NITROGEN OXIDATIVE ACTIVATION IN THE RADIOLYSIS PROCESS OF DIOXIDE HYDROCARBON COMPOSITION, OXYGEN-NITROGEN OVER 3-d TRANSITION METALS

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The radiochemical process of nitrogen fixation in carbon dioxide, oxygen-nitrogen composition in 3-d metal (iron, nickel) was studied. Bifunctional character of surface's role in the generation of radiolysis products was postulated:

a) Chemical sorption of molecular ions (N_2^+, CO_2^+, O_2^+) on the surface of metal and their dissociative neutralization.
b) Coordination of nitrogen and carbon oxide being generated in nitrosyl and carbonyl-nitrosyl complex of iron and nickel.

The recent nitrogen fixation process constitutes reaction "brute force" based on the inorganic catalyst application at high temperatures, pressures or in electric discharge. Attempts to realize nitrogen radiation-chemical fixation were not carried out to the high nitric oxide yield (G=1,0÷1,5 molecule/100eV) [1]. Among them, a great deal of publications concerning usage of soft oxidizing substances (H_2O_2) were dedicated to the search of alternative ways on nitrogen fixation lately [2]. They have enough potential for oxidation N_2 before N_2O with the further creation coordinated to $[ONNO]^{2-}$. Experimental researches on radiolysis of dioxide-carbon–nitrogen composition over dispersed nickel (1) and oxygen-nitrogen over iron (II) were done by us.

Samples (I) were irradiated at quartz vessels with electrons accelerated under the statical condition. Homogenization of the components can be accoplished ampoule rotation. Dosimetry is made by ethylene. Doze rate is 10 kG/hour. For better contact of the composition components with iron a permanent magnet was installed behind ampoule was to create magnet field. Products' chromatographic analysis was carried on IR-spectra. For nitric-oxide (N_2O, NO_2) chromatograph "Svet-102" was used, for nitric oxide and carbon monoxide (NO, CO) "Gasokhrom-3101" was done. Nickel's carbonylnitrosyl complex was identified on "Specord". Technical nitrogen was cleaned at 196^0C by freezing O_2 impurities dioxide carbon was dried by sulphuric acid and cleaned from oxygen by multiplex freezing on vacuum-adsorption plant.

RESULTS AND DISCUSSIONS

Radiolysis of CO_2/N_2 (70/30) homogenous composition leads to the obtaining of nitric oxide and carbon with $G_{(CO)}$=0,8 and $G_{(NO)}$=0,25. Dependence of the radiation-chemical yields CO and NO on components proportion over nickel (P=0,1 MPa) [3] is shown in the figure 1.

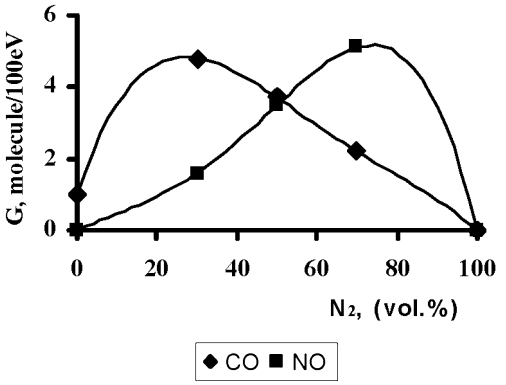

Fig.1 Dependence of the radiation-chemical yields on molecular nitrogen content in the composition.

As one can see from Fig.1, total yield of the products is over the range of 6,4÷7,5, which makes it impossible to explain the contribution of only neutral products to radiolysis. Evidently in the generation of final products, defined contribution brings in molecular ions N_2^+ (N^+) and CO_2^+. Interaction character of these ions with nickel proposes the formation of the relation between unpaired electrons N_2^+ and CO_2^+ with unfilled d-sublevel of these metals with the nickel nitride generation [N_i-N=N^+] and binding energy in ion diazotate decreases as much as twice. During dissociative neutralization of nickel nitride ions, nitrogen atoms become excited N(^{2}D) having 2,38 eV higher in comparison with N(^{4}S) main condition and life-time. Based on the authors' researches [4] it is supposed that atoms reaction of N(^{2}D) with O_2 have nitric oxide NO. Here, the main research demonstrated that [5] during overcharge of positive ions in metal atoms transition from the initial condition to product condition may be carried out through generation of highly excited particles stage.

Total yield of all active intermediate particles of nitrogen radiolysis equals:

$$\sum G_{(N)} = 2G_{\left(N_2^+\right)} + G_{\left(N^+\right)} + G_N^0 = 4,9 + 5,6 = 10,5$$

Consequently, calculated total yields of radiolysis composition products (I) may be

$$10,5 \geq \sum G_{yield} \geq 6,5$$

As it is shown, the calculated and the experimental values of nitric oxide and comparable hydrocarbon obtained indicate correctness of the model selected. Some understated values of observed yields is seemingly related with the oxide insufficiency generated only at a result of radiolysis of CO_2.

The generation of carbon nitrosyl composition of nickel [$Ni(CO)_m(NO)_n$] was spectrophotometrically identified. This radiolysis products without their thermal decomposition was led to gas ditch of the spectrophotometer. At IR spectrum products in the range of stretching vibrations CO= group was observed in the absorption band with ν= 2080 cm^{-1} frequency and NO group is characterized by 1850 cm^{-1}. For NO- group in connection with Ni(NO)(NO_2)- oscillation frequency NO- group was reduced to 1845 cm^{-1}, and in nickel tetracarbonyl [$Ni(CO)_4$] the frequency of stretching vibrations of CO group is 2060 cm^{-1}. Interaction of radiolysis product (NO, CO) with dispersed nickel leads to the rapid combining form [Ni-N=O] generation and week combining form [Ni=C=O] in nickel carbonylnitrosyl complex.

Nitric-oxide samples over dispersed iron was irradiated on the radioisotope plant Co^{60}. Nitrous oxide (N_2O) was identified as the main product, besides the following amount of nitrogen dioxide (NO_2) exists. Seemingly the initial reaction in the radiolytic transition composition components have the iron nitride ion generation (FeN_2^+).

The final reaction with oxygen leads to the generation of iron nitrosyl complex in the reaction:

$$FeN_2^+ + O_2 \rightarrow Fe\left[(NO)^+(NO)\right] \xrightarrow{T} FeO + N_2O$$

Nitrous oxide is admittedly created at thermal dissociation of nitrosyl complex of iron.

The generation of nitrogen dioxide (NO_2) in gas phase is determined by radiolytic transition of composition components:

$$N+O_2 \rightarrow NO+O$$

and slow interaction

$$NO+O_2 \rightarrow NO_2+O$$

In N_2O molecular bond strength of N_2 was decreased twice in comparison with nitrogen molecule, that's why its further oxidation doesn't give thermodynamical difficulties.

The yield of nitrogen dioxide on radiolysis of the air gave G_{NO_2}=0,8±0,2 molecule/100eV which is referred to the data in a good agreement in the literature. Kinetic curve appears rapidly in the saturation. Air radiolysis over iron gave the following results: $G_{NO_2} = 2,75 \pm 0,25$, $G_{N_2O} = 9,0 \pm 1,0$ molecule/100eV. Thus, total yield of radiolysis products is $\sum G = 10,5 \pm 12,0$ molecule/100eV.

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