



PlasTEP

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NO removal from flue gases

NO oxidation by dielectric barrier discharge

NO oxidation is efficient both by O atoms and O₃. The reaction rate for $\text{NO} + \text{O} \rightarrow \text{NO}_2$ is $2.7 \cdot 10^{-12} \text{ cm}^3/(\text{mol} \cdot \text{s})$. The reaction rate for $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ is $x \cdot 10^{-14} \text{ cm}^3/(\text{mol} \cdot \text{s})$. One has to consider also the back-reaction of $\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2$ which has similar reaction rate as oxidation reaction by O. The ozone formation rate by reaction of $\text{O} + \text{O}_2 \rightarrow \text{O}_3$ is also similar to and is competing with oxidation of O. However, the back-reaction with O₃ is not considerable and this is the reason why NO can be oxidized by O₃ even more efficiently than by discharge.

In the presence of unsaturated hydrocarbons, HC-s, the O atoms are initially consumed by these HC-s and the formed partially oxidized VOC species are efficient at reacting with NO whereas back-reactions are missing. Thus, the NO oxidation is expected to improve in the presence of HC-s. When H₂O is also present, the oxidation of HC-s is even more efficient and the subsequent NO oxidation as well.

In presence of water vapor, the oxidation is also going through the formation of HNO_x. The H₂O is used to produce OH groups and the reaction between NO and OH ($x \cdot 10^{-x} \text{ cm}^3/(\text{mol} \cdot \text{s})$) is even faster than reaction between NO and O.

Finally, the presence of photocatalyst in the plasma zone may also improve the oxidation through the adsorption of O atoms on the surface which may aid in preventing the unwanted back-reactions and additionally by harvesting the energy of excited N₂ or O₂ species and UV which results in the production of OH on the catalyst.

Experimental setup

All experiments were carried out at atmospheric pressures. The inlet mixture was usually prepared from 450 ppm NO in N₂ and from synthetic air by the use of flow controllers. For the addition of water vapor, the mixture was led through a bubbler with H₂O at room temperature (22 °C) resulting in 2 % of water in the mixture of humid air. For higher H₂O percentages used at 60°C, a specially designed heated bubbler was used whereas only O₂ was directed through the bubbler. The first experiments were carried out with inlet mixture of about 200-225 ppm NO and 10 % O₂. The flow rate was 1 l/min unless stated otherwise. Experiments at higher flow rates, up to 10 L/min were carried out with separate NO and N₂ cylinders.

The experiments with PlasTEP standard mixture were carried out by the use of additional cylinders with propylene, CO₂ and CO by the use of separate flow controllers. Usually a mixture with 360 ppm NO, 10 % O₂, 5 % H₂O, 5 % CO₂, 500 ppm propylene and 100 ppm CO was used. 360 ppm of NO was used instead of 400 ppm because it was not possible to have 400 ppm NO and 80 % of N₂ from the cylinder of 450 ppm NO in N₂. The difference of results obtained with 360 ppm or 400 ppm of NO was not large (tested without H₂O and CO₂). The concentrations of various species in the mixture





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were sometimes varied to test the effect of each of these species on the removal. Especially important was the effect of H₂O concentration as slight variations in the temperature of the bubbler resulted in considerable variation in the H₂O concentration and was one of the biggest uncertainty.

A coaxial DBD reactor with discharge gap of 0.7 mm, similar to the one described in our earlier work [10] was used for the production of discharge. During heating experiments, the DBD reactor was placed in an electrically heated oven. The inlet mixture and the outlet pipes of the reactor were also heated by the use of heating tape. Commercial Degussa P25 TiO₂ powder mixed in water was pressed on the inner electrode of reactor. The mass of resulting TiO₂ coating was approximately 10 mg/cm². The specific input energy (*SIE*) was determined from the recorded Lissajous figures similarly with our earlier experiments.

Concentrations of NO_x, HNO₃ and O₃ were measured at the outlet of DBD reactor by the optical absorption spectroscopy (OAS) method. The measurement setup consisted from a deuterium lamp (DDS-30), an absorption cell with the length of 30 cm and from Ocean Optics USB4000 spectrometer of 0.7 nm resolution. The wavelengths from 200 to 445 nm were used for the determination of various species. To determine the NO concentration, a calibration curve was obtained by mixing 450 ppm NO in N₂ balance gas and pure N₂ with various ratios and measuring the intensity of absorption band at 215 nm. The concentration of other NO_x species and ozone were determined by using the absorption cross section values from literature.

NO removal by dielectric barrier discharge and TiO₂: experiments

Effect of water vapor

The first experiments carried out at lower NO concentrations (225 ppm) were presented and published in Hakone XII but are shown and briefly discussed in here. At room temperature, it was possible to remove all NO and oxidize it to NO₂. At 100°C, the removal of NO was not as efficient (figure 1). The use of TiO₂ improved considerably the NO oxidation, probably due to improved oxidation at the surface. The presence of H₂O improved the NO removal both with and without the TiO₂. There was also HNO₃ detectable in the outlet. Some of the NO_x compounds were missing in the outlet but this was probably due to the presence of HNO₂.





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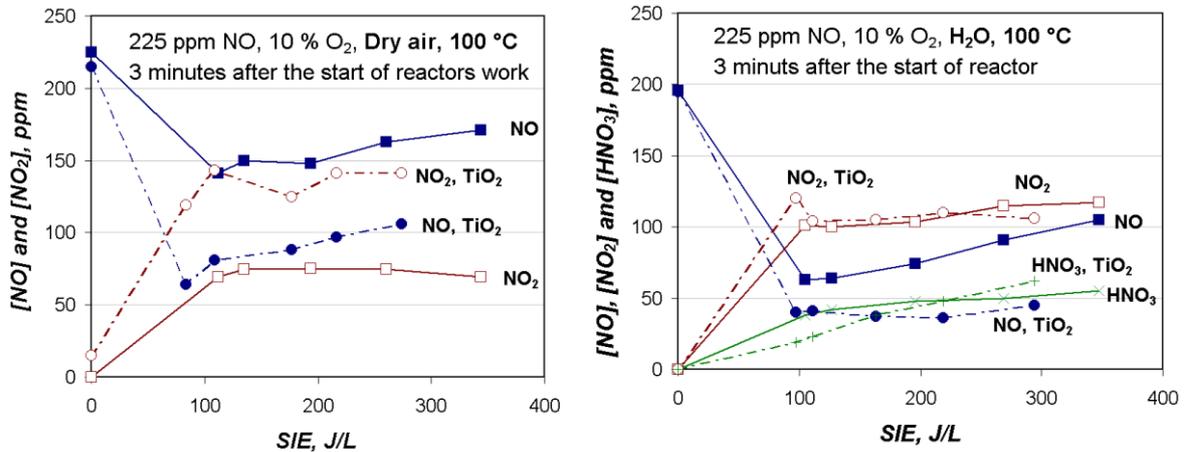


Figure 1. Removal of 225 ppm NO at 100°C with and without the TiO₂ in dry mixture (left) and in mixture containing 2 % of H₂O.

Effect of NO concentration in dry mixtures

The NO concentration did not considerably affect the removal of NO (difference between inlet and outlet concentration) when inlet concentration was between 225 ppm and 400 ppm of NO (fig. 2). At room temperature, the removal of NO was about 250 ppm and it decreased below 100 ppm when temperatures increased above 100°C. Most of the NO was oxidized to NO₂.

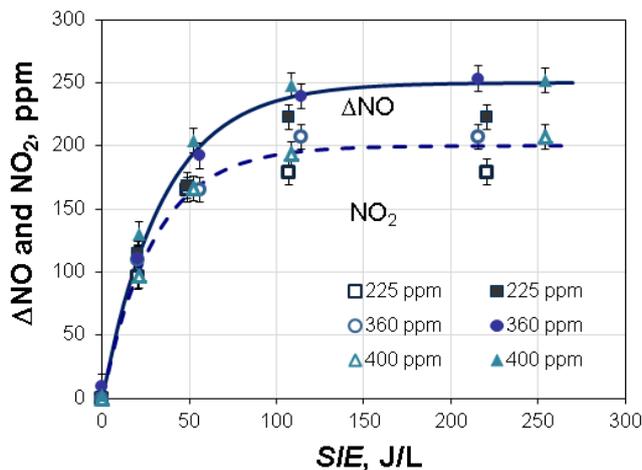


Figure 2. The removal of NO, ΔNO, and outlet NO₂ at various inlet NO concentrations at room temperature.

Effect of CO₂ in dry mixtures

Separate experiments were carried out to investigate the effect of CO₂ in 225 ppm NO, 10% O₂ mixture (fig. 3). The outlet NO concentration at various SIE values was not affected by CO₂ in the limits of measurement uncertainty.





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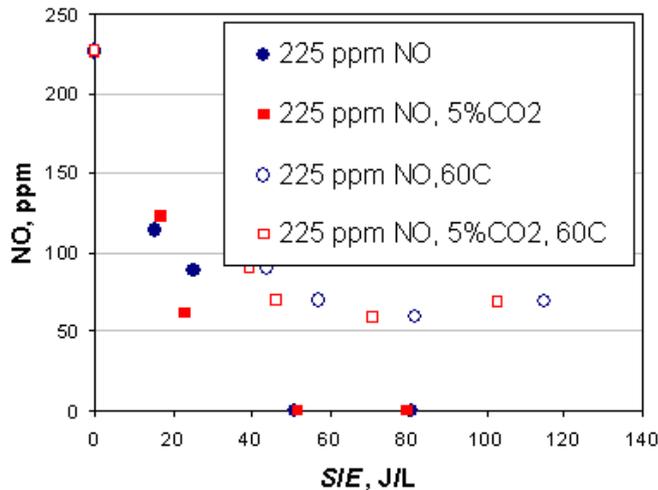


Figure 3. The outlet NO concentration as a function of SIE at two temperatures in the presence of CO₂.

Effect of propylene in dry mixtures

In these experiments, the base mixture was 10 % of O₂ and either 400 ppm or 360 ppm NO. We have a cylinder with 450 ppm of NO in N₂ and thus it will not be possible to obtain the expected mixture of 400 ppm NO when there is also 10 % of O₂, 5 % of CO₂ and 5 % of H₂O. The present experiments demonstrated that used conditions, there was no essential difference between the 400 ppm and 360 ppm of NO, so the results are shown for 360 ppm of NO to allow better comparison with next experiments on more complicated mixtures.

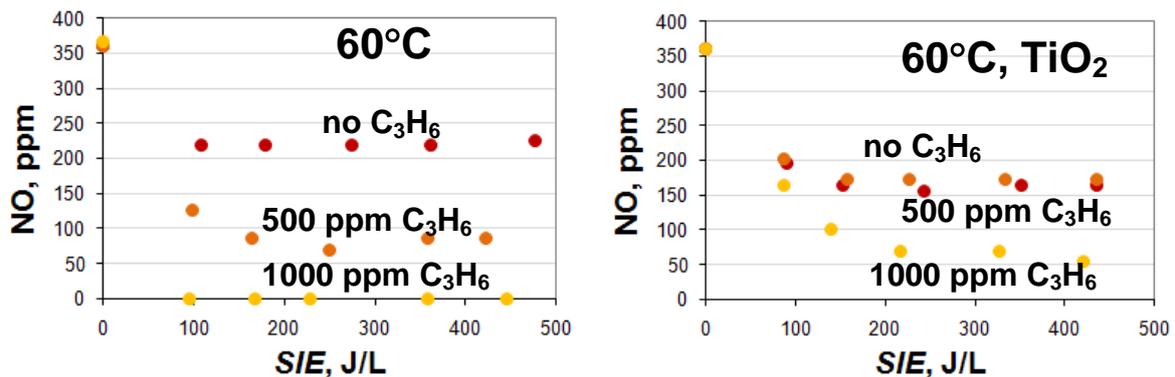


Figure 4. Outlet NO concentration with 360 ppm of inlet NO concentration and 10 % of O₂ with various inlet concentrations of propylene (C₃H₆). The experiments were carried out either without TiO₂ (left panel) or with TiO₂ (right panel).

As expected, the presence of propylene (C₃H₆) generally increased the NO removal and higher propylene concentration resulted in additional increase of the NO removal (fig. 4). The presence of





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TiO₂ also increased NO removal but counteracted the effect of propylene and in the case of 500 ppm of propylene the propylene had practically no effect on NO removal. The main reason may be the preferential decomposition of propylene on TiO₂. As a note, we also carried out the removal of propylene in dry air at room temperature and then the TiO₂ had no effect on propylene oxidation. Our experience with NO oxidation suggests that temperature of TiO₂ has to be higher to have any effect and this may be the reason of the negative effect of TiO₂ in present experiment because 60°C was used as the reaction temperature.

The effect of reactor temperature was also tested for NO oxidation in the presence of propylene. Figure 5 shows the smallest values of NO concentrations in the outlet of plasma reactor obtained at various temperatures with and without TiO₂ and propylene. The SIE values were between 200-300 J/L. Without TiO₂ and propylene, the outlet NO concentration increased at increasing temperatures while TiO₂ allowed to obtain considerably lower outlet NO concentrations. The presence of propylene was even more effective and TiO₂ had negative effect on the NO removal at all used temperatures.

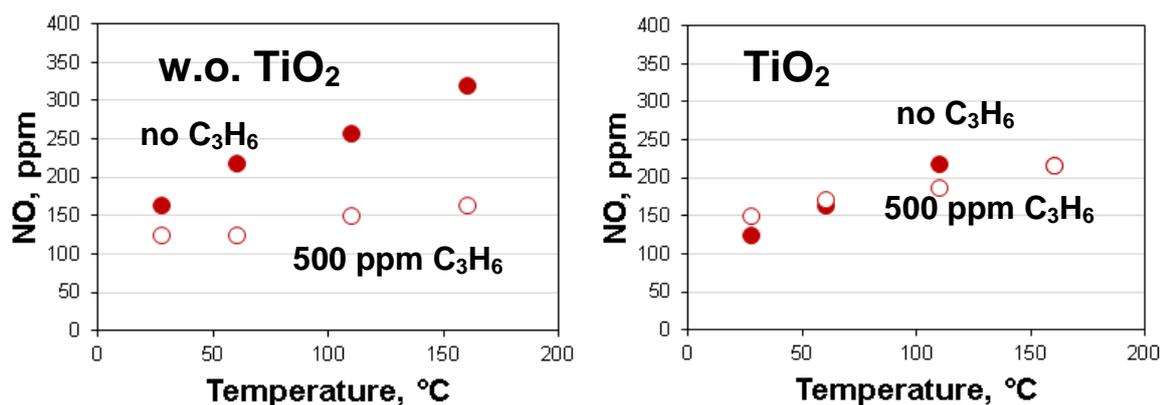


Figure 5. Smallest values of outlet NO concentrations by discharge at various temperatures without (right panel) and with TiO₂ (left panel) and propene (C₃H₆).

There were background shifts in the absorption spectra which we were not able to prevent during the experiments and thus only the NO concentration could be measured with some accuracy. The propene gives a broad absorption feature between 180-200 nm but the measurement error at these wavelengths is large and there was overlap with absorption of other molecules, e.g. NO₂, N₂O₅, HNO₃ etc. During the removal of NO by discharge, this line appeared to disappear indicating that the propene is oxidized in the discharge. There was no ozone present in these experiments with high concentration of NO and thus the NO is only oxidized to NO₂ to some degree and NO₃ or N₂O₅ are not expected in considerable quantities. In the experiments with propene, there appeared additional broad feature at wavelengths around 200 nm which might be due to HNO₃ or maybe due to some oxidized product of propene. The nature of this feature has to be verified in additional experiments where only propene is used.





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The results indicate that the NO removal in complex mixture with CO₂, CO, propylene and H₂O is not affected by the presence of catalyst in contrast to simple NO, H₂O, O₂ and N₂ mixture where catalyst improves the NO oxidation. On the other hand, the catalyst also didn't decrease the NO removal as it did in the case of NO, propylene, O₂ and N₂ mixture. This may be important in the case when the hydrocarbon e.g. propylene concentration in the inlet mixture varies considerably while H₂O concentration is relatively high. At low HC concentrations, the catalyst improves NO oxidation while at higher HC concentrations NO oxidation is improved due to the HC. The oxidation of NO by hybrid plasma-catalytic reactor is also scalable to 10 slm without deterioration of the oxidation capability.

