NO_x - Reduction in Synthetic Air by Dielectric Barrier Discharges

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Abstract - We report our experimental results on the removal of NO and NO_2 from synthetic air by dielectric barrier discharges. The initial NO and H_2O concentrations and gas temperature were varied. The final concentrations of NO and NO_2 were measured as a function of discharge power. A reduction of ([NO]+[NO_2]) by up to 90 % was possible. With increasing $[H_20]_{in}$ the removal becomes more efficient. The measured specific energies range down to 90 eV/molecule.

Introduction

Exhaust gas treatment devices suitable for automotive applications have to be compact and energy-efficient. An additional fuel consumption of less than 7 % is generally believed to be acceptable. A linear model [1] which relates the energy ρ required to remove one NO_x molecule to the additional fuel consumption reveals that ρ should be less than 30 eV to keep the additional fuel consumption below 7 %. In the model calculation it was assumed that the NO_x emission of a Diesel engine which nowadays can be reduced to 5g/kWh by advanced motor concepts alone is to be further diminished to 2 g/kWh which is typical for a spark ignited internal combustion engine fitted with a three way catalytic converter.

Among others non-equilibrium plasma processes are gaining importance [2] as a means for exhaust gas treatment. Corona discharges [3], microwave discharges[4] and surface discharges [5] have already been proposed for exhaust gas cleaning. Dielectric barrier discharges have been used for gas remediation in the form of dielectric packed bed reactors [6] and in planar geometry [7].

The ignition of a dielectric barrier discharge is started by avalanche growth and streamer propagation. In the streamer head energetic electrons are present which are able to excite high-lying molecular states and to dissociate and ionize molecules by collisions [8]. Most of the relevant radicals are created in this phase. After the rather short discharge phase the ions, radicals and metastables continue to react with each other until only stable particles remain. This reaction regime lasts into the millisecond

range [9]. Due to the current self - chopping in the barrier discharge it may be operated with sinusoidal voltage without the need for switching elements. It is these properties that make the barrier discharge a promising candidate for the remediation of automotive exhaust gases. We have therefore investigated the removal of NO_x from synthetic air mixtures containing N_2, O_2, H_2O and NO in barrier discharges with the aim to find out the limits for the degree of decomposition and the specific energy ρ per molecule of toxic gas.

Experiment

The experiments were carried out in a concentric discharge reactor equipped with a gas mixing system, power supply and electrochemical gas detection system. A schematic view of the set-up is given in Fig. 1. In the experiments discharge power, residence time, and initial NO- and H_2O-concentrations $[NO]_{in}$ and $[H_2O]_{in}$ were varied. The concentrations of NO and NO_2 were measured with electrochemical sensors as a function of the discharge power.

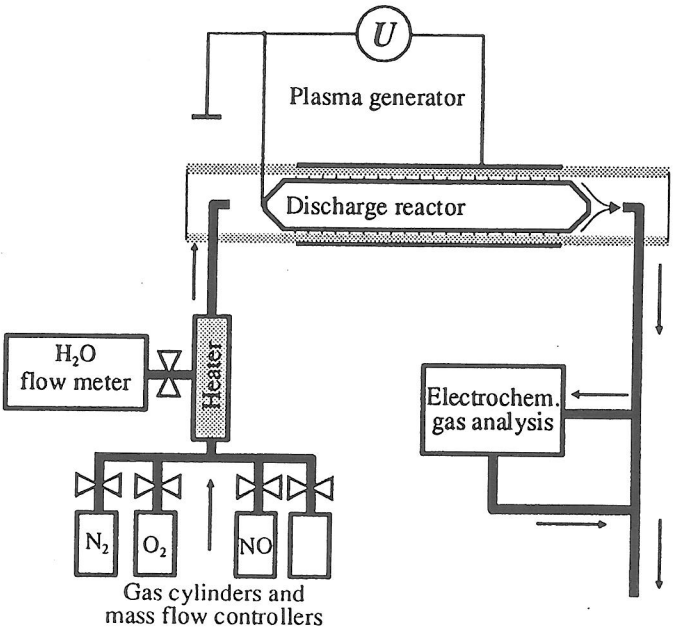

Fig. 1: Schematic view of the experimental set-up used to measure the decomposition of NO and NO_2 in synthetic air in a dielectric barrier discharge.

The reactor consisted of an alumina tube of 47 mm inner diameter, the outer surface of which was coated with a metal layer on a length of 200 mm forming the outer electrode, and a coaxial stainless steel cylinder forming the inner electrode. The

gap width was 0.75 mm in the present experiments. The gas was fed axially through the gap between tube and cylinder with standard flow rates of up to 50 l / min. The gases N_2, O_2, and NO were supplied by gas cylinders and mass flow controllers. H_2O was fed through a liquid flow controller and added to the gas stream in a heated section of the tubing. To ensure well defined temperature conditions, the gas was heated in the tube before entering the reactor, and the reactor itself was also heated to the same temperature. The minimum inlet temperature at the reactor entrance was 100 °C because lower temperatures led to condensation of water on the insulator.

A part of the exhaust gas stream exiting the reactor was pumped through a dryer and an electrochemical sensor unit for composition analysis which provided direct reading of NO, NO_2, CO and SO_2. The values were corrected for the water content known from the liquid water flow.

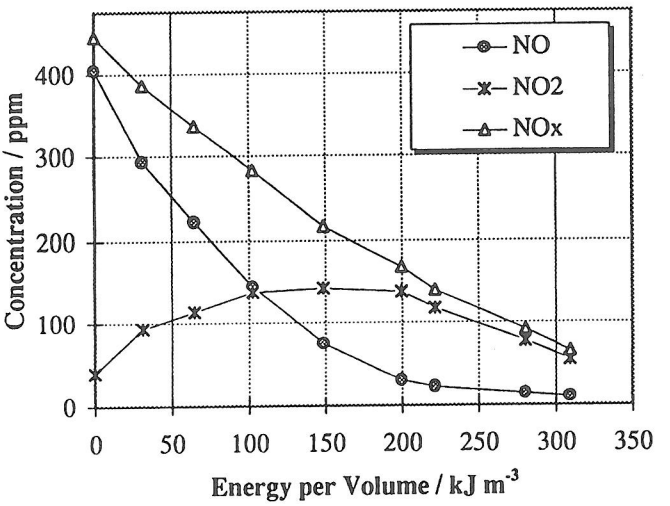

Fig. 2: Removal of NO and NO_2 by a barrier discharge as a function of the discharge power per gas flow. The parameters were: 1 kHz sine-wave excitation, 68 % N_2, 12 % O_2, 20 % H_2O, 500 ppm NO, 100 °C.

High voltage was applied between the coaxial electrodes of the reactor by either a high voltage transformer at mains frequency (50 Hz), a pulse generator delivering bipolar high-voltage pulses with rise times of 5 µs and repetition rates between 0.5 and 5 kc/s, or a power amplifier with an impedance matching network at frequencies between 30 and 100 kHz. In either case the discharge power was measured by integrating the voltage - charge curve measured on a digital storage oscilloscope as described in [10].

Experimental results

The removal of NO / NO_2 from synthetic air in the barrier discharge reactor is shown in Fig. 2 as a function of the ratio of discharge power and gas flow rate at standard conditions. The later quantity equals the energy coupled into the discharge per standard gas volume. This will be used as variable throughout this paper instead of discharge power. The initial NO concentration was 500 ppm. The observed initial NO_2 - concentration without discharge is formed from NO in thermodynamic equilibrium according to the equation $2\ NO + O_2 \rightarrow 2\ NO_2$ [11]. For low power a drastic reduction of [NO] with increasing power is observed while NO_2 is formed. At higher power $[NO_2]$ goes through a maximum and then starts to decrease again. The sum of both concentrations is always decreasing with increasing energy per volume.

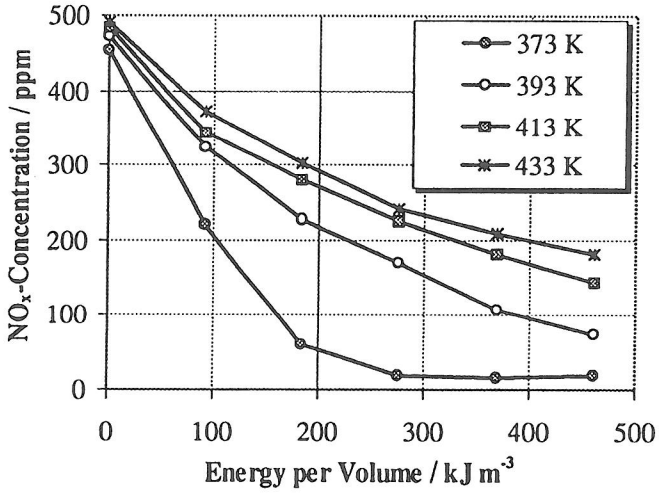

Fig. 3: NO_x removal versus specific discharge energy for various inlet gas temperatures. Pulsed excitation, f = 1 kHz; $[NO]_{in}$ = 500 ppm; $[H_2O]$ = 20 %; $[N_2]$ = 64 %; $[O_2]$ = 16 %;

The formation of NO_2 from NO in the presence of a discharge is mostly due to reactions with O, N, NO_3, HO_2, and O_3 [11]. If a certain degree of reduction is to be achieved the number of discharge pulses applied to a volume element passing through the reactor has to exceed a minimum value.

It is observed in the experiments that the removal efficiency drastically increases with increasing NO content. This behavior can be understood if one takes into account

that for very low concentrations of NO many reactive radicals do not encounter a toxic molecule before they recombine and thus are lost. This result does not limit the applicability of the method since in practical applications it will not be important to reduce the toxic content to a certain fraction of the initial value but rather to a constant fixed value. Therefore for lower toxic concentrations a lower degree of removal may also be sufficient.

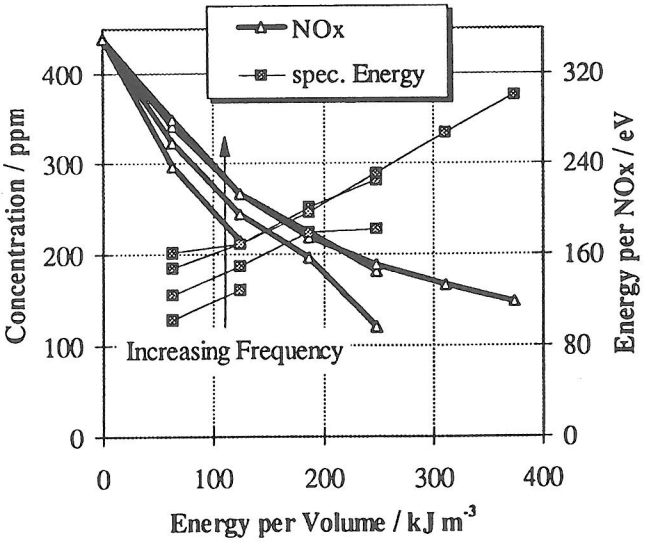

Fig. 4: NO_x concentrations (bold curves) and energy ρ per NO_x molecule versus specific discharge energy for pulsed excitation at frequencies 250 Hz, 500 Hz, 1000 Hz and 2000 Hz (increasing in direction of arrow); inlet gas temperature 120 °C; $[NO]_{in}$ = 500 ppm; $[H_2O]$ = 20 %; $[N_2]$ = 64 %; $[O_2]$ = 16 %;

In Fig. 3 the influence of increased inlet temperatures on NO_x decomposition is shown. Higher temperatures lead to a reduction in removal efficiency as compared to 100 °C. The reason is the temperature dependence of the heavy particle gas-phase reaction constants.

In Fig. 4 the influence of the excitation frequency on the removal efficiency is shown together with the energy input per molecule of removed NO_x.. For low powers the energy ranges down to ρ = 90 eV while it increases for higher power values. A

linear model [1] leads to the requirement $\rho \approx 30$ eV if the additional fuel consumption for the post treatment is to stay below 7 %.

Conclusions

We have shown that the dielectric barrier discharge is an effective means to remove NO and NO_2 from mixtures of O_2, N_2 and H_2O and NO. The H_2O molecules resulting from all combustion processes of organic fuel provide OH radicals via the reactions $H_2O + N_2 (A^3\Sigma) \rightarrow H + N_2 + OH$ and $H_2O + O (^1D) \rightarrow 2\ OH$ [11]. These radicals are needed to further oxidize the NO_2 molecules produced from NO. For the future we will investigate the chemical reduction of NO to N_2. Furthermore the specific energy input per toxic molecule still has to be reduced to efficiently use the dielectric barrier discharge techniques for automobile exhaust remediation. Therefore more advanced concepts of reactors are being developed in our laboratory. Particularly for Diesel engines this last issue is a very critical one since their main advantage against spark ignited engines is their lower specific fuel consumption and associated CO_2 emission by about 15 %.

Acknowledgments

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