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Removal of NO by simultaneous action of dielectric-barrier discharge and TiO₂ photocatalyst

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Abstract. NO oxidation by simultaneous action of a dielectric barrier discharge and TiO₂ photocatalyst was investigated as a function of the inlet gas composition (NO, O₂, N₂) and the input energy. Concentrations of various NO_x species and ozone in the outlet were detected by the optical absorption spectroscopy. Higher content of O₂ (10% and higher) increased the removal of NO and resulted in a higher output of N₂O₅. TiO₂ coating on a reactor electrode resulted in the time-depending oxidation of NO. Initially the concentration of untreated NO fell below the level achieved without TiO₂ but after few minutes the positive effect of TiO₂ diminished. The initial decrease in NO level due to the presence of TiO₂ coating is explainable by surface reactions of NO species and absorbed oxygen. After few minutes, the surface states responsible for the initial removal of NO saturated and the effect of TiO₂ vanished.

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Title: Removal of NO simultaneously by dielectric-barrier discharge and TiO₂

1. INTRODUCTION

NO_x is a harmful by-product in flue gases whereas NO is the most abundant NO_x species. Non-thermal plasma sources, such as corona discharge or dielectric barrier discharge (DBD) are considered as an efficient method for the treatment of NO_x [1-6]. Another possibility for

the treatment of NO_x is to use photocatalysts, such as TiO_2 [6-8]. The main route for the removal of NO from flue gases is the oxidation of NO to NO_2 . In the case of plasma, NO_2 can be further oxidized to NO_3 and finally to N_2O_5 [3,4]. It has been reported that the simultaneous action of DBD and TiO_2 coating inside the reactor decreases in the outlet both NO and NO_x concentrations [9-12]. In these studies only NO and NO_2 concentrations were measured and it was not clear whether NO_x was adsorbed on the TiO_2 surface, oxidized to NO_3 and N_2O_5 or reduced to N_2 and O_2 .

The aim of the present study was to investigate the effect of TiO_2 -coated DBD electrode on the removal of NO_x using different NO and O_2 concentrations in the inlet gas mixture and varying the specific input energy. The effect of TiO_2 on the oxidation of NO was studied by recording the final concentrations of different NO_x species (NO, NO_2 , NO_3 , N_2O_5).

2. EXPERIMENTAL SETUP AND METHODS

The experimental setup is shown in Figure 1. All experiments were carried out at atmospheric pressure. The mixture of $\text{NO}/\text{O}_2/\text{N}_2$ was prepared from separate gases of N_2 , O_2 and 450 ppm NO in N_2 by the use of flow controllers. The inlet fractional concentration of NO was varied in the range of 0-450 ppm; the percentage of oxygen was 0, 5, 10 or 20 %. The total flow rate, F_r , was varied from 0.9 to 2.2 l/min.

Figure 1 gives a schematic representation of experimental set-up. DBD reactor had a coaxial design. The inner electrode of the reactor was a stainless steel tube, whose outer diameter was 14 mm. The outer electrode was a winding on the quartz tube. The discharge gap spacing was approximately 0.7 mm. The length of the active discharge region was approximately 100 mm. A commercial Degussa P25 TiO_2 powder (grains of 80 % of anatase and 20 % of rutile) was pressed on the inner electrode or painted on it using a mixture prepared by stirring the powder in water or ethanol. In the latter case, the mass of the TiO_2 coating was varied by using different number of painting steps.

The barrier discharge was ignited applying to the inner electrode voltage pulses, V , of $\approx 15 \mu\text{s}$ half-width and 1–2 kHz repetition rate. The peak value of pulses was varied from 5 to 10 kV. The outer electrode was grounded through a 23 nF capacitance. The voltage, V , was measured by the capacitive voltage divider 1. The charge transferred through the discharge during one voltage pulse, was measured by the capacitor 2. The voltages were recorded by the PC oscilloscope PCS 500.

The mean input power, P , was calculated from the recorded Lissajous figures according to the procedure described in a paper of Rousseau *et al.* [13]. The specific input energy, SIE , was calculated according to the formula $SIE = P/F_r$. Details about the waveforms of the voltage pulses and determination of SIE are described elsewhere [14].

Concentrations of NO_x species and ozone were measured at the outlet of the reactor by the optical absorption spectroscopy (OAS) method and by an electrochemical gas detector QRAE+ 2000 (only for determination of NO concentration). The OAS measurement setup consisted from radiation source (a deuterium or a tungsten lamp), an absorption cell of 10 cm length, a spectrometer MDR-23 and a CCD camera system Alta U1107. The wavelengths region of 200 – 230 nm was used for the determination of NO, N_2O_5 and O_3 concentrations. The region of 400 – 430 nm was used for the determination of NO_2 concentration. The detection of NO_3 by absorption in 640-670 nm region was not successful. Unless specified otherwise, the concentrations of NO_x species and O_3 were determined from spectra obtained after 2 minutes of reactor's work.

3. RESULTS AND DISCUSSION

3.1. Removal of NO without the TiO_2 coating

At a fixed gas composition and varying flow rate, F_r , voltage, V , and repetition rate, f , it appeared that the remaining concentration of NO depended only on SIE (Fig. 2a) and not separately on the parameters counted above. Thus, similarly to earlier studies [2], SIE is a relevant parameter controlling the NO removal. As expected, at the same SIE , the concentration of untreated NO was higher for higher initial concentrations of NO.

There was a slight discrepancy in the concentrations of NO measured by chemical NO analyzer and OAS method and this discrepancy is most likely due to the remnant NO signal of the NO analyzer.

Fig. 3 shows that at 330 ppm fraction of NO and at 5 % of O_2 , NO was only partially converted to NO_2 while both N_2O_5 and O_3 were practically missing. It should be pointed that in the absence of NO in the initial mixture, the O_3 was present also in the mixtures with 5 % of O_2 [14]. Higher O_2 percentage resulted in the total removal of NO and both O_3 and N_2O_5 became detectable (fig. 3b).

These results indicate that at lower concentrations of O₂, both O and O₃ produced in plasma are totally removed by reactions

and because of the depletion of O atoms, N₂O₅ was not found. At higher percentage of oxygen, NO₂ is further oxidized to NO₃ and N₂O₅ by the reactions

The rate constant of reaction

is small and it was not considered. The oxidation of NO to NO₂ proceeds until NO is totally removed and thus there appear only NO₂, N₂O₅ and O₃ in the outlet.

3.2. Removal of NO in the presence of TiO₂ photocatalyst

The TiO₂ coating increased the removal of NO during the first few minutes of reactor operation, whereas later the concentration of NO increased again and reached a constant value (Fig. 4a). The effect of TiO₂ on the removal of NO increased with the increasing mass of the TiO₂ coating (not shown) and with the increase of *SIE* injected into the reactor (Fig. 4a). At energies below 100 J/l, the effect of TiO₂ was negligible. The dependence of NO removal on the TiO₂ mass indicates that the surface of TiO₂ is involved in the process. In the absence of O₂, the presence of TiO₂ coating had no effect on the removal of NO. Thus, the oxygen is involved in the initial increase in the removal of NO.

The temporal change of the concentrations of different NO_x species and ozone is demonstrated in figure 4. After 15 s of the reactor operation, the concentrations of NO and NO₂ were low (Fig. 4b-c) whereas the concentration of ozone was high. The concentration of NO₂ increased with time while the O₃ concentration decreased. When the resources of O₃ were exhausted, NO₂ concentration reached a constant level. After this moment, NO concentration also started to increase. The time period after which the concentration of O₃ diminished and that of NO₂ reached saturation, increased with the increasing concentration of O₂ and with the decrease of the initial concentration of NO. The NO concentration remained always below the detection limit if the concentration of O₂ was 10 %.

After 2 minutes of reactor's work the concentrations of NO_x species and O_3 stabilized. Compared to the case of uncoated electrodes (Fig. 3), the presence of TiO_2 resulted in the lower final concentration of O_3 (Fig. 5). In the mixture of 330 ppm NO and 5 % O_2 , the reduced production of O_3 (or O) led to higher amount of untreated NO (Fig. 5a). At higher concentrations of O_2 , the NO was totally removed and there was still O_3 present in the outlet (Fig. 5b). Compared to the case with uncoated electrodes, the O_3 concentration remained lower. As a result there was more NO_2 in the outlet while the concentration of N_2O_5 remained lower (Fig. 5b).

The TiO_2 coating started to affect the NO_x removal only at SIE values higher than 100 J/l. The growth of SIE increases both the intensity of UV radiation and/or the concentration of atomic oxygen. Higher intensity of UV radiation enhances the photocatalytic effect of TiO_2 possibly creating OH radicals and O_2^- on the surface [8]. In addition, atomic oxygen can be adsorbed on TiO_2 without the activation of surface by UV radiation [15,16]. In both cases, NO will be oxidized to NO_2 and NO_3 on the surface of TiO_2 . The importance of adsorption processes was determined by the observation of recovering of the removal properties of TiO_2 coating during a break in the reactor operation (15 s – 10 min), whereas longer breaks resulted in increased recovering effect.

The effect of UV radiation was checked by switching off the reactor and illuminating the reactor with TiO_2 coating by Hg lamp (500 W). A slight decrease of the concentration of NO and growth of concentration of NO_2 was recorded. Thus, the TiO_2 coating has a small photocatalytic effect. This effect is most likely due to the photocatalytic adsorption of O_2 as the TiO_2 had no effect when only NO and N_2 mixtures were used. However, the increased intensity of UV radiation at higher SIE alone is not able to explain the initial increase in the removal efficiency of NO and the increase in the concentration of atomic oxygen seems to have a higher impact.

A possible explanation for the temporal effect of TiO_2 coating is as follows. Initial enhanced removal of NO occurs only in the presence of O_2 and thus the surface states responsible for the initial removal of NO have to be initially activated by the presence of O or O_2^- adsorbed on TiO_2 surface [8, 16]. When the surface is activated, NO reacts with the O or O_2^- on TiO_2 surface whereas the reaction products (NO_2 , NO_3) remain on the surface [8, 16]. As part of NO_x is now bound to the surface, the concentration of NO in the gas remains lower, and the amount of O_3 in the treated gas becomes higher. When the surface states responsible for NO removal are saturated, the oxidation of NO to NO_2 consumes the oxygen species in the

plasma. If the amount of O and O₃ is insufficient for the oxidation of NO, the concentration of NO starts to increase in the mixture. When the reactor is switched off, the surface of TiO₂ will recover in time due to the desorption of NO_x products.

4. CONCLUSIONS

- Without TiO₂, the NO removal increased with specific input energy and higher amount of O₂. In the presence of O₂, NO is oxidized initially to NO₂ and then to N₂O₅. Ozone became detectable when NO was almost completely converted to NO₂.
- Effect of TiO₂ coating depended on time. Initially, TiO₂ coating enhanced NO_x removal due to the surface reactions. After few minutes the active surface states saturated and effect of TiO₂ coating diminished.
- The main reason for initial increase in the NO removal efficiency is due to adsorption of atomic oxygen whereas photocatalytic effect of TiO₂ had only slight effect on the NO removal.

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FIGURE CAPTIONS

Figure 1. Schematic representation of experimental setup. 1 – capacitive voltage divider, 2 – capacitor for the measurement of the charge stored on the dielectric barrier.

Figure 2. Concentration of NO, c_{NO} , in the outlet recorded by the electrochemical NO analyzer as a function of SIE in the case of mixtures with various inlet concentrations of (a) – NO (0 % of O_2) and (b) – O_2 (220 ppm of NO). Squares, triangles, circles and crosses denote curves measured at various flow rates or pulse repetition rates. The continuous curves are used as an eye guide whereas dashed lines indicate the initial NO concentration.

Figure 3. Concentrations of O_3 and different NO_x species as a function of SIE in the case of different inlet mixtures: (a) – 330 ppm of NO and 5 % of O_2 ; (b) – 220 ppm of NO and 10 % of O_2 .

Figure 4. Temporal changes in the case TiO_2 coated electrode; (a) – the concentration of remaining NO at different SIE values (330 ppm NO and 5 % O_2); (b), (c) and (d) – concentrations of NO_x species and O_3 at $SIE = 400$ J/l.

Figure 5. Concentrations of different NO_x species and O_3 as a function of SIE in the case of reactor with TiO_2 coated electrode and with different initial gas mixtures: (a) – 330 ppm of NO and 5 % of O_2 ; (b) – 220 ppm of NO and 10 % of O_2 . In figure b, the concentrations of NO_2 and O_3 obtained without the TiO_2 coating are also indicated for comparison.

FIGURES

Jõgi et al. Figure 1.

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