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Spectroscopic Study of Positive Corona Discharge in Mixtures Containing N₂, NO, CO₂, O₂ and H₂O

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Abstract

The positive DC corona discharge in the hemi cylindrical discharge reactor was applied to mixtures containing N_2 , NO, O_2 CO₂ and H_2O while NO_x chemiluminescence analyzer and infrared spectrometry was used to analyze the products of the process in the discharge chamber. The removal efficiency of 80% for NO, and the energy costs 256 eV/molecule was achieved. The attention was paid to the influence of CO₂ on discharge, its character, performance and products of the process. Besides the main components of the mixtures (NO, NO₂, CO₂ etc.) also other compounds and functional groups (e.g. amides HII, amines, imides, NCO) had been identified in the spectra

1. Introduction

The increasing concern about the environmental problems facing the world (acid rain, ozone depletion, global warming, smog) has determined the interest towards developing new and more effective gas cleaning technologies in the last decades. Corona discharge is one of solutions how to remove nitrogen oxides and other toxic compounds from flue gases. This technique has been widely used in many laboratory and pilot-scale experiments over last decades $^{(1-3)}$. The process of NO_x treatment, chemical reactions, final products, energy consumption and process efficiency can be influenced by change of many different parameters and discharge conditions (shape of HV waveform, discharge polarity, initial gas composition, chemical additives, etc.). Among different chemical additives used in deNO_x process (e.g. NH₃ or hydrocarbons) influence of CO₂ had been studied only partially, detailed description of CO₂ effect on the process has not been probably published yet as well as the chemical reactions and products of the process.

In the mixtures containing NO_x and CO_2 treated by discharge, it is believed NCO radical plays an important role. This radical is responsible for removal of NO_x and can also be incorporated in different heterogeneous organo-metal compounds on a surface of electrodes (e.g. copper or brass) having significant catalytic properties. It is quite apparent that discharge process in mixtures including CO_2 -N₂-H₂O can eventually cause formation of some essential aminoacids. Here again the responsible agent seems to be NCO radical. Its reaction with the H₂O (presence of H₂O is necessary for the process) in mixture leads to origin of amide group ⁺NH₂-COO, which is the beginning of the essential aminoacids' (e.g. glycine) formation process⁽⁴⁾. The question is whether similar process also exist in NO_x - CO_2 - H_2O mixtures, while NO_x and CO_2 would be removed simultaneously.

The aim of the research was to perform measurements in the mixtures containing N_2 , NO, CO₂, O₂ and water and describe the discharge process, its efficiency and products. Our intention was to provide measurements using positive DC corona discharge in different modes, while positive DC streamer corona discharge was used mainly. Although the elementary process and chemical reactions are very complicated, several ideas about the discharge process and the analysis of the products are presented at least.

2. Experimental Setup



Fig.1 Experimental apparatus

The experimental setup is presented in the **Fig. 1** Hemi cylindrical type of corona discharge reactor with length 20 cm was employed in the experiment and DC corona discharge of positive polarity was used in all experiments. The gases mixtures of N₂, NO (250 or 500 ppm), CO₂ (0-50%), O₂ (20%) and water were used. All measurements were performed in a flow regime with the total gas flow set to either 1 or 2 l/min respectively. The concentration of NO and NO_2 was monitored with NO_x chemiluminescence analyzer and the overall analysis of the gas products was done by FT-IR spectrometer using 2.4 m long gas cell

3. Experimental Results

The experimental measurements consisted of two parts. First we performed several measurements in the gas mixtures containing N₂-NO-CO₂-H₂O, while deNO and deNO_x treatment efficiency was monitored with the help of NO_x chemiluminescence analyzer in a way to ascertain the general influence of CO₂ and partially also H₂O on NO_x treatment. Then in the second step we concentrated on overall analysis of all components of the gas mixture and analyzed the products formed in the discharge process with the use of IR spectrometry.

The effect of individual components of the mixture on the discharge character was very significant. Compared with pure N₂, an admixture of NO caused a decrease of the corona onset voltage V and hindered breakdown. Increasing discharge current, streamers gradually appeared with fast growing amplitude and frequency. An increase of CO₂ concentration in the mixture (3-5% of CO₂) caused the discharge volume utilization by streamers and their distribution in discharge gap became more homogenous. In the mixtures with initial NO, streamers appeared from early stages of the discharge and an admixture of CO only enhanced the streamers improving their space distribution in the discharge gap, while in the mixtures without initial NO steamers appeared only after CO₂ was introduced. Too much of CO₂ however, caused the streamers gradually died out in the gap and also led to discharge instabilities. With very large amount of CO₂, corona discharge onset voltage could be significantly increased and streamer corona may terminate.

The instant concentration of the nitrogen oxides in the gas mixture was measured by chemiluminescence NO_x analyzer and later also analyzed with FTIR spectrometer. The maximum deNO treatment efficiency of more than 80% was achieved with energy consumption 256 eV/NO while at the same time total deNO_x treatment efficiency was 70% with the energy consumption 287 eV/NO_x⁽⁵⁾. The presence of CO₂ in the mixture lead to both deNO/deNO_x effects decrease, caused either by gradual change in the discharge character described earlier and also by the fact that CO₂ itself also undergoes changes under the influence of the discharge action, while its concentration is several times higher than a concentration of NO_x. The presence of H₂O in the mixture of N₂-NO_x-CO₂ caused improvement of deNO_x efficiency, as OH radicals play an important role especially in NO2 oxidation process and nitric acid formation. The considerable improvement was found especially in the deNO₂ removal efficiency. Generally the presence of water vapor in the mixture as well as OH and HO₂ radicals can significantly intensify the chemical process.

The water vapor or OH radicals enhance also the oxidation of nitrogen gas to N_2O and the presence of H_2O is necessary also for potential and eligible formation of aminoacids⁽⁴⁾.

The analysis of the gas mixture by means of IR spectrometry is very effective method for monitoring the changes of the gas mixture composition caused by electric discharge and products identification. The absorption bands of the main components of the initial gas mixtures are presented in the **Tab. I**.

Tab. I Characteristic absorption bands [cm ⁻¹]	
NO	1920-1900 monomer, 1840 dimer
NO_2	1750, 1630, 2930-2900 overtone
N ₂ O	2240 (between CO ₂ and CO bands)
CO_2	3800-3700, 2400-2300 , 677
CO	2220-2020

The figure **Fig. 2** is the example of absorption spectra of N₂-NO-O₂-5%CO₂ mixture treated by positive corona discharge, where the overall effect of the discharge action on the gas composition can be seen. The figure is composed by three spectra successively representing pure N₂, gas composition before and after the discharge action (at I_{mean} = 1000 μ A). Based on the results of spectrometric measurements and the development of the individual concentrations of the main components of the gas mixtures, the following conclusion can be made:



Fig.2 IR spectra of N₂-NO-O₂-5%CO₂ mixture

The NO removal process in the mixtures without initial CO₂ was strongly reductive. The process lead to formation of N2O and molecular N2, while only a small amount of NO₂ was produced. A small amount of CO₂ (1%) in the mixture improved deNO efficiency a little bit, although the production of NO₂ at the same time increased. However, the further increase of CO₂ concentration in the initial mixture had negative effect on NO removal. The concentration of NO₂ usually increased in all types of mixtures (except N2-NO), however concentration of CO2 over 10% led to continuous streamer disappearance, contraction of the discharge to the vicinity of the wire, while only a very small amount of NO₂ was formed. The presence of H₂O in the mixture caused improvement of deNOx efficiency, especially deNO₂ removal efficiency.

The concentration of NO₂ apparently increased with power in all mixtures, except N₂-NO mixture, where in the later stages NO₂ concentration decreased with discharge power. In the mixtures with initial NO and O₂, the concentration of NO₂ increased rapidly thanks to immediate oxidation of NO to NO₂. Also an influence of CO₂ might not be neglected. This is mainly caused by intensive streamer discharge in a discharge gap, which support chemistry. On contrary, however, in the mixtures without the initial NO the streamer mode firstly incepts and later vanishes with increasing concentration of CO₂. The concentration of CO₂ over 10% led to continuous streamer disappearance, contraction of the discharge to the vicinity of the wire and thus only a very small amount of NO₂ is formed here.

The production of N₂O in the discharge process is also interesting. The influence of initial O₂ in the mixture on N₂O production was decisive, compared to initial NO concentration, because of the reaction N₂(A)+O₂ \rightarrow N₂O+O. Although further increase of CO₂ concentration caused a decrease of N₂O in N₂-NO-CO₂ mixtures, it was also strongly affected by streamer discharge continuing disappearance already described before.

The discharge action also caused the production of CO. The bigger was the initial concentration of CO_2 , the bigger was CO production. A possible increase of CO concentration might be also caused by decomposition of solid products previously created in the discharge process with high frequency of the pulses. The presence of water in the mixture, however, leads a decrease of CO concentration.

Except the absorption bands of the main components of the gas mixture, there were also other bands, which appeared in the spectra. Analyzing spectra complexly, considering all possibilities, discharge conditions, initial gas composition and intensity of absorption bands also other interesting compounds and functional group were identified.

The analysis of other compounds of the mixture also took into account the fact of possible formation of aminoacids or at least some traces or functional groups. The formation of aminoacids was confirmed earlier⁽⁴⁾. The formation is launched with excitation of N₂ molecules (metastable state $A^{3}\Sigma^{+}$) later incorporated into CO2 while forming important radicals NCO respectively ON-NCO. For possible formation of trivial aminoacids in the discharge the process of water dissociation on electrode surface is necessary to form an amide group. The identification of aminoacids or their traces in the discharge is complicated by their polarization in the volume and formation of zwitter ions, i.e. NH₂⁺COO⁻ or NH₃COO⁻ in the presence of the electric field. It results in the band shifts in the infrared spectra (e.g. protonated amino cation NH_3^+ is shifted down to 2500cm⁻¹ and NH_2^+ 2700cm⁻¹) making possible analysis more difficult. Furthermore aminoacids can be neutral, acidic or basic, depending on the number of NH2⁺ respectively COO

groups in the structure of the molecule, which might also lead to different effects in the infrared spectra.

Considering the infrared absorption spectra, there are several other bands except those aforementioned, which attracted our attention (**Fig. 3**). In the upper region, there are visible bands of amine NH₂ resp. zwitter ion NH₃⁺ in the spectra in the range of 3490, 3467 resp. 2580, 2550 cm⁻¹, while the region around 1900 cm⁻¹ belongs to NO, namely NO monomer band at 1920-1900 cm⁻¹ and NO dimmer at 1840 cm⁻¹.

The region from 2000 cm⁻¹ down to 1600 cm⁻¹ is the region of carbonyls (ketones, esters, carboxyl acids, etc.), i.e. the compounds including C=O group. Especially the range of 1850-1600 cm⁻¹ is very important as this is the range of carbonyls with the double bond, which are very strongly dependent on their surrounding and associations resulting in the shift and position of the absorption bands in the spectra. In our case the following bands are visible in the spectra: carbonyl of carboxyl acid at 1720 cm⁻¹, carbonyl of imide at 1700 cm⁻¹ (which is stronger as it is twice in one compound), then carbonyl of non-specified neutral aminoacids at 1680 cm⁻¹.

At the bottom side of this region a strong band of NO₂ is present at 1630-1620 cm⁻¹, along with C=C conjugated resp. C=C, C=N conjugated and carboxylate ion COO (v_{as}). At the right side of the NO₂ absorption band a small band representing amide I (1640 cm⁻¹) is well visible especially in the spectra of N₂-NO-CO₂ mixture. In the mixtures with initial concentration of O₂ and comparably bigger production of NO₂ caused the band interfered with band of NO₂ and so the band is invisible.

Then in the range of 1600-1500 cm⁻¹ absorption band of amide II (β , δ NH_x) can be seen. Especially the region of 1560-1510cm⁻¹ is full of sometimes small but sharp absorption bands, which corresponded to amide II.



Fig.3 Part of differential spectra of mixtures N₂-O₂-CO₂ and N₂-NO-O₂-CO₂, where each curve represents the same power while concentration of CO₂ varies from 0 to 30%

Further in all three types of mixtures a small band at 1460 cm⁻¹ appeared, which represented the combination of bands of standard amide III band in his neutral state. This band is associated with the band of NCO radical, imide group 1490 cm⁻¹ and carboxylate ion COO⁻ (v_s) at 1465 cm⁻¹. In the polarized state of zwitter ion aminoacid the band is shifted down to region 1300-1250 cm⁻¹, where it interferes with C-N and C-O bands.

Finally a small and sometimes hardly visible absorption in the range 1140-1130 cm⁻¹ represented βNH_2 amine and amide III, which usually appears in the range of 1190-1038cm⁻¹.

4. Conclusions

The positive DC corona discharge in the hemi cylindrical discharge was applied to mixtures containing N_2 , NO, Q CO₂ and H₂O. Except the changes in the

concentration of the main gas components also other bands were identified in the spectra including amides I, II and III, βNH_2 amines, NCO radical and imide.

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