INVESTIGATION OF DISSOCIATION AND SYNTHESIS IN PLASMA CHEMICAL REACTORS BASED ON PLASMA-BEAM DISCHARGE

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Keywords: Synthesis, dissociation

ABSTRACT

Synthesis of NO in plasma-chemical reactor based on plasma-beam discharge (PBD) is treated both theoretically and experimentally. Experimental results presented were obtained on PBD plasmatrons with different configurations of the discharge. Experimental results on dissociation of $C_2Cl_3F_3$ are also given.

INTRODUCTION

It was shown in (1,2) that plasmatrons based on stationary PBD are the most promissing from technological point of view. High degrees of ionization ($\alpha=10^{-4}\div1$) can be achieved in this type of a discharge under working gas pressure ranging from 10^{-4} to 10 tor. The discharge was stable despite whether noble gases or electronegative gases were used. Physical principles of PBD plasmotrons are briefly described in (1,2). The paper deals with investiggtion of chemical reactions in PBD plasmatrons with ribbon-like and pipe-like beams.

I.PBD PLASMATRON WITH RIBBON-LIKE ELECTRON BEAM.

Device. Schematic diagram of plasmatron is shown on Fig.1. Electron gun (1-anode, 2-catode) injects electron beam (3) along axial magnetic field. Vacuum resistance (5) separates electron gun from high pressure reaction zone. Collector of an electron beam (6) cooling by water operates as calorimeter used to determine the part of beam energy dissipated in plasma. Electron beam power is about 30KW (I=5A, U=6KV). Working gas flow is formed by the system (4) and passesthrough the discharge zone (7). Products of chemical reaction were sampled by spesial collector (8) providing flow rate G= 120 l/sec or G=1500 l/sec which assure expenditures of working gas from $5\cdot10^{19}$ part/sec to $5\cdot10^{22}$ part/sec depending on gas pressure and velocity of pumping. Products were analysed by mass-spectrometer of omegatron type.

Synthesis of NO in PBD.

Theory. Synthesis of NO preceeds most efficiently when nitrogen is vibrationally excited according to reaction (4):

$N_2(v) + O \underset{K_3}{\overset{K_1}{\rightleftarrows}} NO + N$ (1), $O_2 + N \underset{K_4}{\overset{K_2}{\rightleftarrows}} NO + O$ (2)

Here $N_2(v)$-vibrationally excited N_2, K_i -rate constants of direct and inverse reactions.If each particle of working gas is staying in the discharge zone during τ_0 ,then degree of processing of N_2 in thedischarge zone can be estimated by the formula: $\Delta[NO]/N_0 \simeq (A/N_0) K_0 N_0 \tau_0$

Here A-concentration of N,N_0-concentration of N_2,K_0=10^{-11} cm^3/sec -rate constant of the process.In our experiments A/N =10^{-2},N_0=10^{16}cm^3, τ_0 =10^{-5}sec.Then degree of processing equals to 10^{-2}.Synthesis of NO in plasmatron based on PBD proceeds in two stages:1) passing of working gas through the discharge where molecules gain vibrational energy and partly dissociate.2)Chemical reactions of nitrogen oxidation in afterdischarge zone.Let us consider the first stage.Since degree of processing increase in accord with increasing of vibrational energy it is necessary to learn the dependence of $\bar{\mathcal{E}}_v$ upon discharge parameters(α , T_e) in the regime of saturation,i.e. when $\tau_0 \to \infty$ .Then maximal degree of processing can be evaluated.To obtain this dependence the system ofequations discribing time variations of nitrogen vibrational levels populations was calculated numerically(5).Rate constants were taken from (6).The results obtained are shown in Fig.2.It can be easily seen that for all α : $\bar{\mathcal{E}}_v \leq T_e$. Then to achieve highest processing of NO nitrogen have to stay in the discharge zone during time τ_0 ,which can be estimated from this obvious relation:

$$T_e \simeq \bar{\mathcal{E}}_v \simeq \hbar\omega K_{e\text{-}v} N_0 \alpha \tau_0 \qquad (3)$$

where $K_{e\text{-}v}$ -rate constant of vibrational excitation of N_2 by electron, $\hbar\omega$ -vibrational quantum.However collisions of electrons with N_2 results not only in vibrational excitation but in dissociation of N_2 excitation of electronic states and ionization of molecules and atoms as well.To achieve better efficiency energy spent on those perposes have to be much less than $\bar{\mathcal{E}}_v$ .Consider some model gas taking into account all these processes except for excitation of electronic states.It was shown in (7) that $K_D = \xi K_I$ (K_D, K_I -rate constants of dissociation and ionization, ξ -some coefficient equals to 10).Ionization rate constant can be obtained from balance equation for electrons in the discharge.Since α =10^{-3}÷1 in PBD life-time of electrons is restricted by ambipolar diffusion or by dissociative recombination.Thus we obtain

$$K_I = (\tau_{a.d.} N_0)^{-1} + \alpha K_{d.r.} \qquad (4)$$

Where $\tau_{a.d.}$ -characteristic time of ambipolar diffusion, $K_{d.r.}$ -rate constant of dissociative recombination.We may conclude that when the condition

$$\xi \frac{\mathcal{D}}{\hbar\omega} \left\{ \frac{1}{\tau_{a.d.} K_{e\text{-}v} N_0} + \frac{T_e}{\hbar\omega} \frac{K_{d.r.}}{K_{e\text{-}v}} \frac{1}{K_{e\text{-}v} N_0 \tau_0} \right\} < 1 \qquad (5)$$

(D -dissociation potential) is valid the major part of energy input into gas is spent on vibrational excitation.Making use of equation (4) one obtains the concentration of working gas which assures optimal vibrational excitation

$$N_0 > N_* = \frac{1}{2}\xi \frac{T_e \mathcal{D}}{(\hbar\omega)^2} \frac{K_{d.r.}}{K_{e-v}} \frac{1}{K_{e-v}\tau_0} + \left\{\left(\frac{\xi}{2} \frac{T_e \mathcal{D}}{(\hbar\omega)^2} \frac{K_{d.r.}}{K_{e-v}} \frac{1}{K_{e-v}\tau_0}\right)^2 + \xi \frac{\mathcal{D}}{\hbar\omega} \frac{N_0}{\tau_{a.d.} K_{e-v}}\right\}^{1/2} . \quad (6)$$

For characteristic parameters of PBD plasmatron $\tau_0 = 10^{-5}$ sec, $\mathcal{D}/\hbar\omega \simeq 20$, $T_e/\hbar\omega \simeq 3$, $\xi = 10$, $K_{d.r.} \approx K_{e-v} \simeq 10^{-8}$ cm^3/sec, 10^{-19} N_0, we obtain $N_0 \simeq 6.10^{15}$ cm^{-3}.

Consider now the second stage. It is supposed that gas on outlet from discharge is partly dissociated and it's mean vibrational energy equals $\bar{\mathcal{E}}_v$. Since cross-sections of vibrational excitation for O_2 and NO are about two orders of magnitude higher then that of N_2 and on the outlet from discharge $\bar{\mathcal{E}}_v^{(N_2)} \simeq T_e$ then $\bar{\mathcal{E}}_v^{(NO)} \simeq \bar{\mathcal{E}}_v^{(O_2)} \simeq T \ll T_e$ where T-gas temperature. Nonresonant v-v exchange between O_2, NO and N_2 is not quick enough to change appreciably mean vibrational energy of NO and O_2- $\bar{\mathcal{E}}_v^{(NO)}, \mathcal{E}_v^{(O_2)}$ -during reaction time and therefore the only mechanism resulting in increasing of $\bar{\mathcal{E}}_v^{(NO)}$ and $\bar{\mathcal{E}}_v^{(O_2)}$ is chemical reaction itself. Neglecting the dissociation processes in afterdischarge zone and making use of quasistationary approximation for concentration of atoms of oxigen and nitrogen we obtain from (1) and (2):

$$\frac{d[NO]}{dt} = 2A \frac{K_1 K_2 [O_2][N_2] - K_3 K_4 [NO]^2}{K_1 [N_2] + K_2 [O_2] + (K_3 + K_4)[NO]} , \quad (7)$$

where A= O + N = const. It follows from (4) that rate constants of endothermal reaction K_1 and K_4 depend upon mean vibrational energy of the molecules involved, but K_2 and K_3 depend upon T. Thus equation (7) and equations for time variation of vibrational energy and gas temperature describe the whole process of NO synthesis. Indicated system of equations was solved numerically by means of computer. Rate constants of reactions (1) and (2) were taken from (8). It was supposed that 10% of energy in excess of threshold energy of vibrational excitation is transfered in heating of the gas. On Fig.3 relative concentration of NO in equimolar mixture is plotted against time for different values of initial gas temperature T and $\bar{\mathcal{E}}_v^{(N_2)} = 1$ eV ($\tau = (A/N_0) K_0 N_0 t$). Dependence of energy cost of one NO molecule on vibrational energy for equimolar mixture is shown on Fig.4. Almost the same results were obtained when air was taken.

Thus the calculations presented here demonstrate the possibility of NO synthesis in PBD plasmachemical reactor with degree of processing about 10-12% and energy cost of NO molecule about 6-8 eV.

<u>Experiment</u>. Prior to consideration of main results of NO synthesis it is instructive to consider briefly experimental evidence of effective relaxation of an electron beam in plasma. Variation of energy gained in plasma W_p with increasing of beam power W_B under constant current of the beam I=1A (curve 1) and constant density of the beam (curve 2) are shown on Fig.5. Air pressure in reaction zone was 5.10^{-2} tor with gas flow rate 2.10^{20} part/sec. It is seen that energy input in plasma is strongly dependent upon relation between beam current I and it's voltage U.

Consider now experimental results on NO synthesis. Fig.6 shows the variation of NO concentration in gas on outlet from the discharge with increasing of energy input in plasma W_p under gas pressure in reaction zone $P_0 \simeq 5.10^{-2}$ tor and gas flow rate 2.10^{22} part/s. The current of the beam in this experiment was hold constant. It is seen that degree of NO processing is increased with increasing of W_p. Comparing the results shown on Fig.5 and 6 one may come to conclusion that in order to increase the output of the reaction concentration of the beam have to be increased under being fixed at the optimal value. Fig.7 demonstrates dependence of NO concentration on the output of reactor on beam power W_b under different gas pressure P_0 and gas flow rate G. Beam energy was increased due to increasing of its current (and therefore its density), the voltage of the beam was varied only slightly. Saturation which is seen on Fig.7 is evidently caused by the fact that during the time needed for gas to come through thedischarge zone vibrational energy reaches it's stationary level $\mathcal{E}_v \simeq T_e$ (Fig.2). On Fig. 8 energy cost of one NO particle is plotted against beam power W_b ($p=10^{-1}$ tor, das flow rate -1500 ℓ/sec). It must be noted that energetic efficiency of NO synthesis in plasma-beam discharge is about two times as high as in the other types of discharge (10). Thus the possibility of NOsynthesis from air in plasma-beam discharge is experimentally shown with degree of processing about 10-20% and energy cost of each NO particle about 10eV. These experimental results are in good agreement with theory presented in the first part of the paper.

PIPE-LIKE ELECTRON BEAM. Plasmatron with pipe-like electron beam were used with the aim to obtain high-intensity atomflows due to dissociation in the discharge. Experiments were undertaken on the device differing from that described in (2) by the exchange of the cylindrical beam for pipe-like hollow beam 40mm in diameter and 1mm width. Molecular gas was injected into inner volume of pipe-like discharge. The products were analysed by mass-spectrometer of omegatron type.

Dissociation of $TiCl_4$. Final products of dissociation can be collected on quenching target in the form of films or thin powders. Under power regime when 30 eV was spend on each particle of $TiCl_4$ intensive deposition of TiCl, $TiCl_2$, $TiCl_3$ was obtained on the cooling target. The rate of deposition was about 0,5 mkm/min. It is supposed that the rate of deposition can be increased by instantaneous increase of the discharge power and gas flow rate. The products deposited on the target can be easily cleaned out by means of pumping velocity decreasing. In this case Cl_2 is in excess in the reaction zone ,and part of it dissociates in the discharge. Interaction of atomic Cl with clorides deposited on the target results in creation of gaseous $TiCl_4$. Thus etching of previously deposited products occurs.

Dissociation of freons-113 .In order to obtain atomic flows of Cl and F ,dissotiation of $C_2Cl_3F_3$ was investigated in plasma-beam discharge.Electron beam power was varied from 0,6 up to 2,5 kW,gas pressure of $C2Cl_3F_3$ in the reaction zone was about $(1-3).10^{-2}$ tor.In the absence of the discharge the presence of heavy component and small part of Cl was indicated by mass-spectrometer.The present of Cl was evidently caused by dissociates of $C2Cl_3F3$ in the mass-spectrometer lamp.Ad the power of the discharge was increased prononced peaks of Cl,Cl_2,F_3,HF were obtained. The traces of atomic F were obtained when power was as high as 2,5 kW.On Fig.9 the ratio of peak intensities of light components to heavy component is plotted against discharge power.Molecules Cl_2,F_2,HF are evidently the secondary products which resulted to recombination of atomic Cl and F in the tube connecting reaction zone and mass-spectrometer ter.Experiments described here demonstrate that atomic flows of high intensity can be produced due to dissociation of appropriate products in plasma-beam discharge.

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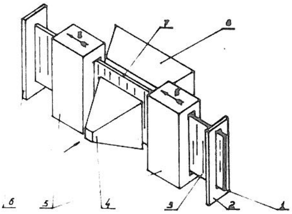

Fig. 1

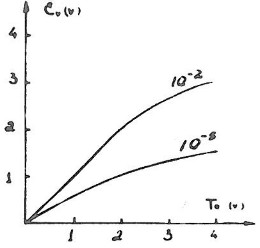

Fig. 2

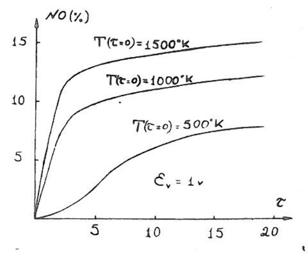

Fig. 3

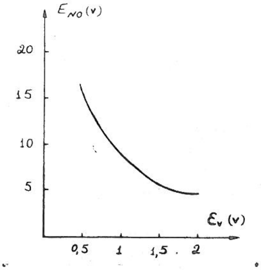

Fig. 4

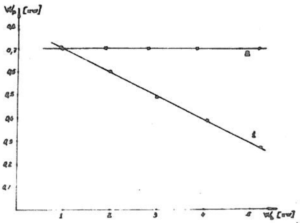

Fig. 5

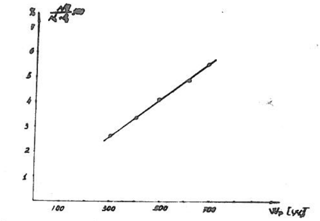

Fig. 6

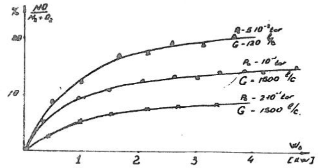

Fig.7

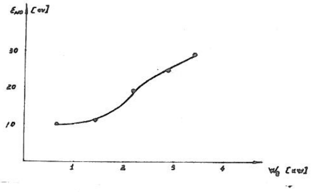

Fig.8

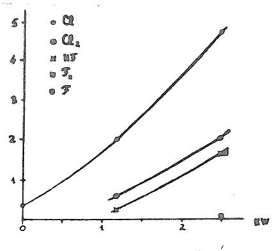

Fig.9