LEAN NO_X REDUCTION BY PLASMA ASSISTED CATALYSIS

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INTRODUCTION

The widespread use of light duty diesel engines in the United States would naturally lead to a large reduction of fuel consumption, due to their generally higher efficiency. By extension, savings in fuel consumption would decrease the total CO_2 emitted from mobile sources. Although this is a desirable goal, at present a major stumbling block to increased diesel engine use is the difficulty in reducing noxious exhaust components, mainly NO_x and particulates, to acceptable levels. We are studying the possibility of reducing NO_x emissions through the combination of non-thermal plasma with appropriate catalysts. The broad outline of how this technique works has been worked out both experimentally and theoretically.[1-3] The presently accepted model is that a non-thermal plasma in the presence of water, oxygen and hydrocarbon will efficiently convert NO to NO_2, while only partially oxidizing the hydrocarbon present. Some catalysts will reduce NO_2 (but not necessarily NO) in the presence of excess oxygen if the proper hydrocarbon is present. In this paper we report results using non-thermal plasma in conjunction with a commonly available zeolite catalyst, NaY, to treat synthetic diesel exhaust. We focus on details of the heterogeneous chemistry on NaY by comparing the thermal and plasma driven chemistry.

EXPERIMENT

Details of our experiment have been published elsewhere, so only a brief summary is included here.[4] Synthetic exhaust gas was created by blending gases from cylinders of known composition using mass flow controllers. Besides NO, the exhaust mixture included CO, CO_2, propylene, water, oxygen and nitrogen. A typical mixture contained 6% oxygen, 2% water, and, unless otherwise noted, a 3:1 ratio of propylene to NO_x. This corresponds to a 9:1 ratio on a C1 basis. CO and CO_2 were sometimes included, but we found that their presence did not materially affect our results. For nitrogen balance experiments we omitted CO and CO_2 and replaced the nitrogen bath gas with helium.[4]

The bulk of the data was obtained using a chemiluminescent NO_x analyzer (CLA) to monitor NO and NO_2. Nitrogen was determined by GC analysis. The N_2O concentration was monitored by either GC or FTIR.

Sodium Y was obtained as extrudates and in powder form from Zeolyst International as CBV 100 molecular sieve. The extrudates were used as received in a packed bed configuration. The powder was used to coat standard untreated honeycomb monoliths such as are commonly used to support automobile catalysts.

For the experiments reported here we separated the discharge and heterogeneous chemistry into separate steps as shown in Figure 1. A double dielectric barrier discharge reactor was used to cre-

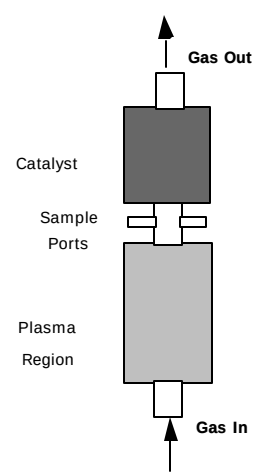

Fig. 1: Conceptual design of a 2-step discharge reactor.

ate a plasma catalyst. The plasma chemistry was studied by sampling between the plasma and catalyst. The power deposited into the reactor was measured with a capacitive circuit and a high voltage probe.[5,6]

RESULTS AND DISCUSSION

The gas phase plasma chemistry has been discussed in detail in earlier publications.[1-3] Basically oxygen atoms formed by the discharge react fastest with hydrocarbons, creating organic peroxides and other oxidized species. The peroxides react with NO to yield NO_2. The presence of hydrocarbons thus encourages NO conversion to NO_2 while inhibiting formation of nitric oxide (from ambient nitrogen) and nitric acid by sinking most of the O and OH radicals formed.

Figure 2 illustrates the dependence of the NO_x and NO concentrations on the deposited plasma energy. Only a very small amount of N_2O was formed, with the rest of the NOx loss probably due to nitric acid or organic nitrate or nitrite formation. As can be seen, at roughly 15J/l of energy deposited NO was efficiently converted to NO_2. The precise energy required depends linearly on the NO concentration, and also varies with plasma temperature. No significant chemical reduction occurs in the plasma, as experiments have demonstrated that the missing NO_x can be recovered by placing a heated platinum catalyst downstream of the plasma.[7] The NO to NO_2 conversion is completed at an energy where the propylene is only 30-50% oxidized. This is an important result, as the remaining hydrocarbon is therefore available as a reductant in the catalytic step.

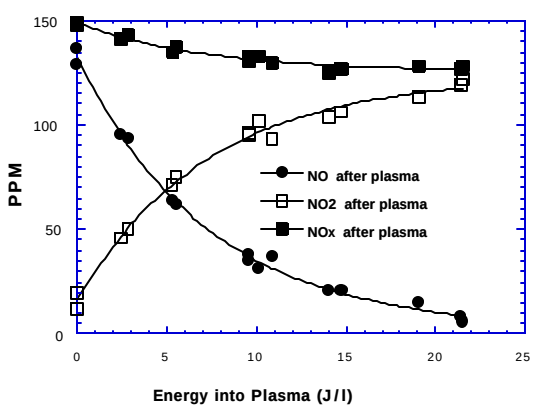

Figure 2: Plasma energy dependence of NO, NO_2 and NO_x concentrations in synthetic diesel exhaust.

As shown in Figure 3, at constant plasma energy the oxidation of NO to NO_2 is greatly facilitated by added hydrocarbon. We find that a C1 to NO ratio of between 6 and 9 to 1 is necessary for optimum conversion of NO to NO_2.

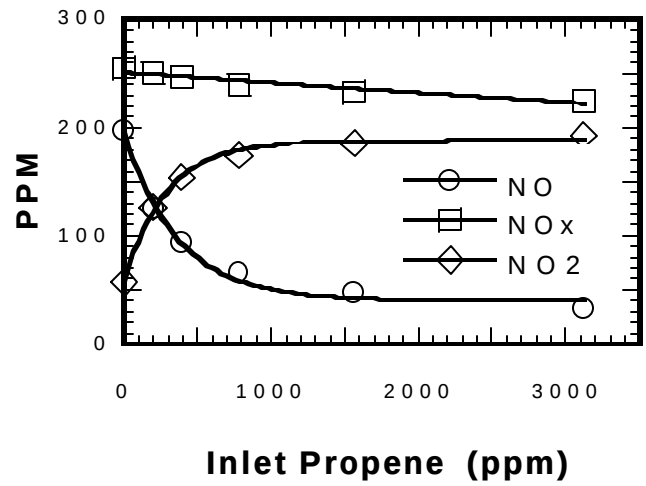

Figure 3: Propylene dependence of NO, NO_2 and NO_x concentrations in synthetic diesel exhaust at constant plasma energy. NO_x in was 250 ppm; a 9:1 ratio of C1: NO_x occurred at 750 ppm propene.

If the output of our non-thermal plasma is passed over a bed of NaY held at 180° C the total NO_x detected drops quite dramatically as a function of the deposited energy. Figures 4 and 5 illustrate the effect of varying the deposited energy or the hydrocarbon concentration. The similarity of both the energy and hydrocarbon dependence with the gas phase NO_2 production is striking. We note that with the plasma turned off there is essentially no conversion, indicating that NO does not react with propylene on this catalyst. As we discuss later, when we change NO to NO_2 in the feed gas we do see a thermal reaction, although the reaction is slow and the overall NO_x loss is limited to roughly 25%. These results suggest that the dominant heterogeneous chemistry involves reactions of NO_2 rather than NO.

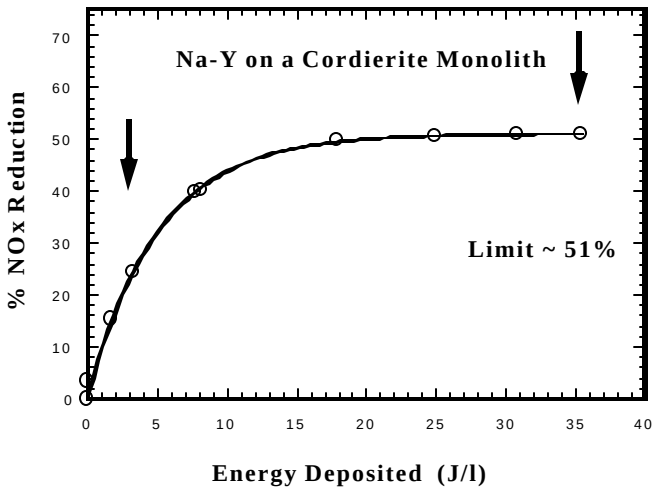

Figure 4: NO_x **reduction over Na-Y as a function of plasma energy. Thermal conversion is very low. Arrows correspond to values of curves in Figure 5.**

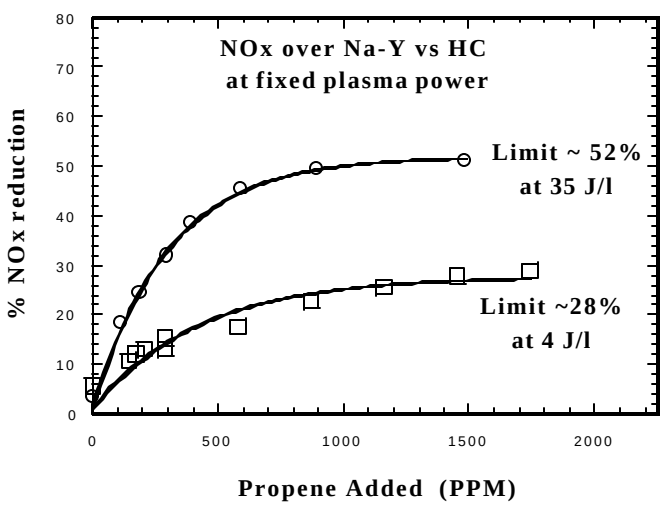

Figure 5: NO_x **reduction over Na-Y as a function of propylene input concentration at 2 different plasma energies. Data were taken where the arrows on Figure 4 indicate.**

We have measured the efficiency of NO_x reduction over NaY between 150° to 400° C. These experiments were done over extrudates, at a space velocity of 12000/Hr, calculated from the volume of catalyst used. As shown in Figure 6, a relatively high % conversion was observed over a broad temperature range. There was some scatter in the data due to changes in plasma energy, the space velocity and the form of the catalyst. However the shape of the high temperature drop-off was always similar to that shown. The maximum efficiency was found near 200°C. Below 175° the efficiency drops again, but our data was less certain due to the large amount of NO_2 adsorption that occurs. With green (i.e. new) catalyst in our reactor we sometimes observe over 70% peak conversion, but after running a few hours the conversion typically drops to between 60 and 70%. For light duty diesel applications the range of greatest interest is between 180 and 300 °C.

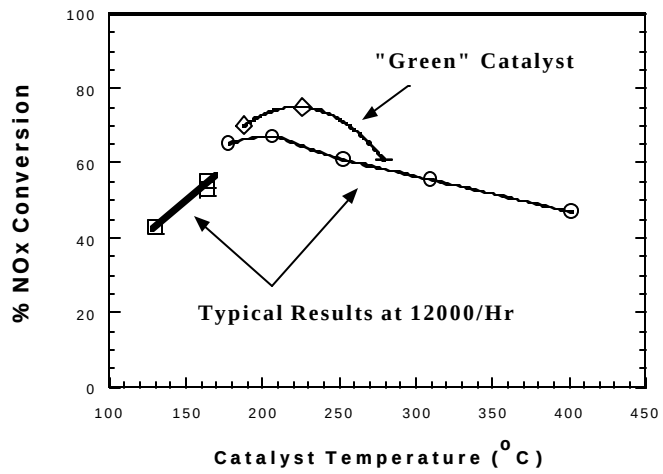

Figure 6: Temperature dependence of the NO_x **conversion over Na-Y extrudates. Data is from 3 separate experiments. Diamonds were with green catalyst.**

The experiments described above actually only report the NO_x lost as determined by a chemiluminescent NO_x meter. The possibility exists that the missing has been either adsorbed on the catalyst or simply converted to nitrogen containing species that are undetectable in the CLA. In order to determine whether NO_x "loss" could be due to simple adsorption onto the zeolite we measured the NO_x conversion at steady state in an experiment, which lasted approximately 70 hours. At the end of the experiment the catalyst was heated to 570 °C while monitoring for any desorbing NOx. Surface nitrates or nitrites would decompose as NOx under these conditions. As can be seen in Figure 7, the total NO_x recovered only accounted for 3% of the total NO_x missing. Furthermore there is no sign of NO_x breakthrough, even after 70 hours.

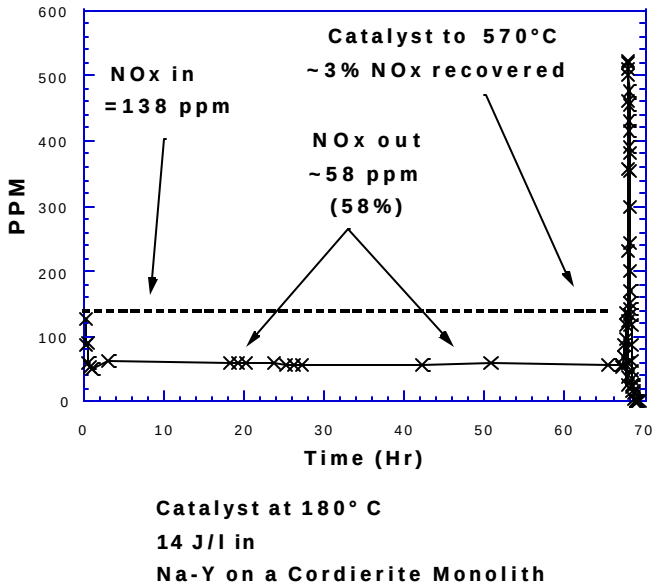

Figure 7: The reactor was operated at constant energy, flow and temperature for nearly 3 days. Only 3% of the converted NO_x was recovered upon heating the catalyst to 570 °C.

Experiments such as the one illustrated in Figure 7, as well as post-experiment examination of the catalyst indicated that only a small fraction of the conversion could be explained by absorption on the zeolite itself. Nevertheless we cannot definitively conclude that the NO_x is being chemically reduced since we are unable to detect product N_2. In order to do so we ran a series of experiments in which the nitrogen in our synthetic exhaust was replaced by helium. Although the energetic requirements of our plasma were drastically reduced, we could see no change in the plasma chemistry, at least as far as NO to NO_2 conversion was concerned. With the nitrogen removed we used a gas chromatograph to detect product nitrogen. For these experiments we reduced the oxygen to 2% in order to ensure a good separation between the oxygen and nitrogen peaks.

Figure 8 illustrates the NO_x reduction behavior of NO in helium at 227 and 280°C. With the plasma off, we observed only a small, transient NO absorbance. The thermal conversion was less than 10%, as expected (see Fig. 3). Turning the plasma on converted the NO to NO_2 and led to an immediate disappearance of NO_x in the outlet gas. The measured NO_x out, which was nearly 100% NO, actually undershot the final value, taking over 20 minutes to stabilize. The detected N_2 and N_2O signal had the same equilibration time. When we raised the catalyst temperature to 280°C, there was a short burst of both NO and N_2, after which the system stabilized at a lower NO_x destruction efficiency.

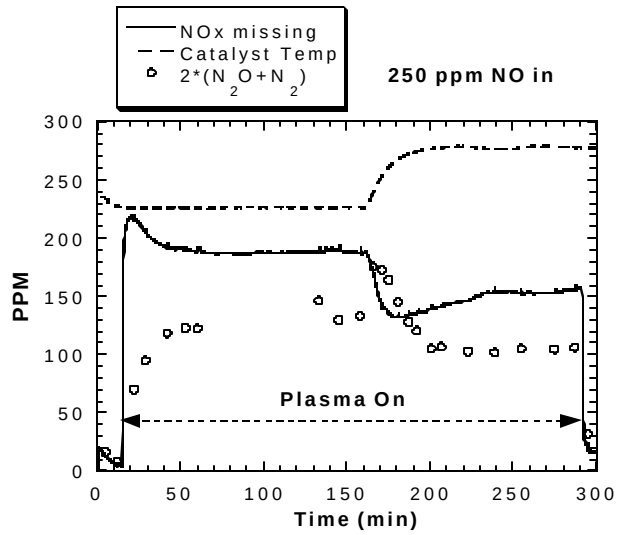

Figure 8: Nitrogen balance experiment for NOx as NO on NaY. NOx in was 250 ppm NO.

At the power level used we know that essentially all NO was converted to NO_2 in the plasma. The long equilibrium time suggests that reduction occurred only after a sufficient surface coverage of NO_2 (and possibly partially oxidized hydrocarbon) was attained. The final NOx destruction efficiency as measured by the CLA was 71%, but the reduction efficiency as measured by product N_2 and N_2O was only 53%. At higher catalyst temperature the overall reduction efficiency dropped, with nearly the same percent nitrogen recovered.

We also monitored the propylene, CO, CH_2O and methanol concentrations. The overall propylene loss held steady at 225 ppm, with no noticeable change from raising the catalyst temperature. Essentially all of the propylene reaction occurred in the plasma, which suggests that propylene is *not* the reductant. We were not able to identify which organic species is the reductant, but we can say that neither formaldehyde nor CO appear to be involved.

Figure 9 shows our results at lower temperatures. Surprisingly we find essentially complete nitrogen balance at 135 °C, but lose the balance as the temperature is raised. Even though the NOx conversion is higher at 165 °C, the net recovery of N_2 and N_2O is not significantly changed. It appears that an unknown loss channel opens up in this temperature range. The net nitrogen recovery at 165 °C is very similar to that found at higher temperatures, suggesting that the branching ratio to

this undetected species is relatively constant between 165 and 280 °C.

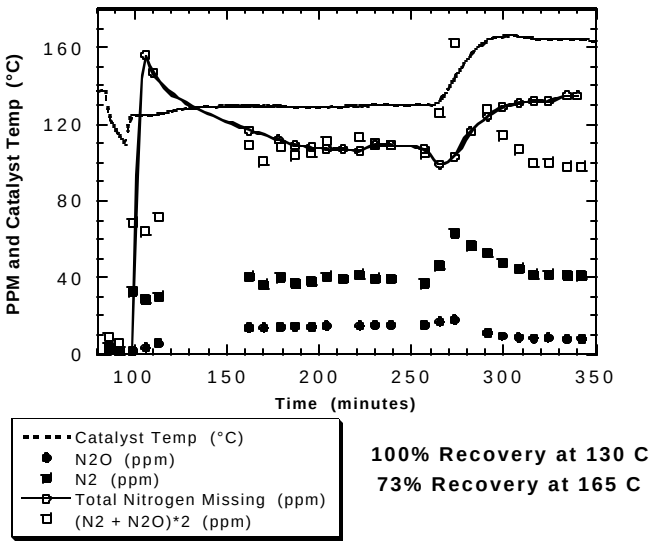

Figure 9: At 130 °C we recover 100% of the missing NOx as N_2 or N_2O. Raising the temperature to 165 increases the apparent NO_x conversion without any net increase in nitrogen recovered as N_2O + N_2.

In order to test the hypothesis that the important reactions over Na-Y involve NO_2 we ran similar nitrogen balance experiments using NO_2 in the feed gas rather than NO. As can be seen from the figure, at 230°C NO_2 is very strongly absorbed by NaY.

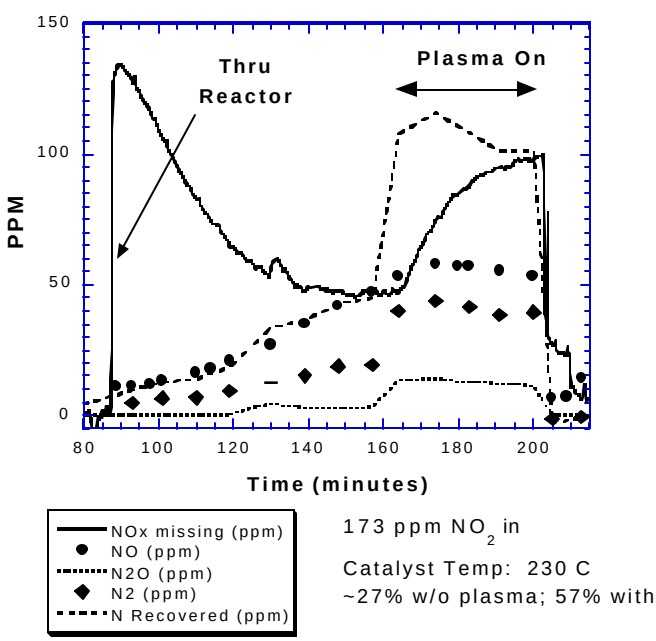

Figure 10: Nitrogen balance for NO_2 on NaY. Note the extremely long time constant for thermal equilibrium.

The time constant for thermal equilibrium of the NO_x out and the N_2 and N_2O detected are the same. Furthermore at equilibrium 100% of the nitrogen missing is detected as N_2 + N_2O. However, the overall conversion is disappointingly low when compared to the plasma + NO case. A signifycant increase in the NO_x conversion occurred when we turned on the plasma, even though there was no apparent change in the NO concentration. The size of the effect is quite large, with the NO_x missing increasing from 27 to 53%. This observation strongly supports our earlier suggestion that NO_x reduction over NaY is more efficient with one or more partially oxidized propylene products than with propylene itself.

Conclusion

We have looked closely at the plasma assisted catalytic reduction of NO_x on one candidate catalyst, NaY. Our data suggest that the importance of the plasma is twofold. First, in the presence of sufficient hydrocarbon, the plasma efficiently oxidizes NO to NO_2. The subsequent reaction of NO_2 on NaY is greatly enhanced by the presence of partially oxidized hydrocarbon produced by the plasma. Plasma-catalysis treatment of NO_x as either NO or NO_2 produces comparable amounts of N_2 and N_2O products. However the apparent reduction is much higher for NO due to an unidentified product formed in the process.

Acknowledgments

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