CATALYTIC EFFECTS OF SOLID SURFACES ON OZONE FORMATION IN AIR[1]

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Catalytic action of silica on ozone formation in air was investigated by means of a semi-corona ozonizer.

In presence of granular silica in the discharge gap both higher ozone concentrations and a higher yield of energy were obtained. The influence of temperature on this phenomenon was examined, too. In experiments with air the catalytic action of silica was not stable, probably due to the poisoning effect of nitrogen oxides.

I. INTRODUCTION

Recently there has been a considerable interest in studying the role of plasma-surface interaction in the mechanism of chemical reactions under the conditions of electric discharges [1]. In previous works [2, 3] we stated that various solid dielectrics, e.g. silica or alumina, exhibit some catalytic activity in ozone formation in silent or semi-corona discharges. Similar effects were observed when some metals or metal oxides were inserted into the discharge gap of a silent discharge ozonizer [4—6]. While investigating the ozone synthesis from oxygen in a semi-corona ozonizer an increase of ozone concentrations was observed when the discharge gap was filled with granular silica [3]. Moreover, in the presence of silica also the yield of energy was higher. In the same paper it was pointed out that the discharge under those conditions might have the characteristic of a surface discharge. The observations concerning the catalytic effects mentioned above suggest that some dielectrics, like silica, might be useful as catalysts in the commercial production of ozone. The aim of this work was to continue our study of the catalytic action of silica on the ozone synthesis in a more complex system, in air. As it is well known in the presence of nitrogen various nitrogen oxides are formed simultaneously.

II. EXPERIMENTAL.

A semi-corona ozonizer K2/86 used in experiments is given in Fig. 1. A high voltage electrode made of stainless steel was placed at the centre of a "Pyrex" tube (22 mm internal diameter) which acted as a dielectric barrier. It was inserted in the cooling jacket in which constant temperature was maintained by means of a stream of water flowing through the jacket from the thermostat circuit. This was a ground electrode of the ozonizer at the same time. From a high voltage transformer (50 Hz), a voltage of up to 20 kV was applied to the central electrode. The input power was measured by a wattmeter at the primary circuit. A packing of granular silica was inserted into the discharge gap (7 mm
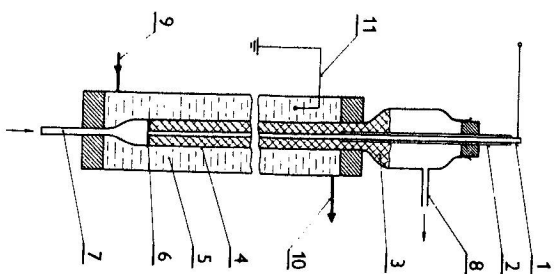

Fig. 1. Semi-corona ozonizer K2/86. 1 — High voltage electrode; 2 — insulator; 3 — bed of granular dielectric (silica); 4 — dielectric barrier (Pyrex tube); 5 — cooling liquid; 6 — perforated insert; 7 — air inlet; 8 — air and ozone outlet; 9 — cooling liquid inlet; 10 — cooling liquid outlet; 11 — ground lead.

wide) between the central electrode and the "Pyrex" tube. Ozone concentrations in the gas stream from the ozonizer were measured photometrically by observing the UV absorption at 225 nm. The apparatus used in the present work was quite similar to the one described in [3]. For the determination of nitrogen oxides (NO$_x$) these were oxidized with hydrogen peroxide. Then the nitrate, the product of that oxidation, was determined photometrically with phenolo-disulphonic acid — the method being in common practice. It should be added, however, that using that method we were not able to determine N$_2$O, and so its contents were not known.

III. RESULTS AND DISCUSSION

Experiments were carried out under the following conditions: Voltage: $U = 6$ —20 kV; Air flow: $\dot{V} = 25$, 100 and 200 dm^3/h; Cooling liquid temperature: $t_L = 2$, 25 and 50 °C; Packing: granular silica 1.25—5 mm (or 1.25—3.15 mm).

From current-voltage characteristics (Fig. 2 and 3) a strong influence of the packing on the ozonizer current i_{oz} was found (at constant voltage). In the
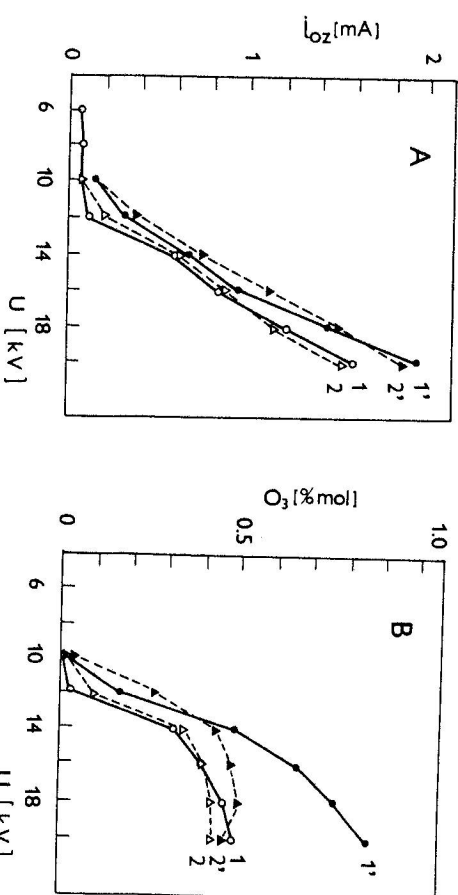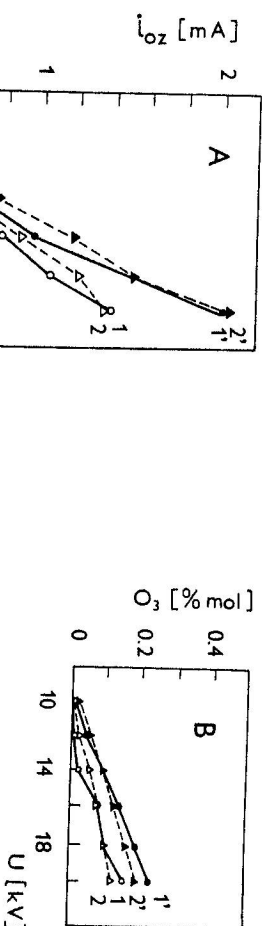

Fig. 2. Current-voltage characteristic (A) and ozone concentrations (mol. % O$_3$) vs voltage (B). 1 — without packing, $T_L = 2$ °C; 2 — without packing, $T_L = 50$ °C; 1' — with silica 1.25—5 mm, $T_L = 2$ °C; 2' — with silica 1.25—5 mm, $T_L = 50$ °C. Air flow $\dot{V} = 25$ dm^3/h.

Fig. 3. Current-voltage characteristic (A) and ozone concentrations (mol. % O$_3$) vs voltage (B). 1 — without packing, $T_L = 50$ °C; 2' — without packing, $T_L = 2$ °C; 1' — with silica 1.25—5 mm, $T_L = 50$ °C; 2 — with silica 1.25—5 mm, $T_L = 2$ °C. Air flow $\dot{V} = 200$ dm^3/h.

presence of silica the starting voltage was much decreased (e.g. from 12—13 kV to 8—9 kV) and the ozonizer current was higher especially in the lower part of the characteristics, i.e. just above the starting voltage. When discussing the current-voltage characteristics it must be taken into consideration that ozone concentrations in the presence of the packing were higher as well. This fact must influence the ozonizer current, too.

An increase of the ozone concentrations in the presence of silica was observed under various experimental conditions (Fig. 2 and 3). This effect was quite distinct especially at the lowest temperature range ($t_L = 2°C$), and two points should be noted in particular:

— within the voltage range $U = 8—12$ kV ozone concentrations were much higher with silica than without packing. This should be connected with the decrease of the starting voltage, mentioned above,

— with silica in some circumstances (e.g. $\dot{V} = 25$ dm³/h, $t_L = 2°C$) the ozone concentrations rose with the increasing voltage even above 18 kV, whereas without packing the ozone concentrations were nearly stable within this voltage range. On the other hand, the dependence of ozone concentrations vs. voltage in the presence of the packing shows a maximum when $\dot{V} = 25$ dm³/h and $t_L = 50°C$.
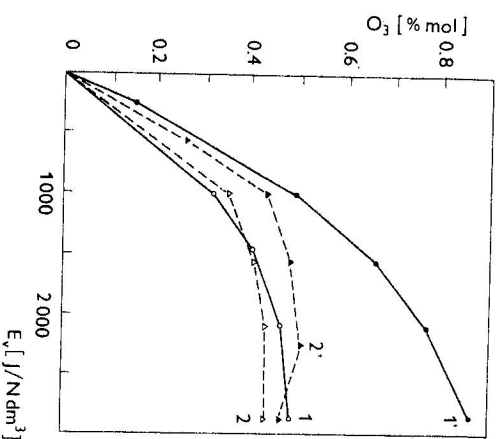
Fig. 4. Ozone concentrations (mol. % O₃) vs energy density E_v, J/Ndm³. 1 — without packing, $T_L = 2°C$; 2 — without packing, $T_L = 50°C$; 1' — with silica 1.25—5 mm, $T_L = 2°C$; 2' — with silica 1.25—5 mm, $T_L = 50°C$. Air flow $\dot{V} = 25$ dm³/h.
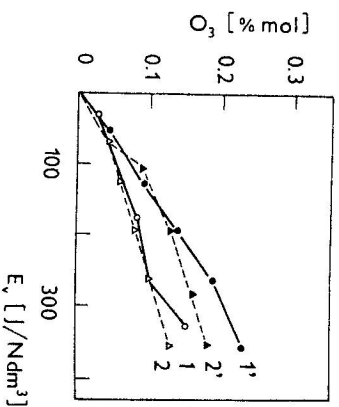
Fig. 5. Ozone concentrations (mol. % O₃) vs energy density E_v, J/Ndm³. 1 — without packing, $T_L = 2°C$; 2 — without packing, $T_L = 50°C$; 1' — with silica 1.25—5 mm, $T_L = 2°C$; 2' — with silica 1.25—5 mm, $T_L = 50°C$. Air flow $\dot{V} = 200$ dm³/h.

The catalytic action of the silica packing can be better seen (Fig. 4 and 5) when comparing the dependences of ozone concentrations on the energy density E_v, defined as:

$$E_v = \frac{P}{\dot{V}_N}, \quad J/Ndm^3, \qquad (1)$$

P — input power at the ozonizer, $\dot{V}_N$ — air flow, Ndm³/h (0°C, 760 mm Hg). Fig. 6 shows the dependences of ozone concentrations on air flows $\dot{V}$ and Fig. 7 — on the cooling liquid temperature t_L. In the presence of the packing higher ozone concentrations as well as higher energy yields were obtained (Fig. 8).
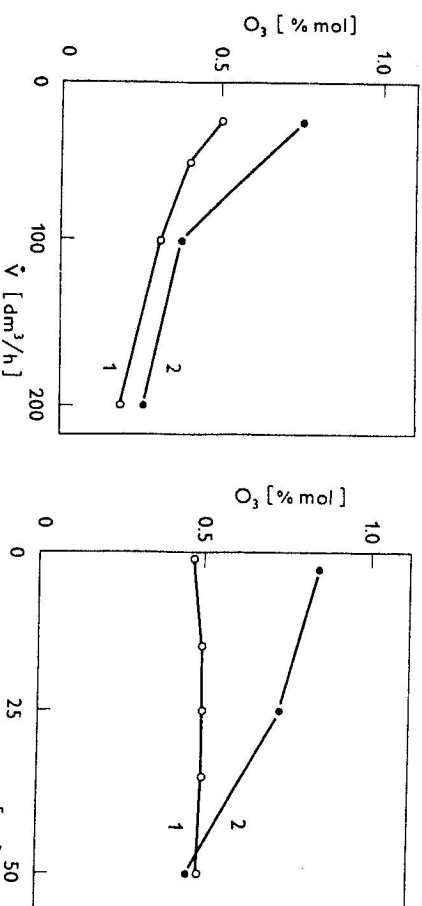
Fig. 6. Ozone concentrations (mol. % O₃) vs air flow $\dot{V}$. 1 — without packing; 2 — with silica 1.25 — 5 mm; $U = 20$ kV, $T_L = 25°C$.

Fig. 7. Ozone concentrations (mol. % O₃) vs cooling liquid temp. T_L. 1 — without packing; 2 — with silica 1.25—5 mm; $U = 20$ kV, $\dot{V} = 25$ dm³/h.

These effects were quite similar to those observed during the ozone formation in oxygen [3]. In our opinion, those were catalytic processes occurring at the plasma-solid interface responsible for both effects. Thus, silica catalyzed the ozone formation in air in a similar way as in oxygen. An essential difference, however, should be noted: the catalytic effect observed in this work, i.e. in air, was not stable contrary to that in oxygen. The silica packing lost its catalytic activity probably due to being poisoned under experimental conditions.

When discussing these results it should be taken into consideration that as the ozone synthesis was carried out in air, nitrogen oxides were produced as well.

We found their contents from 0.01 to 0.06 mol. %. The "poisoning effect" of nitrogen oxides on the ozone formation under silent discharge conditions is well known [7—9]. It is thought that the adsorption of nitrogen oxides, especially N_2O_5, on the surface of the glass wall (barrier) of ozonizers is responsible for this effect [10]. Thus, it is quite possible that in our experiments nitrogen oxides being adsorbed on the silica surface inhibited its catalytic action in the ozone formation. This assumption was supported by the measurements shown in Fig. 9. During the run of the experiment without packing (Fig. 9A) ozone concentrations were stable (at the level of 0.5—0.55%), and concentrations of NO_x were nearly stable, too (0.03—0.04%). When silica packing was taken (Fig. 9B), at
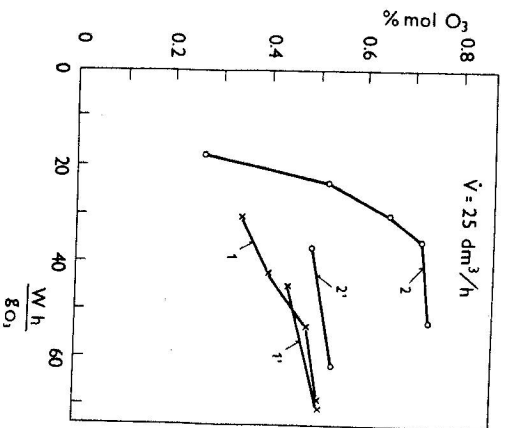

Fig. 8. Dependence of energy consumption on ozone concentrations. Air flow $\dot{V} = 25$ dm³/h, cooling liquid temp. $T_L = 25°C$, voltage $U = 12$—20 kV. 1 — without packing, at the beginning of the run; 1′ — without packing, at the end hours of the run; 2 — with silica 1.25—5 mm, at the beginning of the run; 2′ — with silica 1.25—5 mm, after 30 hours of the run.

the beginning the ozone concentrations were found higher (above 0.8%); however, they fell off quickly during the first period of the experiment (i.e. during the first four hours). At the same period of time NO_x concentrations were staying low but next, after four hours, they began to rise abruptly. At the end of the experiment we found the ozone and the NO_x concentrations as high as those without packing. The connection between the ozone formation rates and the presence of NO_x was evident. Probably during the first period of the experiment almost the whole amounts of NO_x generated in the discharges were adsorbed on the surface of silica grains. At the same time the silica surface of the packing dropped step by step. After several hours the silica surface became "saturated" with NO_x and therefore it lost the catalytic activity completely in the ozone formation process. In our opinion that was the "poisoning effect" of NO_x demonstrated in the experiment under discussion.

The amount of silica taken for the next experiment (Fig. 9C) was first inserted in a urea solution and carefully dried. In the presence of silica prepared in such a way the first period of the experiment, with high ozone and low NO_x concentrations, was found to be much longer than in the case of pure silica. However, the final results were nearly the same as in the measurements discussed above. The effect observed with urea can be understood when it is taken into account that urea can react with nitrogen oxides decomposed in this way. When the amount of urea deposited on the silica surface had been consumed by the reaction with NO_x, the process conditions became the same as in the previous experiment, Fig. 9B. So were the ozone and NO_x concentrations. The "poisoning effect" of NO_x is also clearly seen when the dependence of energy consumption on ozone concentrations is considered (Fig. 8). Finally it should be mentioned that in the present experiments with air we found the discharge structure (in the presence of silica and without packing) similar to that in oxygen. Still, the current flowing through the ozonizer was now more stable.

As it was shown earlier [3], in our ozonizer, in the presence of the packing, the discharges had a feature of surface discharges. This fact facilitated the catalytic action of the packing surface and made it more effective. It also resulted in the current — voltage characteristic changes as it can be seen in Figs. 2 and 3.

IV. CONCLUSIONS

1. Catalytic action of silica was observed under conditions of semi-corona discharges in air.

2. It was found that the catalytic action of silica was not stable under those conditions, probably due to the poisoning effect of nitrogen oxides.
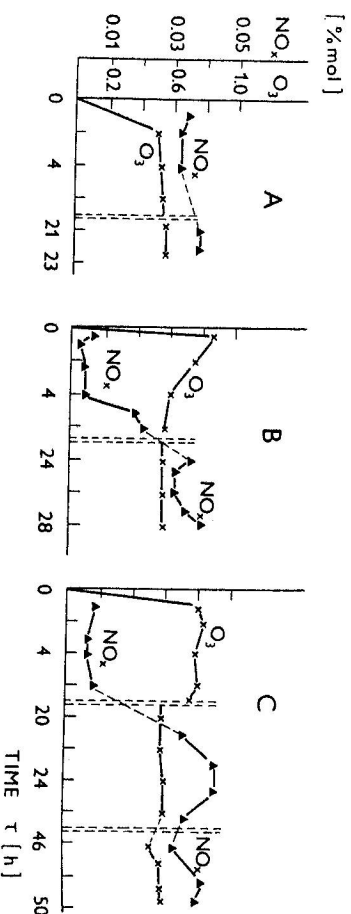

Fig. 9. O_3 and NO_x concentrations (mol. %) vs time, h. A — without packing; B — with silica 1.25—5 mm; C — with silica 1.25—5 mm, urea deposited.

3. In the presence of the granular silica packing in the discharge gap the semi-corona discharges in air had a feature of surface discharges, similar to the semi-corona discharge in oxygen.

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КАТАЛИТИЧЕСКИЕ ЭФФЕКТЫ ТВЕРДЫХ ПОВЕРХНОСТЕЙ ПРИ ФОРМИРОВАНИИ ОЗОНА В ВОЗДУХЕ

Каталитическое действие кремнезема на формирование озона в воздухе было исследовано при помощи полукоронного озонатора.

В присутствии гранулированного кремнезема в разрядной щели были получены повышенные концентрации озона, также как и повышенная отдача энергии. Было исследовано влияние температуры на эти эффекты. В экспериментах с воздухом каталитическое действие кремнезема не было стабильным, что, вероятно, можно объяснить эффектом отравления окислами азота.