The Conversion of NO by a Corona Discharge through a Catalyst Bed

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Abstract

Plasma-induced heterogeneous reactions are studied for the low T removal of NO as a function of the composition of the gas mixture. In a number of cases, the presence of a large silica or alumina surface area enhances the energy efficiency of the process several times. The most promising reaction is the so called 'fixation' of NO on γ-alumina. An energy efficiency of 16 and 32 eV/NO_x at respectively ~65% and ~95% NO conversion is obtained at an initial [NO] = 1000 ppm. This result is at least a factor 5 better than the plasma-induced heterogeneous reactions with NO reported before [1,2].

1 Introduction

The deNO_x/deSO_x of flue gas by plasma treatment has been a subject of research for several decades. The energy efficiency of the plasma process has been studied with respect to the type of discharge, the composition of the flue gas, and additives such as NH_3 and H_2O_2.

The aim of our work is to investigate the possibilities of plasma-induced heterogeneous (catalytic) reactions for the conversion of NO. The efficiency of several types of active materials are studied in relation to the composition of the gas mixture. Based on the results of our experiments, we propose a heterogeneous reaction mechanism with plasma species. Only Henis and Suhr studied such similar reactions [1,2]. These authors showed that the energy efficiency of the NO conversion can be improved by the presence of certain solids in the discharge zone. This effect has not been explained at that time.

2 Experimental information

The experiments are performed in a laboratory scale setup at atmospheric pressure. The micro-flow reactor consist of a quartz tube, i.d. 9 mm, with a stainless steel wire electrode of 1 mm diameter through the center, and a grounded foil of 1 cm width around the quartz tube (see figure 1). The discharge gap can be filled with a packed bed of (catalyst) particles. It is realized that the discharge only proceeds through the voids in the bed since micropores are too small for the discharge to exist. The dielectric barrier discharge is generated by a high voltage spark gap circuit. The energy input in the plasma is typically 6 to 7 mJ/pulse and rather independent of the gas mixture. The gas mixture is composed by a gas manifold with gases from bottles. The gas tubing from the reactor to the mass-spectrometer is heated to avoid condensation of products.

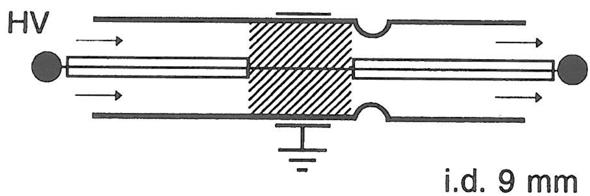

Figure 1: *The dielectric barrier reactor with optionally a packed bed of catalyst particles in the discharge gap.*

3 Experimental results

The plasma-induced conversion of NO is studied with and without a catalyst in the discharge gap, and as a function of the composition of the gas mixture [5]. Only a small subset of the results is presented here. The experiments are performed with 1000 ppm NO in a carrier gas at a total flow of 100 Nml/min, and a reactor temperature of 90 °C. The energy efficiency of the process is expressed in eV per converted NO molecule, further denoted by 'eV/NO'.

- *Diluted NO in* <u>*dry*</u> *He or* $N_2 + x\%\ O_2$*:*

The conversion of NO is studied as a function of the $[O_2]$ in presence of highly porous Grace 332 silica (300 m^2/g, V_p=1.65 ml/g) and AKZO γ-alumina (200 m^2/g, V_p=0.6 ml/g). These materials are frequently used as support for catalysts. The experiments are performed at approximately constant energy input

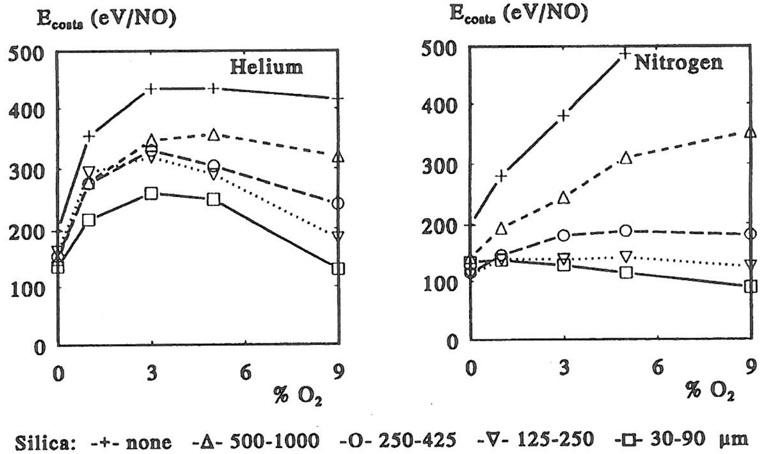

Figure 2: *The energy costs per removed NO molecule versus the $[O_2]$ in presence of Grace 332 silica of different sieve fractions at approximately constant energy input of ~ 0.6 - 0.7 W. The $[NO]_0$ is 1000 ppm NO.*

in the plasma of 0.7 W for He and 0.6 W for N_2 as bulk gas.

The results for silica are plotted in figure 2. The presence of a large silica surface area decreases the energy costs of NO conversion over the entire range of $[O_2]$. However, the reaction mechanism differs when O_2 is present or not. In absence of O_2, the NO is dissociatively converted to N_2 and O_2 by highly excited He or N_2 molecules [3]. In presence of O_2, the dissociative conversion of NO is depressed strongly since O_2 is the energy sink in the plasma [3]. The homogeneous oxidation reaction of NO to NO_2 by $O^{\bullet}$ is very inefficient due to the reduction of NO_2 by $O^{\bullet}$ also [3]. Hence, the energy costs increases rapidly by the addition of O_2. However, the presence of silica enhances the oxidation reaction as is clearly observed from figure 2. We explain this fact by a heterogeneous oxidation reaction of NO by probably $O^{\bullet}_{ads}$, which is efficient due to the transfer of reaction energy to the solid.

The heterogeneous reaction mechanism is confirmed by the use of γ-alumina as bed material. Surface reactions should depend on the type of surface. Indeed, the NO is also oxidized on γ-alumina in a plasma of 1000 ppm NO + 5% O_2 in He, but remains adsorbed as NO_3-groups. This appears from the regeneration of γ-alumina by temperature programmed desorption (TPD) from 90 to 450 °C. An example of the experiment is plotted in figure 3. The different nature of the NO 'fixation' reaction is stressed even more by the initial energy costs of only 16 and

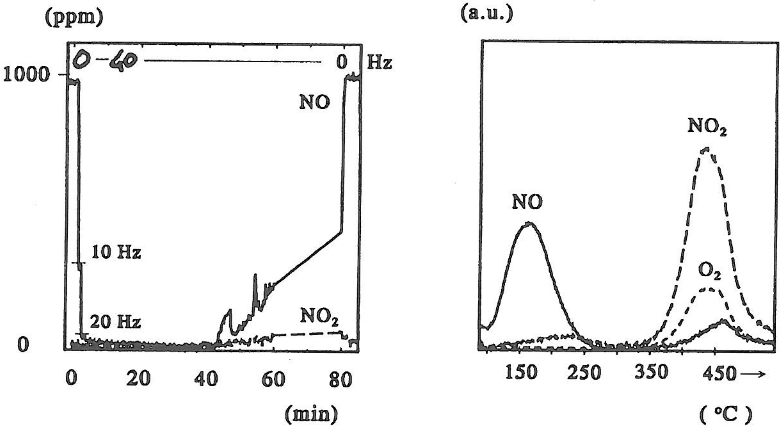

Figure 3: *Left: the NO concentration during the plasma treatment of a mixture of 1000 ppm NO in dry He + 5% O_2 in presence of γ-alumina, which is saturated with NO before the plasma reaction. Right: the TPD mass-spectrum of the γ-alumina immediately after the reaction.*

32 eV/NO_x at respectively ~65% and ~95% NO conversion (compare silica: ≥250 eV/NO for the same gas mixture, figure 2). The low energy costs are caused at least partially by the fixation of the N-oxides, which avoids the reduction in the homogeneous plasma phase.

- *Diluted NO in* <u>*moist*</u> *He or N_2 + x% O_2:*

The conversion of NO is studied as a function of the [O_2] in presence of H_2O and silica of sieve fraction 125 - 250 μm. Helium is used as bulk gas. Water is added to the gas mixture by saturation. The [H_2O] used in the experiments is given in the legend of figure 4, in which the results are plotted.

This experiment shows firstly that the addition of H_2O at [O_2]=0% leads to a strong increase in the energy costs of the NO removal. $OH^\bullet$ alone is not very reactive for the oxidation of NO neither on the silica surface nor in the gas phase. This result agrees with the one of Tokunaga [4]. Secondly, the NO conversion as a function of [O_2] differs completely in presence or absence of H_2O. The immediate decrease in the energy costs when O_2 is added in the presence of H_2O must be caused by the beneficial action of the $HO_2^\bullet$ radical which is formed. From a comparison with experiments in the empty tube reactor, we conclude that the homogeneous free radical oxidation of NO dominates the heterogeneous reactions now.

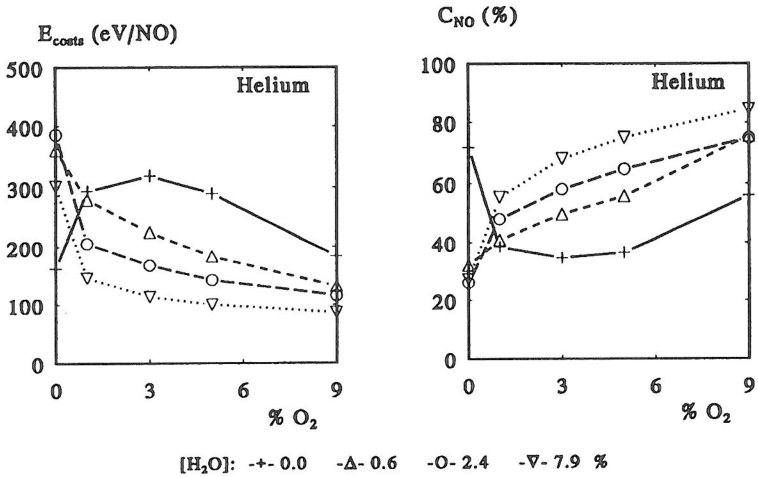

Figure 4: *The conversion of NO in presence of a packed bed of Grace 332 silica particles (sieve fraction 125-250 μm) as a function of the [O_2] at four different [H_2O]. Helium is used as bulk gas with 1000 ppm NO. The energy input in the plasma is approximately equal for all data points.*

4 Conclusions

In a number of cases, the energy efficiency of the NO conversion in a plasma can be increased by heterogeneous reactions. The mechanism and effect of the heterogeneous reaction depend strongly on the composition of the gas mixture and the type of bed material.

The heterogeneous mechanism is well understood for diluted NO in a dry He or N_2 mixture with a few percent O_2. The oxidation of NO to NO_2 is enhanced several times by the presence of the silica surface area in the plasma. The presence of γ-alumina induces a very efficient oxidation of NO to NO_3-groups on the surface, which are stable at T $\leq$ 200 °C. These surface reactions can be understood from the fact that O_2 is the energy sink of the plasma which leads to an efficient production of $O^{\bullet}$. We propose that the adsorption of $O^{\bullet}$ is the primary step in the plasma-induced heterogeneous reaction. The reaction of NO with the $O^{\bullet}_{ads}$ depends on the type of surface.

$$
\begin{array}{llll}
O^{\bullet} + \square & \longrightarrow & O^{\bullet}_{ads} & \\
NO + O^{\bullet}_{ads} & \xrightarrow{+O_2} & NO_{3,ads} & for\ \gamma - alumina \\
 & \longrightarrow & NO_2 + \square & for\ silica
\end{array} \qquad (1)
$$

in which $\square$ denotes a surface site. The homogeneous oxidation of NO to NO_2, followed by adsorption of NO_2 on the γ-alumina is excluded by the very inefficient oxidation of NO by $O^\bullet$ in the gas phase (see figure 2).

The surface reactions belonging to the dissociative conversion of diluted NO in the pure bulk gas is not well understood. The effect of the surface is observed for He and N_2 which indicates that the enhanced dissociation of NO cannot be explained only by the stabilization of plasma radicals on the surface. In analogy with the previous mechanism, we propose that surface radical sites are also produced by other highly excited plasma species. NO dissociates on these radical sites, finally leading to N_2 and O_2 formation. For *silica*, the mechanism is proposed:

$$\begin{array}{lll} M^+,\ M^*,\ M^\bullet & \longrightarrow & M + \square^\bullet \\ & \longrightarrow & M^\bullet_{ads} \\ NO + \square^\bullet & \longrightarrow & O_{ads} + N_{ads} \rightsquigarrow N_2 + O_2 \end{array} \qquad (2)$$

in which $\square^\bullet$ denotes a surface radical site.

For H_2O and O_2 containing gas mixtures, the plasma-induced free radical oxidation of NO to its acid by the combination of $O^\bullet$, $O_3^\bullet$, $OH^\bullet$, and $HO_2^\bullet$ is fast and efficient. The role of heterogeneous reactions is less clear for these compositions of the gas mixture.

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