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NO REMOVAL FROM FLUE GASES BY OZONATION

The implementation of stringent regulations on NO_x emission requires the development of new technologies of NO_x removal from exhaust gases. The main objective of this investigation was to identify the products of nitric oxide ozonation as well as to establish the influence of molar ratio and gas mixture flow rate on the reaction progress. The results of FTIR spectroscopy indicate that the main products of the ozonation were NO_2, N_2O_4 and N_2O_5. Only 2 moles of ozone per mole of NO proved to be sufficient for 94% NO oxidation.

1. INTRODUCTION

Nitrogen oxides are nowadays a subject of international concern. Several types of nitrogen oxides exist in the environment: N_2O, NO, NO_2, N_2O_3, N_2O_4, NO_3, N_2O_5. The abbreviation NO_x usually relates to: nitrogen monoxide NO, nitrogen dioxide NO_2 and N_2O nitrous oxide which from photochemical point of view can be called 'fresh' nitrogen oxides since in this form they reach the atmosphere. All three are considered as air pollutants. NO and NO_2 contribute to the formation of troposphere ozone, photochemical smog and acid rains. It is known that N_2O is one of the greenhouse gases and what is more it takes part in the complex reactions in stratosphere which can lead to a depletion of the ozone layer (ANEJA et al. 2001). As greenhouse gas it absorbs infrared radiation with 270 times higher intensity than carbon dioxide (CO_2) does (WRIGHT 2003). Furthermore, both NO and NO_2 are toxic and harmful to humans, animals, vegetation and materials. Nitrogen monoxide inhaled in high concentrations causes enlarged susceptibility to diseases in living organisms, directly acts on nervous system and reacts with the haemoglobin in the blood (PAUL et al. 2008, WOODROW 1998). NO is less toxic than NO_2 however, it is extremely active and rapidly oxidizes to NO_2. Nitrogen dioxide irritates pulmonary track in worst cases causing lungs oedema (PAUL et al. 2008). In contrary to NO and NO_2, nitrous oxide (N_2O) is not toxic and additionally it is commonly used as anaesthetic as well as aerosol spray propellant in food industry.

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Changes in the composition of the atmosphere are mainly prompted by fossil fuels combustion processes occurring in power plants, engines of vehicles and aeroplanes (GOMEZ-GARCIA et al. 2005). It is also true for NO_x emission but there are also other sources of these gases, such as: adipic acid manufacture for Nylon 6.6 production, the use of fertilizers and production and application of nitric acid (GOMEZ-GARCIA et al. 2005). Additionally, these pollutants can be also formed by natural processes including lightening, oxidation of NH_3 (produced by microbial decomposition of proteins in the soil), fires and volcanic activity. However, these amounts produced in natural phenomena are of low importance (GOMEZ-GARCIA et al. 2005, KAMPA and CASTANAS 2008).

Increased combustion of fossil fuels since the last century has been a primary source of NO_x leading to the increase of pollutants concentration in the atmosphere. However, other sources of NO_x such as the production and the use of nitric acid should not be neglected. During nitric acid plant operation as well as nitrification and oxidation of organic compounds with the use of nitric acid, nitrous gases in varying concentrations are formed (DYER-SMITH and JENNY 2005)

In the case of rising restrictions regarding NO_x emission which are being imposed by Gothenburg's and Kyoto's protocols, development of new technologies and improvement of currently used methods for nitrogen oxides removal are necessary. Currently, two trends in secondary emission reduction methods are dominating. They are generally based either on the reduction of NO_x to environmentally harmless substances like N_2 and O_2 or on its oxidation to higher oxides followed by scrubbing techniques. Selective catalytic reduction is probably the most popular method used for exhaust gases from combustion processes (MOK and YOON 2006). For that reason many researchers are focused on finding new better catalysts which will give higher reduction efficiency, not as much on finding new method (BROER and HAMMER 2000, MOK et al. 2003, NAKATSUJI et al. 1999). MOK et al. (2006) has recently proposed a new way for NO_x and SO_2 simultaneous removal from flue gases which combines two trends by using ozone injection and absorption-reduction technique. Firstly, simulated exhaust gases mixture is ozonated to NO_2 which is further reduced to N_2 by reducing agent, in this case Na_2S. The reducing agent is also able to remove SO_2. Obtained efficiencies were satisfactory: 95% for NO_x and 100% for SO_2 (MOK and LEE 2006).

The removal of NO_x from waste gases discharged from nitric acid towers and chemical reactors using nitric acid is usually conducted by means of dry as well as wet techniques such as catalytic absorption and adsorption. The main drawback of the wet techniques is the low solubility of nitric oxide (THOMAS and VANDERSCHUREN 1997). The reduction of its emission must be conducted by first oxidizing NO to higher nitrogen oxides (with better solubility) which next in water are converted to HNO_2 and HNO_3. The aim of this study was to determine if NO, which is present in exhaust gases, can be oxidized by means of ozone injection to higher nitrogen oxides like N_2O_5 and to assess the influence of molar ratio and gas mixture flow rate on reaction progress.

2. METHODS

An overview of the experimental set-up is given in figure 1. The simulated exhaust gas was prepared by mixing N_2 (1) with small amounts of NO nitric oxide (2) with the use of mass flow meters Brooks Instruments 5850 TR(4). Both gases were purchased from Linde-Gas. NO and N_2 mixture was supplied to gas tube reactor (9) (inner diameter and length were 5 cm and 50 cm respectively) where it contacts with ozone-oxygen mixture.

Oxygen was obtained from air by the PSA (Pressure Swing Adsorption) oxygen generator AirSep (3). After dehumidification in a drying jar (5), oxygen was fed into Ozone Generator BMT 802 (6). Next, oxygen-ozone mixture passed through Ozone Analyzer BMT 963 (7), which measures ozone concentration in the gas at the reactor inlet.

Gaseous reagents were analyzed in Fourier Transform Infrared Spectrometer Jasco FT/IR-4200 (10) equipped with 0.4 dm^3 gas cuvette and additionally by Ozone Analyzer BMT 964 which measures outlet ozone concentration (11).

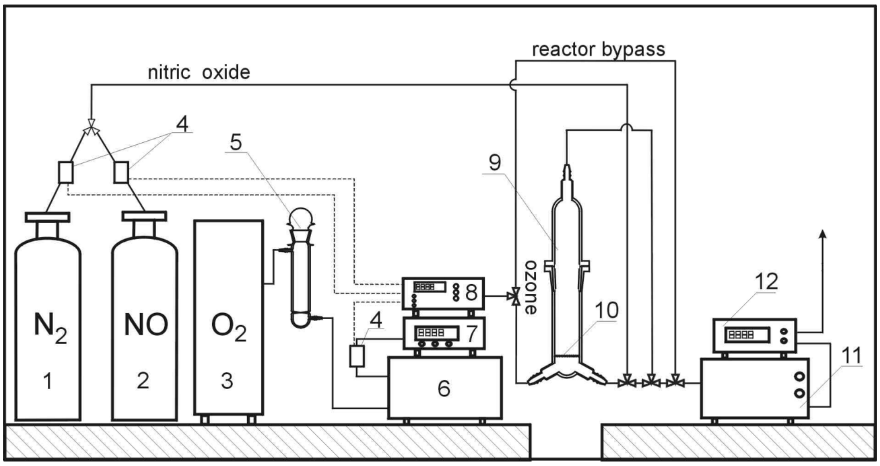

Fig. 1. 1 – nitrogen gas cylinder, 2- nitrogen oxide gas cylinder, 3 – oxygen generator, 4 – mass flow meters, 5 – drying jar, 6 – ozone generator, 7 – ozone inlet concentration analyzer, 8 – mass flow meters regulator, 9 – glass tube reactor, 10 – porous glass plate, 11 – Fourier Transform Infrared Spectrometer, 12 – ozone outlet concentration analyzer

Two series of experiments were conducted. In the first one the inlet concentrations of the mixture were adjusted to approximately $1.8\cdot10^{-5}$, $3\cdot10^{-5}$, $4\cdot10^{-5}$, $5\cdot10^{-5}$, $6.5\cdot10^{-5}$ mol/dm^3 in the total gas flow rate equal to 1.5 dm^3/min. In this experiment the simulated exhaust gases mixtures were introduced into plug flow reactor, where they contacted with ozone oxygen mixture, in such concentrations as to obtain molar ratio of O_3/NO equal to 1, 2, 3, 4, 5. The second experiment was conducted for one chosen NO concentration (around $3\cdot10^{-5}$ mol/dm^3) and three molar ratios 1, 2 and 3 of O_3/NO for different flow rates of reaction gases adjusted to 1, 1.25, 1.5, 1.75, 2, 2.25 and

2.5 L/min. However, calibration curves for NO and NO_2 were firstly determined. All calculations were performed for standard conditions. During all FTIR measurements the spectra from 4000 cm^{-1}–700 cm^{-1} were monitored with the 4 cm^{-1} resolution. All reactions were conducted at ambient temperature.

3. RESULTS AND DISCUSSION

During these studies numerous spectra were obtained, few of which are shown in figure 2. They represent the dependence of mixture composition on molar ratio (MR) of O_3/NO. In the case of the spectrum acquired for gases before reaction, peaks representing NO (1907 cm^{-1}) and NO_2 (1628 and 2920 cm^{-1}) are present. The same peaks are present on the spectrum for MR = 1 however, the height of peaks changes because the following reaction takes places:

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (1)$$

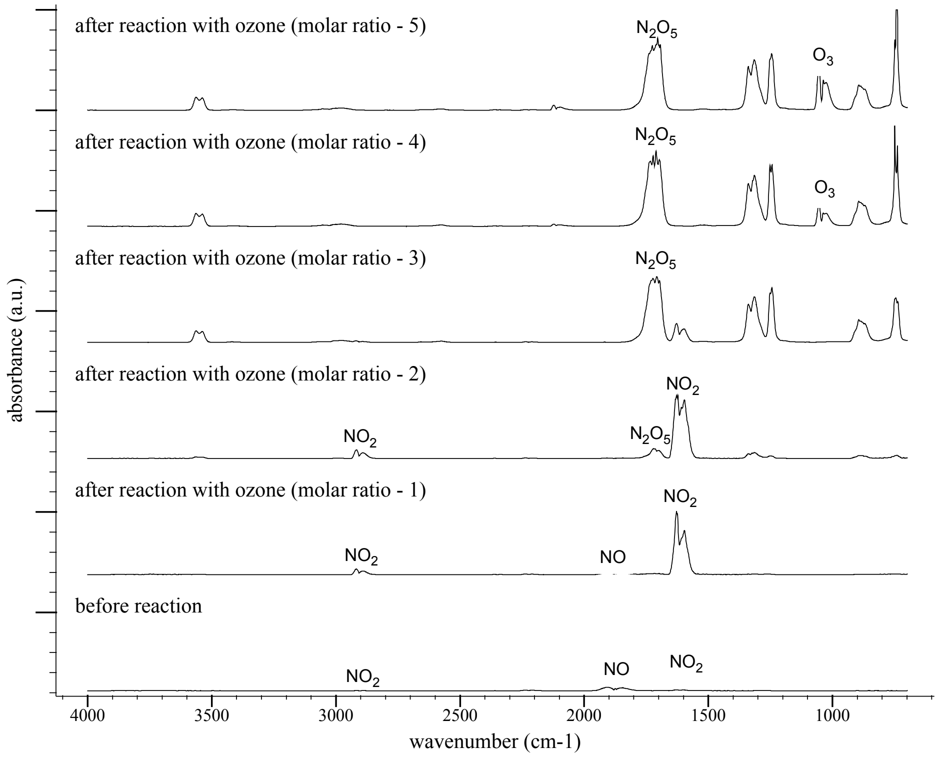

Fig. 2. The FTIR spectra obtained for the exhaust gases mixture (flow rate: 1.5 dm^3/min, initial NO concentration: 3.94E-05 mol/dm^3)

The increase of the molar ratio results in further rise in the amount of formed NO_2 but also a new peak representing N_2O_5 starts to be visible at 1727 cm^{-1}. No peak for NO is present. These changes are due to oxidation of earlier formed NO_2 to NO_3 following the reaction:

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (2)$$

Since NO, NO_2 and NO_3 are radicals they can associate to form higher molecular weight dinitrogen compounds according to reactions (GRASSIAN 2005):

$$NO + NO_2 \rightarrow N_2O_3 \qquad (3)$$

$$NO_2 + NO_2 \rightarrow N_2O_4 \qquad (4)$$

$$NO_2 + NO_3 \rightarrow N_2O_5 \qquad (5)$$

In the next spectrum another five peaks are observed, three of which (897, 1315 and 3564 cm^{-1}) are probably representing N_2O_5 similarly to this one at 1727 cm^{-1}. The remaining two ones (742 and 1245 cm^{-1}) correspond probably to N_2O_4. However, the amounts of N_2O_4 and N_2O_5 are difficult to assess at this point of our research. Furthermore, in the spectrum obtained for gas mixture when it reacted with ozone in concentrations adjusted to give MR equal to 4 and 5, one more peak is visible at 1055 cm^{-1}. It is connected with the presence of unreacted O_3 in the outlet gases.

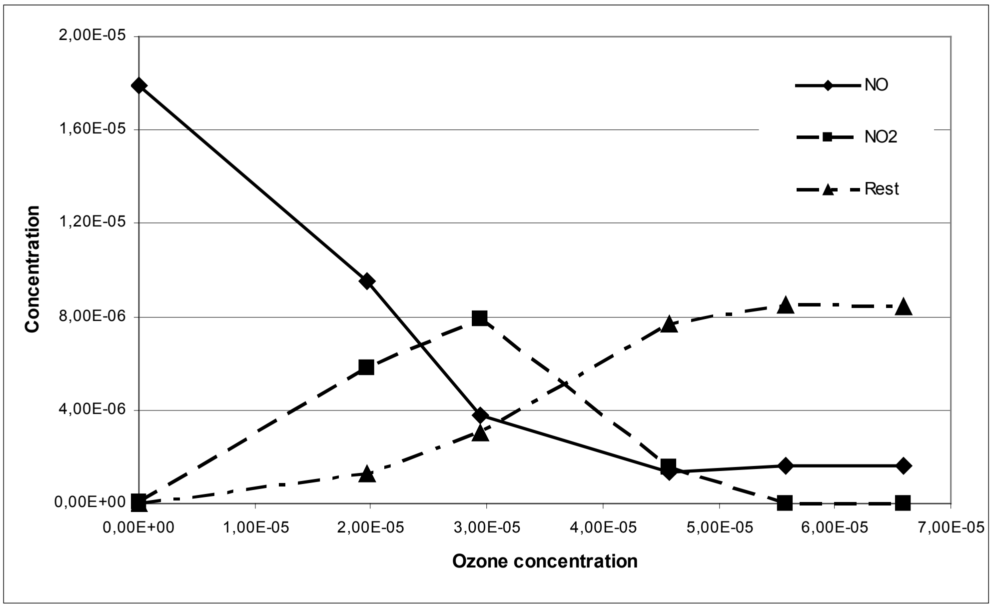

Fig. 3. The dependence of the NO oxidation process on the amount of ozone added (flow rate: 1.5 dm^3/min; initial NO concentration: 1.79E-05 mol/dm^3)

After analyzing both figures 2 and 3 it is getting more clear what happens during increasing of the molar ratio. As it can be seen the concentration of NO decreases with the increase of the ozone concentration. NO_2 concentration rises to certain maximum reached for molar ratio equal to 2, then it starts to decrease since it is faster consumed in the reactions 2, 4 and 5 than it is formed in reaction 1. In connection with the absence of peaks representing N_2O_3 it can be assumed that reaction 3 does not take place in our system. The sum of formed N_2O_4 and N_2O_5 rises with the increasing ozone concentration until it reaches maximum. The small amounts of N_2O_5 are already formed for equimolar reaction as it was reported earlier by MOK and LEE (2006) as well as by WANG et al. (2007). Mok and Lee state that as the concentration of the added ozone to the exhaust gas increases beyond initial NO concentration the amount of formed N_2O_5 abruptly increases. For the concentrations of ozone and NO both equal to 280 ppm, 1.2 ppm N_2O_5 was produced (MOK and LEE 2006). WANG et al. (2007) also confirms that NO_2 is the main product when O_3/NO molar ratio is smaller than 1.

Results obtained in the second experiment have been gathered in figure 4. It presents NO oxidation percentage as a function of ozone added for seven different flow rates of exhaust gases. The percentage of oxidized NO augments with the increase of the flow rates until it reaches maximum that is 94% for 1.75 dm^3/min and molar ratio equal to 2.

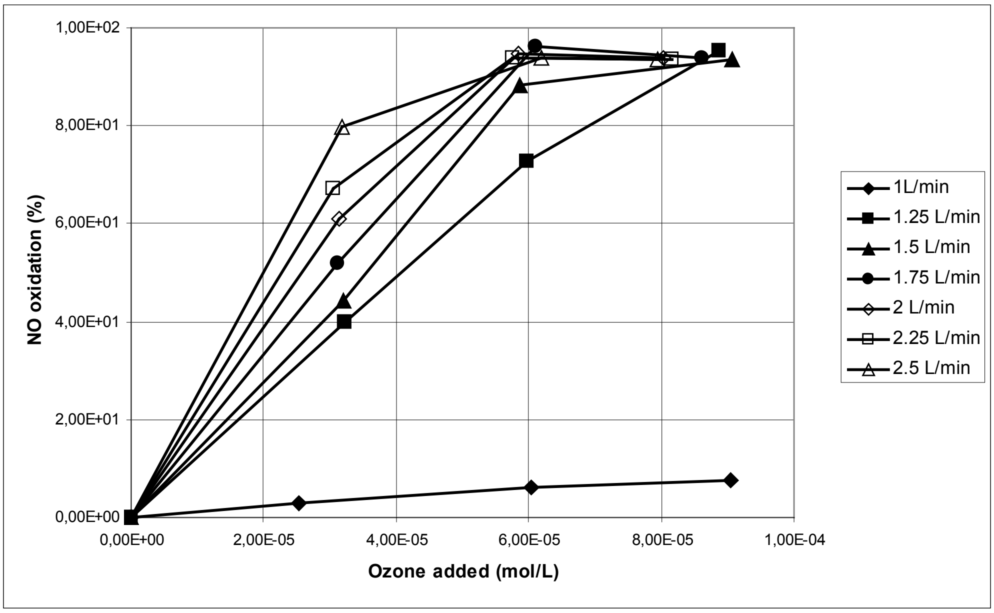

Fig. 4. The dependence of NO oxidation on the amount of ozone added for different flow rates (NO initial concentration: 3.23E-5 mol/dm^3)

This paper presents the results of the preliminary studies of NO removal by its oxidation with the use of the ozone injection. In the future these research are going to be focused on determining the kinetics of NO to N_2O_5 ozonation.

4. CONCLUSION

It seems that oxidation of NO_x followed by the absorption of the generated products is a good, effective and cost efficient reduction method for the NO_x emission from chemical and nitric industries. It requires small financial outlays and can be easily introduced to existing plants. The results of these research suggest that the best levels of NO removal are obtained for gas mixture flow rates equal to 2.25 and 2.5 L/min and that already 2 moles ozone per mole NO are sufficient. This is important since ozone generation is expensive. N_2O_4 and N_2O_5 formed during ozonation are better soluble in water hence the efficiency of their absorption might be higher than in the case of traditional wet techniques.

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