Effects of NOx adsorption on the electrode surface during silent discharge in air

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Abstract

A composition of chemical products obtained during silent discharge in an air-fed reactor strongly depends on the power density of discharge (U/V parameter). At medium value of this parameter stable level of ozone concentration was observed while at big value "non-stationary" process and strong adsorption of nitrogen oxides on the dielectric surface were observed. Changes of concentration of electrosynthesis products in time were observed in "non stationary" region when a HV value, gas velocity and temperature were constant. The maximal air residence time in discharge volume was 1,2 sec. The required time to reach the stationary concentration of electrosynthesis products may be even longer than 10 minutes. The ozone concentration in the gas at reactor’s outlet decreases to zero during the above time and the N2O-, NO- and NO2- concentration increases to stationary level.

1. Introduction

It is well known that during a barrier discharge in air ozone and nitrogen oxides (NOx) are produced [1,2]. The presence of nitrogen in air causes a decrease in energy efficiency of the process and lowers the level of ozone concentration. Independently, the degree of oxygen conversion to ozone is 2,5 time higher. Figure 1 presents typical dependence of the electrosynthesis products concentrations versus high voltage value. At high values of feeding voltage decay of ozone synthesis is observed. The voltage value at which ozone synthesis decay takes place, for the defined reactor and a fixed gas temperature, depends on air velocity. Air velocity increment causes this voltage value growth. Application of mass spectroscopy for an the electrosynthesis products analysis makes possible the "non stationary" kinetics observation. Adsorption of nitrogen oxides on dielectric surface in discharge gap induces a "non stationary" processes. The subject of influence of dielectric surface on the run of chemical processes in discharge volume is not yet explored. Research made up to now [3-7] did not give the answer on to mechanism of occurring processes. Even in the extended numerical models these processes are not considered.[1,8]

2. Experimental

Investigations were performed with the application of system earlier described [10] which consists among the other parts: the both side cooled, flat quartz reactor (discharge gap 1.0 mm) and mass spectrometer placed directly at the outlet of reactor. For discharge HV system (50-4500Hz, 4.0-12.0 kV) is applied. The air residence time was varied from 0,6 to 1,2 seconds. Application of mass spectroscopy directly at the reactor’s outlet makes possible a quick analysis of very active mixture leaving discharge space.
From Figure 1 we can see that at high voltage value \( HV = 7.5 \text{ kV} \) (U/V parameter value 3.6 Wh/dcm-3) stationary level of ozone concentration is zero while nitrogen oxides concentration takes non-zero values and varies depending on the oxide kind. Figure 2 presents fact that in these conditions a zero ozone concentration is not obtained immediately after the start of discharge but only few minutes after. Value of time depends on a gas residence time in discharge volume. Higher air velocity causes faster settlement of chemical dynamic equilibrium and a stabilisation of a electrosynthesis products concentration. Concentrations of individual nitrogen oxides is not stable too and only after few minutes they reach stationary level (Fig. 3-5). It is necessary to stress that changes of the electrosynthesis products concentration at the reactor’s outlet take place when other process parameters (gas velocity, discharge gap and temperature of cooling water) were kept unchanged. High repeatability of results presented in Figures 2-5 was achieved than that reactor was blow through by pure nitrogen for 40 minutes time after each experiment. The blowing time considerably influenced the maximal value of ozone concentration obtained in these conditions. On the basis of these data the required blowing time was found. Dependence between maximal value of ozone concentration and the pure nitrogen blowing time shows Figure 6.

To explain the phenomenon observed gas composition after cleaning dielectric surface was analysed. Experiment was carried out without discharge at first and next with varied power of discharge. Results of gas composition analysis presents Table 1.

Table 1. Concentrations [% vol] of desorption products during dielectric surface cleaning by pure nitrogen [99.9999 %] and by discharge. Gas velocity 3.0 dcm3/h, \( T=313K \)

<table>
<thead>
<tr>
<th>REACTOR INLET</th>
<th>REACTOR OUTLET</th>
<th>Discharge power density (U/V parameter)</th>
<th>Wh/dcm3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>no discharge</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>O2 0</td>
<td></td>
<td>0.025</td>
<td>0.12</td>
</tr>
<tr>
<td>N2O 0</td>
<td></td>
<td>0.001</td>
<td>0.007</td>
</tr>
<tr>
<td>NO 0</td>
<td></td>
<td>0.005</td>
<td>0.0055</td>
</tr>
<tr>
<td>NO2 0</td>
<td></td>
<td>0.007</td>
<td>0.012</td>
</tr>
<tr>
<td>N2 100</td>
<td></td>
<td>no measured</td>
<td></td>
</tr>
</tbody>
</table>

3. Results and discussion

During barrier discharge in an air-fed reactor with quartz dielectric, at high voltage (in our case \( HV=7.5 \text{ kV} \)) “non stationary” processes can be observed. It takes place when a value of U/V parameter is high and a stationary ozone concentration is zero. These phenomena are connected with a electrosynthesis products adsorption on a dielectric surface. Among components of a reactive mixture: N2, O2, O3, NO, N2O, NO2, NO3 and N2O5 only last one can be adsorbed in significant amounts on a dielectric surface in conditions of our experiments. This compound has a temperature sublimation 305.4K.[10], but as a desorption product from dielectric surface is not observed.

The experience of work with ozonizers used in industry, at high discharge power shows that during ozone synthesis from air, after sufficient long period of work (few months) ozone concentration decreases to low values. It is connected with presence of white deposit on dielectric surface, having acid reaction in water solution. The supposition of N2O5 adsorption does not explain the concentrations changes of electrosynthesis products in few minutes time. Ozone not react directly with N2O5. It is final product of nitrogen oxides oxidising process by ozone in a gas phase. There is almost ostensible paradoxical situation. The only gas which can be absorbed on dielectric surface is N2O5, but its adsorption can’t
influence on ozone concentration. It can be explained if we assume that desorption compounds are products of N2O5 decomposition eg.: NO,NO2,NO3, O2 and O-atoms. This process goes spontaneously with temperature, but it can be also forced by electron impact during discharge. Effects of these processes present Table 1.

The relatively high oxygen concentrations in nitrogen which blow through reactor without discharge suggests its presence on the dielectric surface[6] as well as nitrogen oxides. Significant increasing of oxygen concentration when discharge was turn on can result from the electron impact on desorbing nitrogen oxides in discharge space. In these conditions high level, more than 90%, decomposition of NOx to molecular oxygen and nitrogen were obtained[6,9].

The experimental results did not give clear answer concerning these processes influence on composition of desorbing gas from dielectric surface. Nitrogen oxides desorbed at the first part of reactor are exposed to impact of high energy electrons in discharge gap, and consequently: a) NOx are reduced and decomposed to N2 and O2, b) oxidised to higher oxides.

4. Conclusions
1. NOx adsorption on dielectric surface during silent discharge has an important influence on the course of chemical processes in discharge volume.
2. Even at big values of u/v parameter ozone synthesis in silent discharge is possible when surface of dielectric is free from NO mixture.
3. Gases which are desorbing from dielectric surface are O2,N2O,NO and NO2 but not N2O5

5. References

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Fig.1. Concentrations of O3(x0.1) and NOx vs HV value; T= 280K, residence time 1,2 sec., frequency 4500Hz
Fig. 2. Ozone concentrations for different residence time of air at value of $HV = 7.5 \, kV$ vs time.

Fig. 3. Nitrogen oxides concentrations at "non stationary" region of discharge ($HV = 7.5 \, kV$) vs time. Residence time 1.2 sec.
Fig. 4. Nitrogen oxides concentrations at "non stationary" region of discharge (HV = 7.5 kV) vs time. Residence time 0.9 sec.

Fig. 5. Nitrogen oxides concentrations at "non stationary" region of discharge (HV = 7.5 kV) vs time. Residence time 0.6 sec.

Fig. 6. Relation of ozone concentration "C" to maximal ozone concentration "Cmax" vs time of blow through by pure nitrogen.