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DECOMPOSITION AND RE-SYNTHESIS OF NO_X IN NON-EQUILIBRIUM PLASMA IN NITROGEN-OXYGEN MIXTURES CONTAINING WATER VAPOUR

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A b s t r a c t. Processes of nitrogen oxides decomposition in non-equilibrium plasma generated in electrical discharges are accompanied by a re-synthesis of nitrogen oxides. Fathoming of the effect of HV feeder electrical parameters and of gas composition on the NO re-synthesis process can help to inhibit the process and to obtain a higher degree of the NO decomposition and more efficient utilisation of electrical energy that feeds a reactor. Tests have been performed in a flat reactor with a quartz dielectric (discharge gap of 1mm) fed with alternate voltage (50-4500Hz) of 10.0kV. Feeding gas consisted of 9 to 95% of O_2 , 0 - 8000ppm of H_2O with the remaining part being nitrogen.
An analysis of gas composition at the reactor outlet has been performed with a mass spectrometer and it has shown that among the synthesis products aside with ozone there also are N_2O, NO, NO_2 and N_2O_5 there. Along with a growing feeding voltage value the total NO_x concentration increases. The highest total NO_x concentration values have been obtained at the 38% oxygen content in the mixture. Further increase of the oxygen content in the mixture causes a decrease of the N_2O concentration. An increase of the vapour content causes a decrease of the N_2O and NO_2 concentrations. The obtained results indicate that in the process of NO_x removal from flue gases it is possible to inhibit the NO_x re-synthesis by an adequate selection of the HV feeder parameters and the composition of a gas that is subdued to the discharge action.

K e y w o r d s: nitrogen oxides synthesis, NO decomposition, barrier discharge.

INTRODUCTION

Rapidly developing methods for NO_x removal from flue gases and prospects of an application of processes using non-equilibrium plasma for that purpose induce a necessity of fathoming mechanisms of the processes. When discharges occur under the influence of high voltage in the discharge volume the NO re-synthesis runs simultaneously with the processes of nitrogen oxides decomposition [1,2]. Fathoming out the effect HV feeder electrical parameters and gas composition on the re-synthesis processes can be helpful in obtaining a higher

degree of NO decomposition and more efficient utilisation of electrical energy that feeds the reactor.

Efficiency of NO_x decomposition mainly depends on the amount of energy supplied into a gas that flows through the reactor. A discharge power growth can be realised by increasing feeding voltage or frequency, or by introducing changes in the reactor geometry. This work presents results of investigations into the influence of a feeding voltage rise and of changes in frequency and in gas composition on the process of nitrogen oxides synthesis in non-equilibrium plasma.

High energy electrons that show up in barrier discharges influence chemical processes related to nitrogen oxides kinetics in two ways. On the one hand, they initiate processes leading to the nitrogen oxides synthesis through activation and dissociation of active molecules of oxygen and nitrogen :

$$O_2 + e \rightarrow O + O + e \qquad (1)$$

$$N_2 + e \rightarrow N + N + e \qquad (2)$$

$$N + O_2 \rightarrow NO + O \qquad (3)$$

$$N + O_3 \rightarrow NO + O_2 \qquad (4)$$

$$NO + O \rightarrow NO_2 \qquad (5)$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (6)$$

$$NO_2 + NO_3 \rightarrow N_2O_5 \qquad (7)$$

$$NO_2 + N \rightarrow N_2O + O \qquad (8)$$

On the other hand, the electrons cause concentration decrease of the formed oxides through their decomposition :

$$(NO, N_2O, NO_2, N_2O_5) + e \rightarrow (O_2, N_2, NO, N_2O, NO_2) + e \qquad (9)$$

It proves a complex character of the mechanism of nitrogen oxides decomposition and their re-synthesis inside a reactor.

EXPERIMENTAL

Tests have been performed in an earlier described setup [5]. Electrical discharges have been generated in a flat reactor with a quartz dielectric (discharge gap of 1mm) fed with alternate voltage of the value up to 10.0 kV and frequency within the range of 50-4500 Hz. Feeding gas has consisted of 9 to 95% of O_2 , 0 – 8000 ppm of H_2O with the remaining part being nitrogen.

The presented system makes possible to analyse gases directly at the outlet of a reactor which is very important because chemical processes run in gases that leave the reactor. Gases that flow out of the reactor contain excited molecules and atoms of oxygen and nitrogen, ozone and also various forms of nitrogen oxides (N_2O, NO, NO_2, NO_3, N_2O_5). According to the results presented by Vinogradov [6] in such a system very quick reactions take place and they change to a great extent the gas composition. Many authors of earlier works have published results of measurements performed by means of the IR spectroscopy methods [7,8]. Due to analyses performed a few or several tens of seconds after the investigated gas has left the reactor it is possible to determine a total of processes running in silent discharges and after their completion. An application of mass spectroscopy makes possible to quickly reduce the gas pressure down to 10^{-6} mm Hg (which "freezes" chemical processes) and to quickly obtain the analysis results. It gives a chance to learn gas composition directly at the reactor outlet. An analysis of gas composition at the reactor outlet has been performed with a mass spectrometer and it has shown that among the synthesis products aside with ozone there also are N_2O, NO, NO_2 and N_2O_5 there.

RESULTS

The obtained results indicate that HV parameters and gas composition essentially influence the process of nitrogen oxides synthesis in non-equilibrium plasma generated in barrier discharges.

A discharge power increase has been obtained by the application of a higher feeding voltage or a higher frequency. An important indicator that describes discharge conditions is an U/V parameter (energy density) defined as a ratio of discharge power [W] to volumetric gas flow intensity [l/h]. Along with a growing feeding voltage value a total NO_x concentration increases (Fig.1). At the same time an energy density growth obtained by the feeding voltage frequency increase results in obtaining lower N_2O concentration (Fig.2).

A change of oxygen concentration in a nitrogen-oxygen mixture essentially influences composition and concentration level of the synthesised NO_x. The highest total NO_x concentration values have been obtained at the 38% oxygen content in the mixture (Fig.3). For mixtures rich in oxygen (55% and 78%) and for a 21% O_2 mixture the results have been smaller. Higher oxygen concentration in a gas mixture results in a lower N_2O concentration (Fig.4). The highest NO_2 concentration values have been obtained for a mixture of 55% O_2 and 45% N_2 (Fig.5). When water vapour effect has been tested the feeding gas consisted of 9 to 95% of O_2 , 0 – 8000 ppm of H_2O with the remaining part being nitrogen. An

increase of the vapour content has caused a decrease of the N_2O (Fig.6) and NO_2 concentrations (Fig.7). For water vapour concentration of 3500 ppm the highest concentration of nitrogen oxide (NO) and the lowest concentration of nitrogen dioxide (NO_2) occur.

CONCLUSIONS

Chemical processes running in nitrogen-oxygen non-equilibrium plasma generated in barrier discharges lead to the synthesis of a nitrogen oxides mixture. Along with the growing feeding voltage a value of total NO_x concentration increases. Concentration level of individual oxides depends on the HV feeding conditions, energy density and gas composition. The obtained results indicate that in the decomposition process of nitrogen oxides occurring in flue gases it is possible to inhibit the NO_x re-synthesis by an adequate selection of the feeding HV parameters and by changing a composition of the gas that is subdued to the discharge action.

REFERENCES

1. **Tochikubo T., Watanabe T.**, Two-dimensional Measurement of Emission Intensity and NO Density in Pulsed Corona Discharge, Cont. Papers of Int. Symp. on High Pressure Low Temp. Plasma Chemistry HAKONE VII, Greifswald, Germany, pp219-223, 2000.
2. **Dors M., Mizeraczyk J.**, Generation of Ozone and Nitrogen Oxides in Positive Corona and Spark Discharge, Pol. J. of Chemical Technology, 4, 2, pp1-4, 2002.
3. **Wronski M.**, A De-NO_x Process Using High Voltage discharge in Gases, Pol. J. of Chemical Technology, 3, 4, pp37-39, 2001.
4. **Wronski M.**, An Effect of the H20 and CO2 Presence on the Efficiency of NO_x Removal from Waste Gases, Cont. Papers of Int. Symp. on High Pressure Low Temp. Plasma Chemistry HAKONE VII, Greifswald, Germany, pp282-286, 2000.
5. **Wronski M., Pollo I.**, Ozone and Nitrogen Oxides Reactions in silent Discharges, Proc. of Ozone World Congress, Kyoto, Japan, pp181-184, 1997.
6. **Vinogradov I.P., Wiesemann K.**, Absorption and emission spectroscopy of barrier discharge in N_2/NO and O_2/NO mixtures, Cont. Papers of Int. Symp. on High Pressure Low Temp. Plasma Chemistry HAKONE V, Milovy, Czech Republic, pp230-234, 1996.
7. **Braun D., Kuchler U., Pietsch G.**, Behaviour of NO_x in air-fed ozonizers, Pure and Appl. chemistry, 60, pp741-746, 1988.
8. **Kogelschatz U., Bessler P.**, Determination of nitrous oxide and dinitrogen pentoxid concentrations in the output of air-fed ozone generator of high power density, Ozone Sci. Eng. 9, 3, p195-206, 1987.
9. **Eliasson B., Kogelschatz U.**, Nitrogen oxide formation in ozonizers, Proc.8th Int. Symp. on Plasma Chemistry, Tokyo, Japan, pp.737-741, 1987.

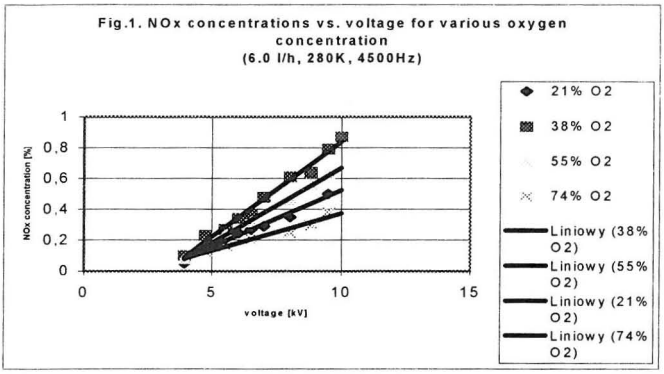


Fig.1. NOx concentrations vs. voltage for various oxygen concentration
(6.0 l/h, 280K, 4500Hz)
NOx concentration [%]
voltage [kV]
21% O2
38% O2
55% O2
74% O2
Liniowy (38% O2)
Liniowy (55% O2)
Liniowy (21% O2)
Liniowy (74% O2)

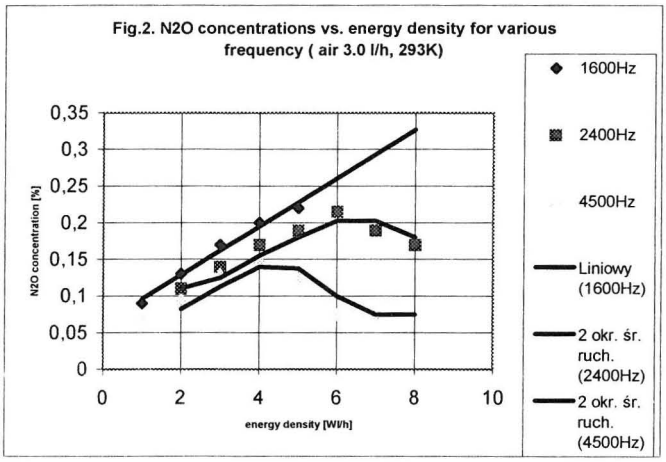


Fig.2. N2O concentrations vs. energy density for various frequency (air 3.0 l/h, 293K)
N2O concentration [%]
energy density [W/h]
1600Hz
2400Hz
4500Hz
Liniowy (1600Hz)
2 okr. śr. ruch. (2400Hz)
2 okr. śr. ruch. (4500Hz)

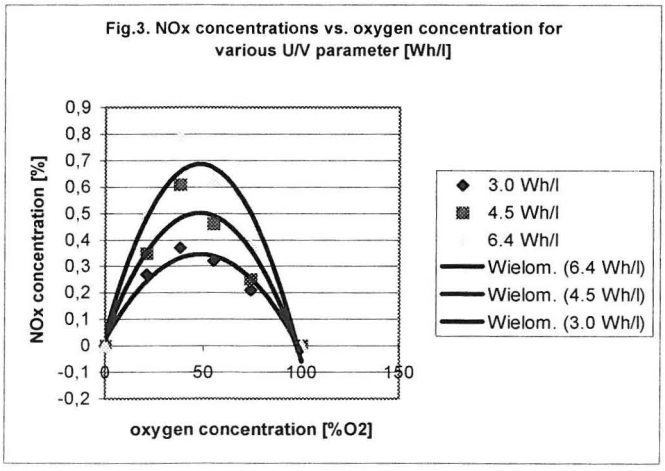


Fig.3. NOx concentrations vs. oxygen concentration for various U/V parameter [Wh/l]
NOx concentration [%]
oxygen concentration [%O2]
3.0 Wh/l
4.5 Wh/l
6.4 Wh/l
Wielom. (6.4 Wh/l)
Wielom. (4.5 Wh/l)
Wielom. (3.0 Wh/l)

Fig.4. N2O concentrations vs. energy density for various oxygen concentration

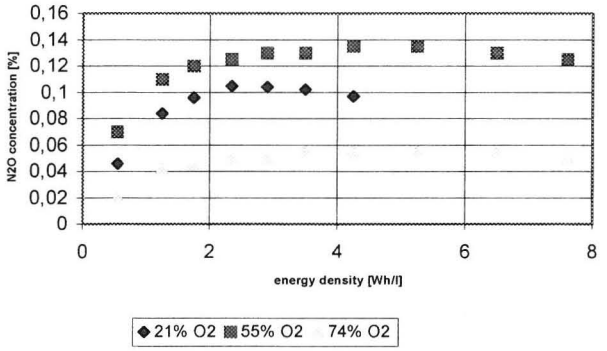


Fig.5. NO2 concentration vs. energy density for various O2 concentrations (293K, 4500 Hz, 6.0 l/h)

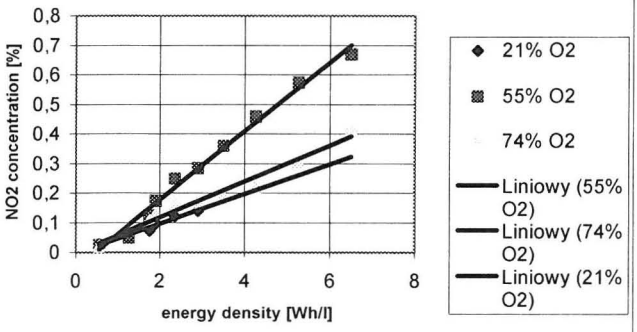


Fig.6. N2O concentration vs. energy density for varioust vapour concentration [ppm] (air, 3.0 l/h, 293K)

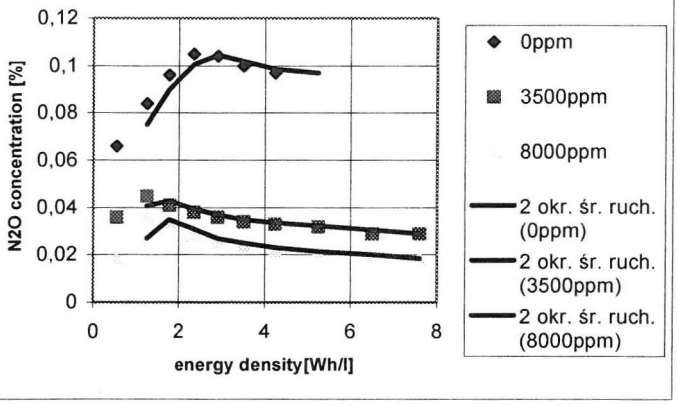
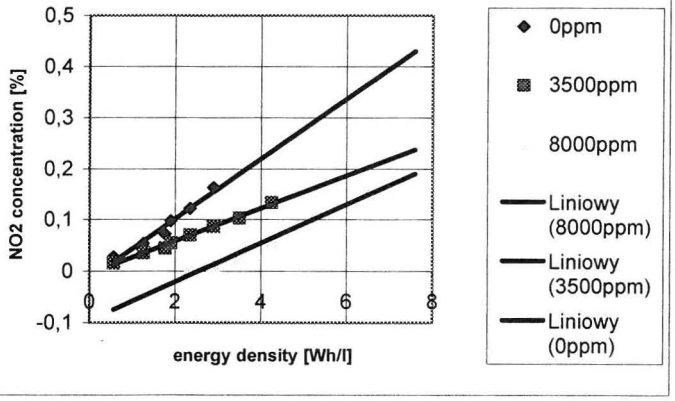


Fig.7. NO2 concentrations vs.energy density for variious vapou concentration [ppm] (air 3.0 l/h,293K, 4500Hz)



ROZKŁAD I RE-SYNTEZA NO_X W PLAZMIE NIERÓWNOWAGOWEJ W MIESZANINACH AZOTOWO-TLENOWYCH ZAWIERAJĄCYCH PARĘ WODNĄ

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S t r e s z c z e n i e. Procesowi rozkładu NO_x w plazmie nierównowagowej towarzyszy powtórna synteza tlenków azotu. Celem pracy było poznanie wpływu warunków zasilania elektrycznego, składu mieszaniny azotowo-tlenowej i obecności pary wodnej na przebieg syntezy NO_x . Uzyskane rezultaty wskazują na możliwość ograniczenia wtórnej syntezy NO_x poprzez odpowiedni dobór zasilania elektrycznego i obecność pary wodnej.

S ł o w a k l u c z o w e : synteza tlenków azotu, rozkład NO, wyładowania barierowe.