA CATALYST D

Metastable aluminas have been reported to have high activity for thermal NO_2 reduction with propylene between 300°C and 600°C [9] and for NO reduction in combination with a plasma at 400°C and 200°C [6,8]. Therefore, the activity of several alumina catalysts in combination with a plasma was investigated. The catalyst was preheated to 150°C under flowing reaction gases and no reaction was observed without plasma. At temperatures lower than 250°C mostly NO_2 adsorption was observed. From 150 to 200°C, with the plasma on, the NOx adsorbtion increased with

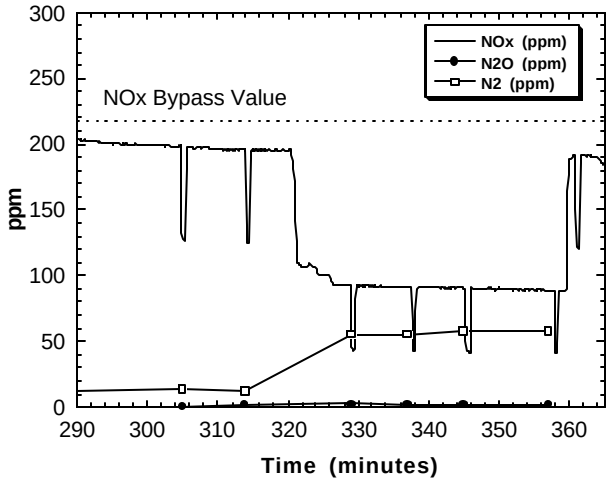

Figure 3. NO_x concentration downstream of the alumina Catalyst D at 340°C (NO_2 200ppm, C_3H_6 715ppm, O_2 8%, H_2O 2%, He-balance Power (20J/l)).

increasing temperature but no significant NO_x reduction was found. Under the experimental conditions (space velocity and NO concentration) at 200°C, alumina was saturated with NO_x after 100 min. At higher temperatures the steady state rate is reached much faster. Above 250°C reaction, rather than adsorption, is taking place. High NOx conversion (81%) with no apparent deactivation was observed when this catalyst was held at 340°C for 18 hours. The observed low temperature NOx uptake can be explained by the fact that NO_2 formed in the plasma, can adsorb on alumina surface in the form of nitrate and nitrite [10]. Thermal decomposition studies of $Al(NO_3)_3$, showed that the mass 30 (NO) profile has two peaks. The major peak is at about 260°C (~80%) and a smaller one is at 600°C (~20%). This data suggests that there should be little nitrate or nitrite formation on the alumina surface at temperatures higher than 260°C. This is consistent with the observation that reaction to nitrogen occurred above 250 °C.

<u>NO_2 experiments and effect of plasma and propylene</u> To confirm the formation of nitrogen during the reaction, nitrogen in the reaction mixture was replaced with helium. In addition, the thermal activity in the absence of plasma with NO_2 replacing NO was investigated. The evolution of NO_x, N_2 and N_2O concentrations during the experiment are presented in figure 3. The plasma was turned on at 320 min and turned off at 260 min. For the alumina catalyst,

with an NO_2 feed and no plasma, 10% NO_x conversion was observed at 340°C. The catalyst is expected to be thermally active at temperatures higher than 400°C, similar to the alumina catalysts reported elsewhere [8, 9]. When the reaction mixture was treated with plasma, the catalyst converted about 65% of NO_2 (350°C) at an input power of 20 J/l. 100% of the converted NO_2 was recovered as N_2, confirming that at this temperature the NO_x loss is not due to adsorption. When propylene was removed from the feed, no NO_x reduction or N_2 formation was found.

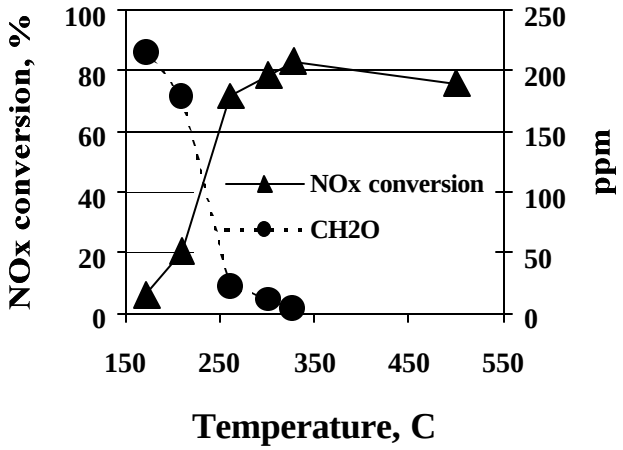

Figure 4. Temperature dependence of NO_x conversion (solid line) and formaldehyde concentration in the gas mixture (dotted line), downstream of the alumina Catalyst D (NO 200ppm, CO 400ppm, C_3H_6 715ppm, O_2 8%, CO_2 7%, H_2O 2%, N_2-balance).

Effect of temperature – The effect of temperature on NO_x reduction over the alumina catalyst when it is downstream from a plasma is shown in Figure 4. The standard simulated exhaust gas composition was used. The catalyst becomes active at 250°C and retains its activity up to 500°C. At high temperatures the catalyst also exhibits some thermal activity in the absence of a plasma (~20% at 500°C). Fig. 4 also shows the change of formaldehyde concentration with temperature.

Aldehydes are formed during plasma treatment of the reaction mixture [11]. The concentration ranges from 150-200 ppm. As seen in Figure, above 250°C the alumina catalyst decreases the concentration of aldehydes from 215 ppm (173°C) to 2ppm (336°C). FTIR data shows that the aldehydes are mostly oxidized to CO.

These experiments and NO_2 experiments revealed that the mechanism for NO_2 reduction may be different for catalysts B and D. While plasma treatment significantly enhances the activity of zeolite catalyst B, this catalyst can also reduce NO_2 to N_2 without prior plasma treatment of the reaction gases. However, at temperatures below 340°C, the alumina catalyst D is not active for NO_2 reduction unless the propylene has been treated by the plasma. During plasma treatment of simulated diesel exhaust, NO is oxidized to NO_2 and propylene is partially oxidized to aldehydes (mainly formaldehyde) [11]. Over the zeolite catalyst, NO_2 can be reduced to N_2 by propylene. However, since plasma treatment improves the NOx reduction performance of zeolite catalyst B, other partially oxidized products formed in the plasma may be more effective reducing agents than propylene. Over alumina Catalyst D, at temperatures less then 340°C, NO_2 is reduced to N_2 mainly by products formed in the plasma, possibly formaldehyde. This assumption is supported by the fact that most of the formaldehyde disappears from the process gas after it passes the alumina catalyst.

TWO LAYER ZEOLITE-ALUMINA CATALYST BED

To achieve good NO_x reduction performance over a larger temperature region, a two-layer catalyst bed was used where alumina catalyst D was placed downstream from zeolite catalyst B. The NO_x removal temperature dependence of the combination of catalysts is shown in Fig. 5 at an overall space velocity of 12,000 h^{-1}.

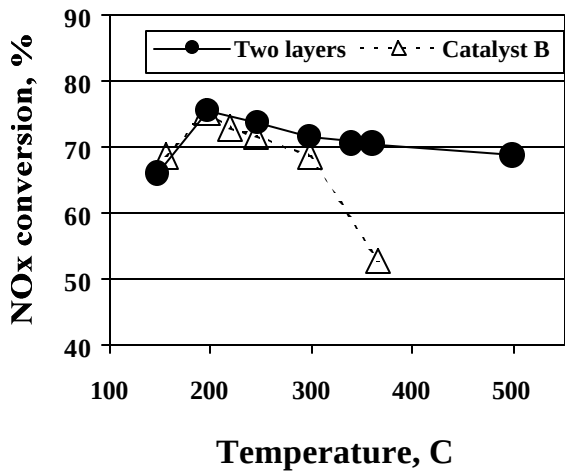

Figure 5. Temperature dependence of NO_x conversion over two-layer (zeolite catalyst B –alumina Catalyst D) catalyst bed (solid line) and zeolite catalyst B (dotted line) (NO 200ppm, CO 400ppm, C_3H_6 715ppm, O_2 8%, CO_2 7%, H_2O 2%, N_2-balance).

Performance of zeolite catalyst B is also shown as a reference. The double layer (alumina Catalyst D – zeolite catalyst B) system exhibited improved performance as compared to the individual catalysts. In particular, the combined catalyst system increased the temperature window over which maximum NO_x conversion is achieved resulting in at least 70% conversion from 150-500°C.

When background nitrogen is replaced with He for the dual catalyst system (physical mixture), complete nitrogen balance was obtained at catalyst temperatures between 260°C and 310°C (Table 2). At 180°C, part of the nitrogen is stored, possibly in a form of NO_2, nitrate and nitrite.

When the temperature increased, the preadsorbed nitrogen compounds evolved mostly as N_2 and N_2O.

FORMALDEHYDE AS A REDUCTANT

As it was mentioned earlier, aldehydes formed during plasma treatment of the simulated exhaust may be active in reducing NO_2 to dinitrogen in the plasma catalyst system.

Table 2: Summary of the nitrogen balance results for the dual catalyst system (space velocity was 20,000 h^{-1} and 2 cm^3 of oxidation catalyst (Pt/Al_2O_3) was downstream of catalysts B and D in the same reactor)

T, °C	NO_x, reacted	N_2, ppm	N_2O, ppm	N recovered as N_2 and N_2O, %
180	117 (48%)	25 (58%)	18 (42%)	73.5
260	164 (67%)	48 (59%)	33 (41%)	99
310	120 (49%)	41 (70%)	18 (30%)	99

Separate experiments were performed to evaluate the NO_2 reducing ability of formaldehyde, one of the major products of partial oxidation of propylene during the plasma treatment.

At 197°C with formaldehyde replacing propylene and NO2 as NOx source, no thermal activity was found when zeolite catalyst B was used as the catalyst. Part of the NO_2 was converted to NO and part of the formaldehyde was oxidized to CO and CO_2. Plasma treatment of the reaction mixture did not bring about any changes in activity

In the case of the alumina catalyst, with formaldehyde as the reductant, 12% thermal conversion was observed at 310°C. As expected, most of the formaldehyde is completely oxidized at this temperature. Similar to zeolite catalyst B, there were some NO_2 to NO conversion.

Results of these experiments suggest that for both catalysts, formaldehyde is not the key compound for reduction of NO_2 to N_2 during plasma catalyst treatment of simulated exhaust.

FORMATION OF N_2O DURING PLASMA-CATALYST REDUCTION OF NOx

Nitrous oxide is a powerful green-house gas. High concentrations of N_2O in the nitrogen balance experiments (Table 2) appear to be due to the presence of the Pt/Al_2O_3 oxidation catalyst downstream of the catalyst bed. When nitrogen was used as the balance gas and the oxidation catalyst was not applied, the concentration of N_2O for all the tested catalysts was decreased to 10-12 ppm. Therefore 12-20% of the reacted NOx is reduced to N_2O. We also found that in an N_2 carrier, N_2O is partially formed in the plasma region (5 - 7 ppm). Alternatively, with He as a balance gas, no N_2O is formed (below the detection limit). This may suggest that N_2O is produced by a reaction with species formed from plasma-treated N_2. The mechanism of nitrous oxide formation during the reaction of simulated diesel exhaust is beyond the scope of this paper and was not studied in detail.

CONCLUSIONS

The effect of temperature, propylene, and plasma treatment on NO_x reduction over two catalysts was investigated. NO is converted to NO_2 in the plasma reactor and NO_2 is reduced to dinitrogen over catalysts. Over the zeolite catalyst B significant thermal NO_2 reduction was observed with propylene as the reductant, but addition of plasma treatment further increased the catalyst's activity. Over alumina catalyst D, at low temperatures, thermal reduction of NO_x with propylene was minor. Plasma treatment of the NO_2 and propylene containing reaction mixture at low temperatures resulted in high catalytic activity. Therefore plasma treatment generates compounds (probably partially oxidized hydrocarbons) critical for NO_2 reduction over alumina catalyst.

One of the major products of partial oxidation of propylene during the plasma treatment is formaldehyde. However, formaldehyde was found unimportant for NO_2 reduction over both, zeolite catalyst B and alumina catalyst D.

The zeolite and alumina catalysts are active in different temperature ranges. A catalyst bed consisting of both catalysts produces a catalytic system active between 150 and 500^{o}C.

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