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REACTIONS OF NITROGEN OXIDES AND OZONE IN THE GAS PHASE FOLLOWED BY ABSORPTION PROCESS

REAKCJE TLENKÓW AZOTU I OZONU W FAZIE GAZOWEJ ORAZ ABSORPCJA PRODUKTÓW REAKCJI

Abstract: The growing emissions of nitrogen oxides into atmosphere endanger the human health and degrade our environment. The presence of nitrogen oxides in the atmosphere is responsible for troposphere ozone and urban photochemical smog. NO and NO_2 (NO_x) are one of the major contributors to harmful acid rains. Various methods exist to reduce NO_x emission. Combustion modification and selective catalytic reduction (SCR) are probably the most widely used techniques to control NO_x emissions from industry. New technologies such as nonthermal plasma and pressure swing adsorption appear to be efficient for the removal of higher concentrations of NO_x but they are still expensive for the treatment of huge volumes of flue gases. Thus, there is a need for environmentally friendly and cost effective methods for treatment of flue gases. One of the solutions to NO_x emission problem can be to couple ozonation process in the gas phase with SCR or absorption process. In this work the application of ozone for the oxidation of nitrogen oxides present in exhaust gases was presented. The main concept of the process is to oxidize nitrogen oxide (NO) and nitrogen dioxide (NO_2) into nitrogen pentoxide (N_2O_5) which reacts with water giving nitric acid. This way NO_x can be absorbed in water with good effectiveness. In presented studies the influence of nitrogen(II) oxide initial concentration on the NO conversion was studied. Furthermore, the two stage process composed of the ozonation process of NO_x and the absorption of reaction gases in the 0.01 M solution of NaOH was performed. These experiments proved that the yield of absorption process is higher for gases containing N_2O_5.

Keywords: nitrogen oxides, emission control, ozonation

Nitrogen oxides are considered to be dangerous air pollutants. They contribute to the occurrence of several environmental problems, ie photochemical smog, acid rain, tropospheric ozone, ozone layer depletion and even greenhouse effect. NO_x (NO and NO_2) can lead to health problems in humans exposed to high doses of these gases. The wide range of NO_x control technologies, eg techniques such as absorption, adsorption or electric discharge were developed. However, all these methods have its limitations and drawbacks.

Therefore, attempts to develop new technologies of reduction of NO_x emission are still carried out all around the world. Most of them as literature survey suggests is focused on NO_x emission control from power plants and mobile vehicles [1]. One of the solutions of the NO_x emission problem can be to couple ozonation process in the gas phase with *selective catalytic reduction* (SCR) or absorption process. In 2001 the process called Low-Temperature NO_x absorption (LoTOx) won the Kirkpatrick Award. In this method the 90% efficiency of NO_x emission reduction can be obtained [2]. High amounts of ozone are needed in this application to obtain N_2O_5. Nitrogen pentoxide (N_2O_5) has high solubility in water around 500 $g \cdot dm^{-3}$ [3], which is significantly higher than solubility of nitric oxide or even nitrogen dioxide. The obtained N_2O_5 gives HNO_3 in the absorption column through reaction with water. The process can be described by sequence of reactions:

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

$$NO_2 + O_3 \longrightarrow NO_3 + O_2 \quad (2)$$

$$NO_2 + NO_3 \longrightarrow N_2O_5 \quad (3)$$

$$N_2O_5 + H_2O \longrightarrow 2HNO_3 \quad (4)$$

The main objective of this paper is to describe the influence of NO initial concentration in reaction gases on the nitrogen oxides ozonation process. Furthermore, series of experiments were performed to confirm that the absorption of higher nitrogen oxides is more effective than absorption of NO_2.

Material and methods

Series of experiments were conducted for nitrogen oxides commonly occurring in flue gases from nitric acid plant. Various initial concentrations of nitric oxide ($1.5 \div 7.7 \cdot 10^{-5}$ mol dm^{-3}) were mixed with oxygen-ozone mixture under different mole ratios of O_3/NO : 0.5÷2.5. The ozonation process was conducted in the temperature of 298 K (25ºC) and the reaction gases flow rate equal to 1.5 dm^3 min^{-1} was applied. An overview of the experimental set-up was described in previous papers [4-6]. The second series of experiments were conducted as a two stage NO_x removal process for concentrations of NO_x presented in Table 1. The process consists of the ozonation part and the absorption part. The absorption process of reaction gases was conducted in the bubble reactor filled with 0.01 M solution of NaOH. The absorption of gases was conducted for 30 minutes. After the absorption of nitrogen oxides was finished the ozonation reactor was purged with nitrogen for 100 minutes. The nitrogen gases were also absorbed in the solution. The solution was analyzed for the NaOH loss.

Table 1

Specification of the experiments conducted in the two stage NO_x removal process with the initial substrates concentrations and the results obtained

	Experiment		
	1	**2**	**3**
Concentration of NO+NO_2 [mol dm^{-3}]	$2.09 \cdot 10^{-5}$	$2.11 \cdot 10^{-5}$	$2.2 \cdot 10^{-5}$
Mole ratio O_3/NO_x	1.2	2.3	2.3
Total selectivity of NO into N_2O_5 and HNO_3 [%]	23.6	61.2	58.1
NO_x absorption yield [%]	21.2	47.4	38.5

Results and discussion

The influence of initial NO concentration on the ozonation process was investigated (Fig. 1). The correlation between the initial NO concentration and the NO conversion can be observed. The increase of the NO concentration results in the increase of NO conversion. The NO conversion increases because higher initial concentration of NO influences the reaction rate. However, this can be observed only for the mole ratios of

O_3/NO lower than 1. Above this value the conversion of NO is almost complete and further reactions occur in the reaction space. Dora et al [3] also studied the influence of initial NO concentration on the NO conversion. In their experiments they applied constant ozone concentration and changed only the initial NO concentration. Therefore, it is difficult to directly compare their results with the ones obtained in our studies. Nevertheless the fact that Dora et al [3] obtained lower effectiveness of NO oxidation in spite of increasing mole ratio O_3/NO suggests that NO conversion is dependent on initial NO concentration.

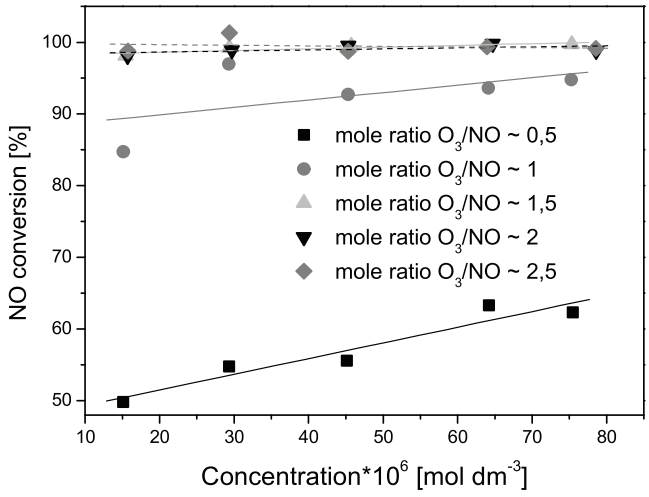

Fig. 1. The influence of initial NO concentration on the NO conversion

In order to elaborate the studies aimed at the development of nitrogen oxide removal technology additional experiments were conducted. The main objective of this series of experiments was to confirm that ozonation leads to better removal of higher nitrogen oxides from exhaust gases than NO_2 when the absorption process is applied. The experimental data are presented in Table 1. The selectivities of NO ozonation into N_2O_5 and HNO_3 were calculated according to:

$$S_{NOtoN_2O_5} = \frac{\left([N_2O_5]_t - [N_2O_5]_0\right)\cdot 2}{[NO]_0 - [NO]_t}\cdot 100\% \tag{5}$$

$$S_{NOtoHNO_3} \frac{[HNO_3]_t - [HNO_3]_0}{[NO]_0 - [NO]_t}\cdot 100\% \tag{6}$$

where: $[NO]_0$ - initial concentration of NO, $[NO]_t$ - final concentration of NO, $[N_2O_5]_0$ - initial concentration of N_2O_5, $[N_2O_5]_t$ - final concentration of N_2O_5, $[HNO_3]_0$ - initial concentration of HNO_3 and $[HNO_3]_t$ - final concentration of HNO_3.

Total selectivity of NO conversion into N_2O_5 and HNO_3 obtained during experiment 1 was around 24%, whereas the absorption yield was around 21%. This experiment was

carried out with the mole ratio O_3/NO_x = 1.2. In this process large amount of NO is oxidized into NO_2 which is soluble in water. In experiments 2 and 3 the mole ratio O_3/NO_x > 2 was applied. Therefore, the observed total selectivity of NO conversion into N_2O_5 and HNO_3 was higher than in the case of experiment 1 and was equal to 61.2% and 58.1%, respectively. The absorption yields obtained during these two experiments were around 47 and 39%, respectively.

Conclusions

Results presented in this paper confirm that the combination of ozonation of flue gases with the absorption process is a promising method for control of NO_x emission from chemical plants. The NO conversion is dependent on the NO initial concentration only for processes carried out with the mole ratio $O_3/NO \leq 1$. Results of these studies confirmed that absorption yield is higher for gases ozonated with the mole ratio $O_3/NO_x > 2$ than for gases ozonated with mole ratio O_3/NO_x close to 1 when the main component of reaction gases is NO_2. Therefore, this method seems to be especially valuable for nitric acid production plants because nitrogen pentoxide forms nitric acid through reaction with water, thus efficiency of nitric acid production might be increased additionally to abatement of NO_x emission.

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REAKCJE TLENKÓW AZOTU I OZONU W FAZIE GAZOWEJ ORAZ ABSORPCJA PRODUKTÓW REAKCJI

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Abstrakt: Rosnąca emisja tlenków azotu do atmosfery zagraża zdrowiu ludzi, a także przyczynia się do degradacji środowiska naturalnego. Obecność tlenków azotu w atmosferze może prowadzić do powstawania ozonu troposferycznego oraz smogu fotochemicznego. NO_x (NO oraz NO_2) są jednymi z głównych zanieczyszczeń przyczyniających się do występowania kwaśnych deszczów. Modyfikacje procesu spalania oraz *selektywna katalityczna redukcja* (SCR) są prawdopodobnie najczęściej stosowanymi metodami ograniczania

emisji tlenków azotu ze źródeł przemysłowych. Nowe technologie, takie jak niskotemperaturowa plazma i adsorpcja zmiennociśnieniowa, wydają się być skuteczne przy usuwaniu wysokich stężeń NO_x, jednak są one nadal drogie w szczególności w przypadku oczyszczania dużych strumieni gazów odlotowych. Dlatego istnieje konieczność opracowania przyjaznych środowisku i tanich metod ograniczania emisji zanieczyszczeń do atmosfery. Jednym z rozwiązań może być zastosowanie technologii łączącej proces ozonowania w fazie gazowej z selektywną katalityczną redukcją (SCR) bądź procesem absorpcji. W niniejszej pracy przedstawiono wykorzystanie ozonu w procesie utleniania tlenków azotu obecnych w gazach odlotowych. Głównym założeniem jest utlenienie monotlenku azotu (NO) i ditlenku azotu (NO_2) do pentatlenku diazotu (N_2O_5), który ulega reakcji z wodą, dając kwas azotowy. W ten sposób NO_x mogą być absorbowane w wodzie z dobrą wydajnością. Zbadano wpływ początkowego stężenia NO oraz stosunku NO/NO_2 w gazach reakcyjnych na stopień konwersji NO oraz selektywności do produktów. Ponadto przeprowadzono eksperymenty w układzie dwustopniowym, składającym się z procesu ozonowania i absorpcji gazów reakcyjnych w 0,01 M roztworze NaOH. Otrzymane wyniki potwierdzają, że wydajność absorpcji jest wyższa w przypadku gazów zawierających N_2O_5.

Słowa kluczowe: tlenki azotu, kontrola emisji, ozonowanie