PHYSICAL-CHEMICAL MECHANISMS OF NO_x OXIDATION STIMULATED BY ELECTRON BEAM.

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INTRODUCTION

EB process is considering now as one of the most perspective technology for the pollution control in particular for the purification of flue gases from NO_x. Development of this technology depends on understanding of NO_x oxidation and NO_x reduction mechanisms. It is considered [1] that NO_x oxidation is taking place sequentially from low oxide to high one. However in additional to this conventional mechanism it is possible that another mechanism occurs when NO oxidize to HNO_3 through negative ion NO_3^- without formation of intermediate NO_2 and HNO_2 oxides. Moreover the existence of the chain ion-molecule mechanism of HNO_3 formation in the gas can be assumed too. The strong effect for the kinetic of NO_x oxidation can has droplets and aerosol particles formed under EB irradiation in the humid air. This effect is associated with good NO_2 and HNO_2 solubility in the water and on the wet surface of aerosols' particles.

This work is devoted to description of kinetic and NO_x oxidation mechanisms in air under EB taking into account electron beam active species production, gas-phase reactions including reactions of exited particles and clusters chemistry, heterogeneous oxidation and reduction reactions including reactions in the droplets.

NO_x OXIDATION MECHANISMS.

It is thought [1] that negative ions in the NOx oxidation process are of little importance and them contribution consists from step of negative cluster formation in the reaction:

$$NO + O_2^- H_2O + M \rightarrow NO_3^- H_2O + M \qquad (1)$$

with following dissociation recombination with positive cluster ion $H_3O^+H_2O_n$:.

$$NO_3^- H_2O_n + H_3O^+ H_2O_m \rightarrow NO_2 + OH + H_2O_{n+m+1} \qquad (2)$$

The proposed ion - molecular oxidation mechanism is related with the formation of negative ion $NO_3^-(H_2O)_n$ that can exist in two isomeric forms[2]. The more stable one has a structure of nitric acid anions and can give nitric acid in the results of recombination with the $H_3O^+(H_2O)_m$.

$$NO_3^- H_2O_n + H_3O^+ H_2O_m \rightarrow HNO_3 + H_2O_{n+m+1} \qquad (3)$$

As is obvious if recombination process takes place in accordance with reaction (2) then NO oxidize to NO_2 and efficiency of NO_x removal is low. If it is assumed that recombination of ion clusters leads to HNO_3 formation then efficiency of NO_x removal increases.

The existence of the chain ion-molecule mechanism of HNO_3 formation in the gas can be assumed:

$e + O_2 + M \rightarrow O_2^- + M$ (4)
$O_2^- + H_2O + M \rightarrow O_2^-H_2O + M$ (5)
$O_2^-H_2O + NO + M \rightarrow NO_3^-H_2O + M$ (6)
$NO_3^-H_2O_n + NO_2 + M \rightarrow N_2O_5^-H_2O_n + M$ (7)
$N_2O_5^-H_2O_n + H_2O \rightarrow 2HNO_3 + nH_2O + e$ (8)

However this process is a possibility only at not much high NO conversation because in the creation of chain both NO and NO_2 take part.

Heterogeneous mechanisms are related with the reactions of the soluble intermediate components like NO_2, HNO_2, $N2O_3$, and $N2O_4$ in the droplets and on the wet surface of aerosols particles. To be dissolved these components exist in ion form and can take part in spontaneous reduction and oxidation reactions.

There are several channels of heterogeneous reactions:

First of all NO_2 molecules being dissolved in the liquid can react with each other in accordance with equation:

$$NO_2(l) + NO_2(l) + H_2O \rightarrow 2H^+ + NO_2^- + NO_3^- \qquad (9)$$

The rate constant of this reaction is $7*10^{-14}$ $cm^3\ c^{-1}$ [3]. Dissolved NO_2 molecules can also react with NO in liquid:

$$NO_2(l) + NO(l) + H_2O \rightarrow 2H^+ + 2NO_2^- \qquad (10)$$

with the same rate constant. NO_2 and NO can also take part in heterogeneous processes indirectly via N_2O_4 and N_2O_3 molecules formed in gas phase:

$NO_2(g) + NO_2(g) \rightarrow N_2O_4$ (11)
$NO(g) + NO_2(g) \rightarrow N_2O_3$ (12)

and then quick reactions in liquid phase

$N_2O_4(l) + H_2O \rightarrow 2H^+ + NO_2^- + NO_3^-$ (13)
$N_2O_3(l) + H_2O \rightarrow 2H^+ + 2NO_2^-$ (14)

Rate constant of these reactions can be estimated as 10^3-10^5 s^{-1} for N_2O_4 and for N_2O_3 10^3 s^{-1} and 10^{-4} s^{-1} in case pH =5 and pH =10 respectively [3].

HNO_2 dissolve in the water rather fast with the subsequent reaction:

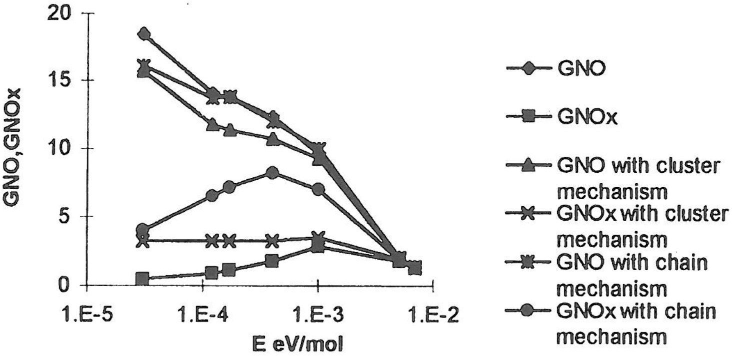
$$3HNO_{2(}(g) \rightarrow H^+ + NO_3^- + H_2O + 2NO(g) \qquad (15)$$

The rate constant of this reaction is unknown but in all cases reaction rate was limited by diffusion and can be estimated as 10^6 s^{-1} .[3]. The same reaction is occur in the cases when HNO_2 is formed in water in the result of chemical reactions (see reactions (9,10, 13,14)

MODELING RESULTS

The modified version of computer program "ELENA" for kinetic modeling of Electron Beam treatment process was used. In addition to gas phase reactions this code allows to consider the influence of heterogeneous chemical reactions on the surface and inside aerosol particles. These reactions were described in frame of simplified approach developed in [3]. More than 500 gas reactions including formation and chemical reactions of clusters and 20 reactions in droplets were taking account. In addition to the conventional radical gas phase NOx oxidation and reduction mechanism ion - molecular oxidation and heterogeneous reactions in the droplets were examined too. NOx oxidation in wet air considered for the initial NO_x concentration one hundred ppmv and more and current density of the Electron Beam in the range 10^{-7} A/cm^2-10^{-1} A/cm^2.

Calculations have shown that when recombination process takes place with accordance reaction (2) maximum GNO_x value is equal 2.5 (Fig.1).



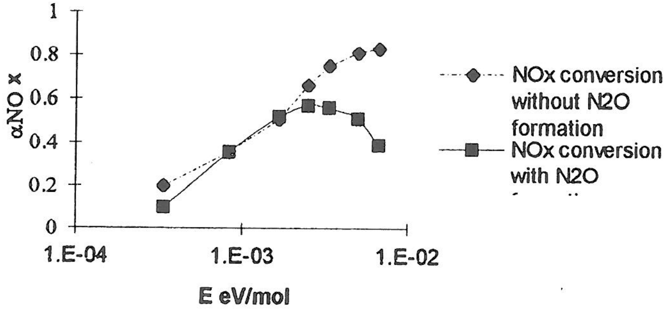
Yield of NO and NOx conversion as a function of input energy.Initial NO concentration is 100 ppm.
J = 1E-5 A/cm2

Fig.1

But if it is assumed that negative ion NO_3^- converts to another isomeric form and recombination process takes place in accordance (3) with directly HNO_3 formation ~~then~~ GNO_x reaches 3.4. On the assumption that chain ion molecule mechanism (4) - (8) ~~exists~~ GNO_x reaches 8.2 but at less dose, because as above has been mentioned this mechanism occurs with the availability in the system NO and NO_2 at one time.

With increasing of dose NO_x conversion reaches 57% and after that decreases (Fig.2).because N_2O forms in the reaction:

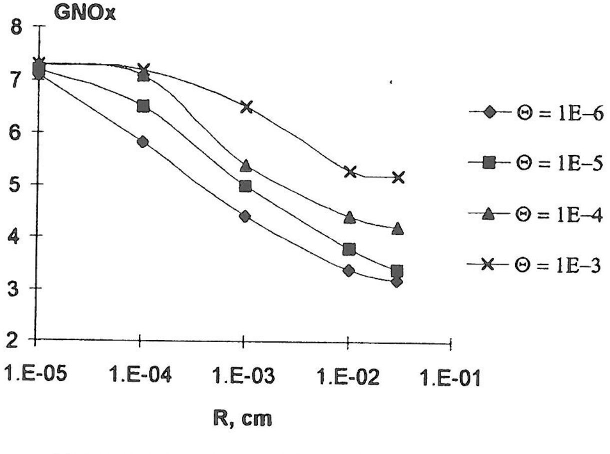
$$NO + N \rightarrow N_2O \qquad (16)$$



Conversion NOx as a function of input energy. Initial NO concentration is 100 ppm, the range of current density is 5E-7 A/cm2 - 1E-5 A/cm2.

Fig.2

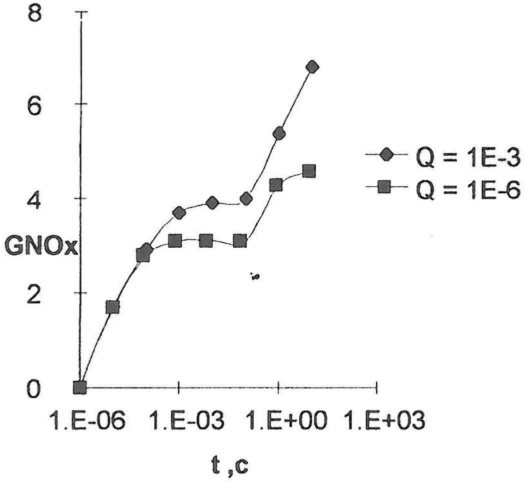
The calculation of NO_x removal process with addition of droplets has shown that with increasing of humidity and decreasing of droplet size GNO_x increases (Fig.3).



GNOx as a function of droplet radius R. Initial NO concentration is 100 ppm, input energy - 5E-4 eV/mol, J = 1E-5 A/cm2, Θ is relative humidity .

Fig.3

An appreciable improvement of heterogeneous process efficiency takes place in time more then irradiation time (Fig.4).



GNOx as a function of time. Initial NO concent 100 ppm, input energy - 5E-4 eV/mol, J=1.E-5. R=30 mkm, tp= 0.58 c.

Fig.4

This fact permits to do conclusion that in many stage irradiation of the mixture the addition of droplet may be efficient between stages of irradiation.

CONCLUSIONS

The modeling shown that ion - molecular oxidation mechanism in clusters at the high relative humidity can lead to the qualitative change in the behavior of NO_x removal efficiency essentially at the low dose. This effect is related with the fact that NO can form HNO_3 directly via proposed ion-molecular mechanism at the same time under conventional radical mechanism at the low dose NO only convert to NO_2 and HNO_2 and $DeNO_x$ process does not occur. The experimental results on the NO_x oxidation have confirmed the possibility of implementation of the direct ion-molecular chain NO oxidation .

It was shown that heterogeneous reactions can have strong effect on the kinetics of the NO_x removal and can increase the removal efficiency in several times with respect to conventional case essentially at the high dose when saturation effect in the behavior of removal degree vs. dose very strong. As it was found the influence of the heterogeneous reactions on the process strongly depends on the size, number density of aerosol particles and current density of the electron beam. The appropriate optimization was performed. These promising results show the possibilities to improve efficiency of NO_x removal in presence of droplets phase.

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