

# MULTI-STAGE SELECTIVE CATALYTIC REDUCTION OF NO<sub>x</sub> IN LEAN BURN ENGINE EXHAUST

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## INTRODUCTION

Many studies suggest that the conversion of NO to NO<sub>2</sub> is an important intermediate step in the selective catalytic reduction (SCR) of NO<sub>x</sub> to N<sub>2</sub> [1 -5]. Some effort has been devoted to separating the oxidative and reductive functions of the catalyst in a multi-stage system [6]. This method works fine for systems that require hydrocarbon addition. The hydrocarbon has to be injected between the NO oxidation catalyst and the NO<sub>2</sub> reduction catalyst, as shown in Figure 1; otherwise, the first-stage oxidation catalyst will also oxidize the hydro-carbon and decrease its effectiveness as a reductant. The multi-stage catalytic scheme is appropriate for diesel engine exhausts since they contain insufficient hydrocarbons for SCR, and the hydrocarbons can be added at the desired location. For lean-burn gasoline engine exhausts, the hydrocarbons already present in the exhausts will make it necessary to find an oxidation catalyst that can oxidize NO to NO<sub>2</sub> but not oxidize the hydrocarbon.

A plasma can also be used to oxidize NO to NO<sub>2</sub>. Plasma oxidation has several advantages over catalytic oxidation. Plasma-assisted catalysis work can well for both diesel engine and lean-burn gasoline engine exhausts. This is because the plasma can oxidize NO in the presence of hydrocarbons without degrading the effectiveness of the hydrocarbon as a reductant for SCR. In the plasma, the hydrocarbon enhances the oxidation of NO, minimizes the electrical energy requirement, and prevents the oxidation of SO<sub>2</sub>.

This paper discusses the use of multi-stage systems for selective catalytic reduction of NO<sub>x</sub>. The multi-stage catalytic scheme is compared to the plasma-assisted catalytic scheme.

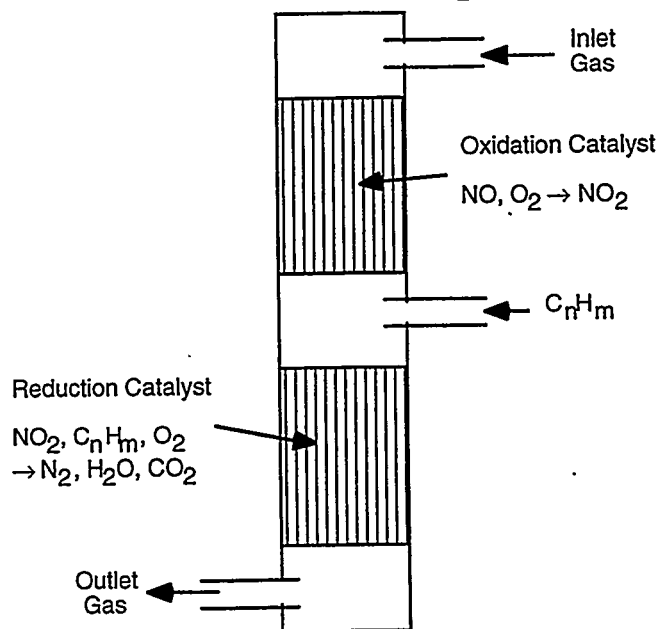


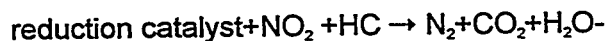
Figure 1. Multi-stage SCR scheme using an oxidation catalyst to convert NO to NO<sub>2</sub> and then a reduction catalyst to convert NO<sub>2</sub> to N<sub>2</sub>.

## MULTI-STAGE CATALYTIC SCHEME

The multi-stage selective catalytic reduction of NO<sub>x</sub> is accomplished in two steps. First, an oxidation catalyst converts NO to NO<sub>2</sub> in the absence of a hydrocarbon:



Then, a reduction catalyst reduces NO<sub>2</sub> to N<sub>2</sub> by selective reduction using hydrocarbons:



Multi-stage SCR has several advantages over conventional SCR. First, the multi-stage scheme offers high NO<sub>x</sub> reduction efficiency from catalysts that, separately, are not very active for reduction of NO. Second, the multi-stage scheme alleviates the problem of

selectivity between NO reduction and hydrocarbon oxidation. The important NO<sub>2</sub> intermediate is formed without consuming the hydrocarbon reductant.

Figure 2 shows the FTIR spectra of the process for a model exhaust gas consisting of 500 ppm NO, 10% O<sub>2</sub> and balance N<sub>2</sub>. The first-stage oxidation catalyst is Pt-based. The second-stage catalyst is essentially the same material but without the Pt. The hydrocarbon, 500 ppm (C<sub>3</sub>) propene, is injected between the oxidation catalyst and the reduction catalyst. The temperature of both catalysts is 3000C.

The spectrum of the inlet gas is shown in the top box ("inlet") of Figure 2. Without the oxidation catalyst (i.e., first stage is removed), the NO<sub>x</sub> reduction efficiency is very low, as shown in the second box ("outlet without oxidation catalyst"). The NO<sub>x</sub> reduction at this temperature is very low even in the presence of a hydrocarbon reductant.

When the gas stream is first passed through the oxidation catalyst, the NO is oxidized to NO<sub>2</sub>, as shown in the third box ("after first catalyst"). The NO<sub>x</sub> reduction is still very low. The same amount of total NO<sub>x</sub> (NO + NO<sub>2</sub>) is left in the gas stream.

When the NO<sub>2</sub>-containing gas stream from the first catalyst is mixed with the hydrocarbon reductant and then passed through the second catalyst, both the NO<sub>x</sub> and the hydrocarbons are eliminated, as shown in the bottom box ("after second catalyst"). The NO<sub>2</sub> is chemically reduced to N<sub>2</sub> on the second catalyst.

### PLASMA-ASSISTED CATALYTIC SCHEME

The oxidation of NO to NO<sub>2</sub> can also be accomplished with a plasma. The chemistry behind the plasma oxidation of NO is presented in an accompanying paper in this proceedings [7].

This section will present the advantages of plasma oxidation over catalytic oxidation.

The multi-stage catalytic scheme requires the injection of hydrocarbon between the NO

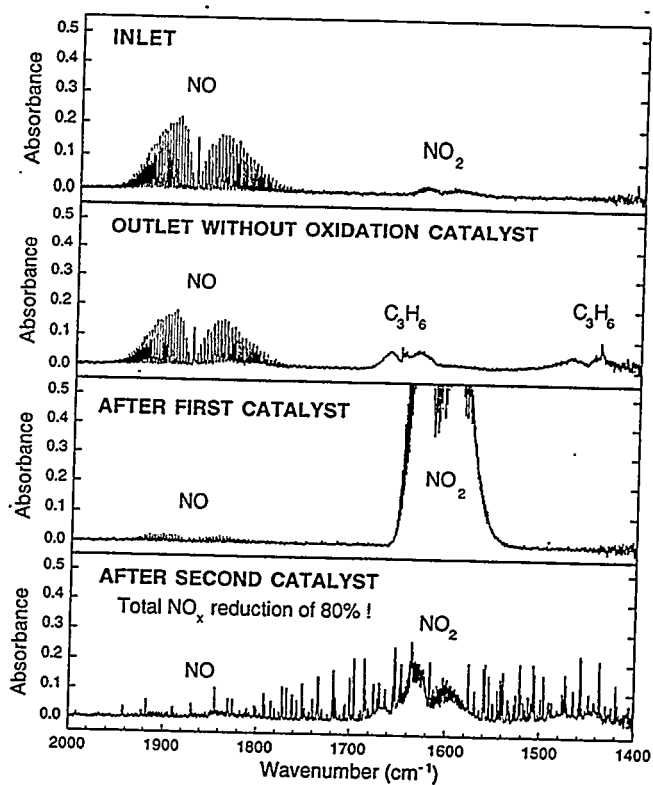


Figure 2. FTIR spectra showing the multi-stage selective catalytic reduction of NO<sub>x</sub>

oxidation catalyst and the NO<sub>2</sub> reduction catalyst. This is necessary because the oxidation catalyst will also oxidize the hydrocarbon and decrease its effectiveness as a reductant. The plasma can oxidize NO in the presence of hydrocarbons without degrading the effectiveness of the hydrocarbon as a reductant for SCR. Plasma assisted catalysis therefore works well for both diesel engine and lean-burn gasoline engine exhausts. The hydrocarbon in the plasma is actually beneficial. In the plasma, the hydrocarbon enhances the oxidation of NO, minimizes the electrical energy requirement of the plasma reactor, and prevents the oxidation of SO<sub>2</sub>. During the oxidation of NO to NO<sub>2</sub>, the plasma oxidizes a fraction of the hydrocarbons, but leaves partially oxygenated hydrocarbon products that are as least as effective as the original hydrocarbons.

Catalytic oxidation has a limited temperature operating range. Figure 3 shows the efficiency for oxidation of NO to NO<sub>2</sub> by a Pt-based catalyst in a model exhaust gas consisting of 500 ppm NO, 10% O<sub>2</sub>, and balance N<sub>2</sub>. The

oxidation efficiency maximizes at 2500C. The efficiency drops substantially at temperatures below 2000C. The efficiency also drops substantially at temperatures above 4000C. It is therefore important to match the temperature operating condition of the oxidation catalyst with that of the reduction catalyst.

Plasma oxidation of NO in the presence of hydrocarbons can have high efficiency over a wide range of temperatures. Figure 4 shows the efficiency for plasma oxidation of NO to N<sub>2</sub> in a model exhaust gas consisting of 500 ppm NO, 1000 PPM (C<sub>3</sub>) propene, 10% O<sub>2</sub> and balance N<sub>2</sub>.

## CONCLUSIONS

Multi-stage SCR offers high NO<sub>x</sub> reduction efficiency from catalysts that, separately, are not very active for reduction of NO, and alleviates the problem of selectivity between NO reduction and hydrocarbon oxidation. In multi-stage SCR, either an oxidation catalyst or a plasma can be used to convert NO to NO<sub>2</sub>, followed by a reduction catalyst to convert NO<sub>2</sub> to N<sub>2</sub>. The use of a plasma for the oxidation of NO offers several advantages over catalytic oxidation. The plasma method works well for both diesel engine and lean burn gasoline engine exhausts. The plasma can oxidize NO in the presence of hydrocarbons without degrading the effectiveness of the hydrocarbon as a reductant for SCR.

## ACKNOWLEDGMENTS

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## REFERENCES

1. Shelef, M., Montreuil, C.N., and Jen, H.W., *Catalysis Letters* 26 (1994) 277.
2. Bethke, K.A., Li, C., Kung, M.C., Yang, B.,

et al., *Catalysis Letters* 31 (1995) 287.

3. Yokoyama C., and Misono, M., *Journal of Catalysis* 150 (1994) 9.

4. Lukyanov, D.B., Sill, G., Ditre, J.L., and Hall, W.K., *Journal of Catalysis* 153 (1995) 265.

5. Beutel, T., Adelman, B.J., Lei, G.D., and Sachtler, W.M.H., *Catalysis Letters* 32 (1995) 83.

6. Iwamoto, M., Hernandez, A.M., and Zengyo, T., *Chemical Communications* Jan 7 (1997) 37.

7. Penetrante, B.M., et al., "Effect of Hydrocarbons on Plasma Treatment of NO<sub>x</sub>", Proceedings of the 1997 Diesel Engine Emissions Reduction Workshop.

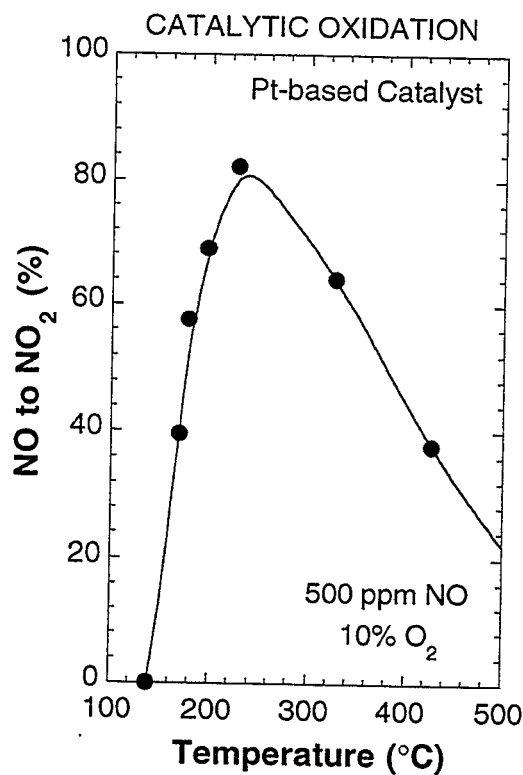


Figure 3. NO to NO<sub>2</sub> oxidation efficiency of a Pt-based catalyst for a model exhaust gas.

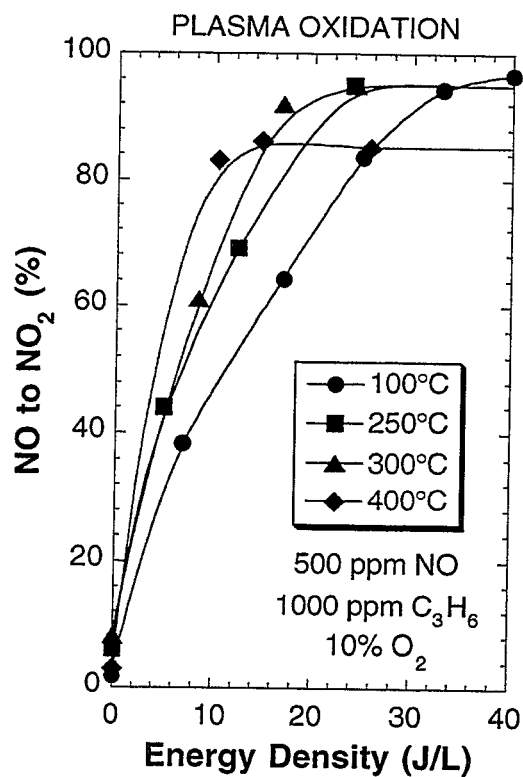


Figure 4. Effect of temperature and input electrical energy density on the efficiency for plasma oxidation of NO to NO<sub>2</sub> in a model exhaust gas.