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OXIDATION OF NITROUS OXIDE TO NITRIC OXIDE IN GLIDING DISCHARGE

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A b s t r a c t. The aim of this work was to investigate the relation between the reactor shape and N_2O conversion to NO, nitrogen and oxygen in the gliding discharge. The discharge was coupled with a catalytic bed. The temperatures of the catalyst were 480°C and 600°C. The object of the studies was to determine the effect of a $CuO/\gamma\text{-}Al_2O_3$ catalyst packed in the discharge space on the conversion of nitrous oxide to oxygen, nitrogen and nitric oxide. The overall conversion of nitrous oxide in the plasma-catalytic process depends on temperature of the $CuO/\gamma\text{-}Al_2O_3$ catalyst. The experimental reactor used enabled to check two kinds of the discharge space. The obtained results showed that the arrangement of the discharge space has a strong bearing on the conversion of nitrous oxide to NO.

K e y w o r d s: Gliding discharge, plasma, nitrous oxide, heterogeneous catalysis.

INTRODUCTION

Nitrous oxide belongs to the group of stable compounds of the so-called greenhouse gases. It is also regarded as being responsible for the destruction of the ozone layer, since such gases are active in the upper layers of the atmosphere. Studies aiming at the reduction of N_2O emission to the atmosphere have been carried out for many years. The studies are concentrated on the following tree approaches [1, 2]:

- Thermal decomposition of nitrous oxide to nitrogen and oxygen
- Catalytic decomposition of nitrous oxide to nitrogen and oxygen
- Oxidation of nitrous oxide to NO

The temperature of about 1500°C needed for the decomposition of nitrous oxide is obtained by combustion of methane in air. Under such conditions nitrous oxide decomposes completely to nitrogen and oxygen. The catalytic decomposition of nitrous oxide to nitrogen and oxygen is carried out using metals, metal oxides, zeolites or carrier-deposited catalysts. Some investigations have been also carried out on partial oxidation of nitrous oxide to NO. This way is the most favourable

because of the considerable amounts of nitrous oxide emitted from the nitric acid and the adipic acid producing plants. The nitric oxide obtained can be used for the production of nitric acid. The oxidation of nitrous oxide to NO can be effected with high yield in the non-equilibrium plasma of the gliding discharge. An advantage of using the gliding discharge is the simple power supply system, its stability under atmospheric pressure, and the high productivity of radicals and low temperatures of the gas mixture. The gliding discharge reactors enable to carry out the reaction under high flow rates. Under the conditions of gliding discharge in the presence of oxygen, nitrous oxide and nitrogen the following reactions can take place:

$$N_2O \rightarrow N_2 + \tfrac{1}{2} O_2 \quad (1)$$

$$N_2O \rightarrow NO + \tfrac{1}{2} N_2 \quad (2)$$

$$N_2 + O_2 \rightarrow 2NO \quad (3)$$

$$2NO \rightarrow N_2 + O_2 \quad (4)$$

The studies carried out in a two-electrode system enabled to obtain a high conversion of N_2O to NO varying within 20 – 37 %. Such results were obtained with flow rates of 150, 200, 300 or 400 Nl/h of gas mixtures having the initial concentration of nitrous oxide of 2.5, 5 or 10% by vol. The overall conversion of N_2O was up to about 80% max [3, 4].

An advantage of the gliding discharge is the possibility of using catalysts under the discharge conditions. The conversion of nitrous oxide was studied with the use of heterogeneous catalysis. The gliding discharge was coupled with catalytic beds of TiO_2, SiO_2 (quartz glass), γ-Al_2O_3, and metal oxides deposited on a γ-Al_2O_3 placed in the discharge space. It has been found that the use of a solid packing material in the reaction space increases the overall conversion of N_2O. The highest overall conversion of nitrous oxide (90%) was obtained with the use of a CuO as the catalyst. However, no significant effect of the catalysts used on the conversion of N_2O to NO was observed [4].

The influence of the discharge space organisation in the gliding discharge process on the conversion of nitrous oxide was also investigated [5]. A conversion of N_2O to NO ranging about 50 % was obtained in a reactor with reduced reaction zone and with the two electrodes forming an acute angle. The overall conversion of N_2O was about 80%. The conversion of nitrous oxide to NO was much higher than those obtained under identical conditions in a quartz reactor of much larger cross-section and knife-shaped electrodes. These results have shown that the process of conversion of nitrous oxide depends on the organisation of the reaction space, in which the electric discharge is effected. However, the changes in the reactor construction resulted in some decrease of the overall conversion of nitrous oxide. It has been found that the nitrous oxide conversion to NO and the overall conversion of N_2O depend on the hydrodynamic conditions of gas flow through the plasma generation zone.

The aim of the studies performed was to determine the conditions of nitrous oxide conversion under the plasma-catalytic process. The studies were carried out with the use of a steel reactor supplied with a layer of $CuO/\gamma\text{-}Al_2O_3$ catalyst and working under isothermal conditions. The temperature of the catalyst was 480^0C or 600^0C. The studies on conversion of nitrous oxide to NO were also carried out in a reactor with modified reaction space.

EXPERIMENTAL

The studies on conversion of nitrous oxide were carried out in a stainless steel reactor supplied with two knife-shaped stainless steel electrodes mounted inside. A quartz glass nozzle was installed within the stainless steel body. The distance between the nozzle outlet and the narrowest interelectrode gap was 5 mm. Placing ceramic filling on both sides of the electrodes reduced the volume of the reaction space. The CuO/Al_2O_3 catalyst was obtained by impregnating a $\gamma\text{-}Al_2O_3$ carrier with aqueous solution of cupric nitrate. The impregnated carrier was then calcined for 5h at 300°C. The CuO/Al_2O_3 catalyst was placed about 8mm below the electrodes. The thickness of the packing layer was about 15 mm (Fig. 1).

The electrodes were connected to a 50 Hz AC supply from a high voltage transformer. The studies were carried out with constant nitrous oxide and oxygen flow rates equal 200 Nl/h. The initial N_2O concentration was 5% by volume. Gas flow velocities 45 and 125 m/s were applied using two nozzles from quartz – glass pipes of 1.25 or 0.75mm diameter. The minimum width of the interelectrode gap was 1mm.

The studies of the reactor with modified reaction space volume (with ceramic filling – Fig. 1b) were also performed using the same interelectrode distance and the nozzle diameters of 0.75 or 1.25mm. The conversion of N_2O to NO and the overall conversion of N_2O were determined versus the electric power applied.

The concentration of nitrous oxide before and after the reaction was determined by gas chromatography. The amount of nitric oxide formed was determined by titrimetric and gravimetric methods [6].

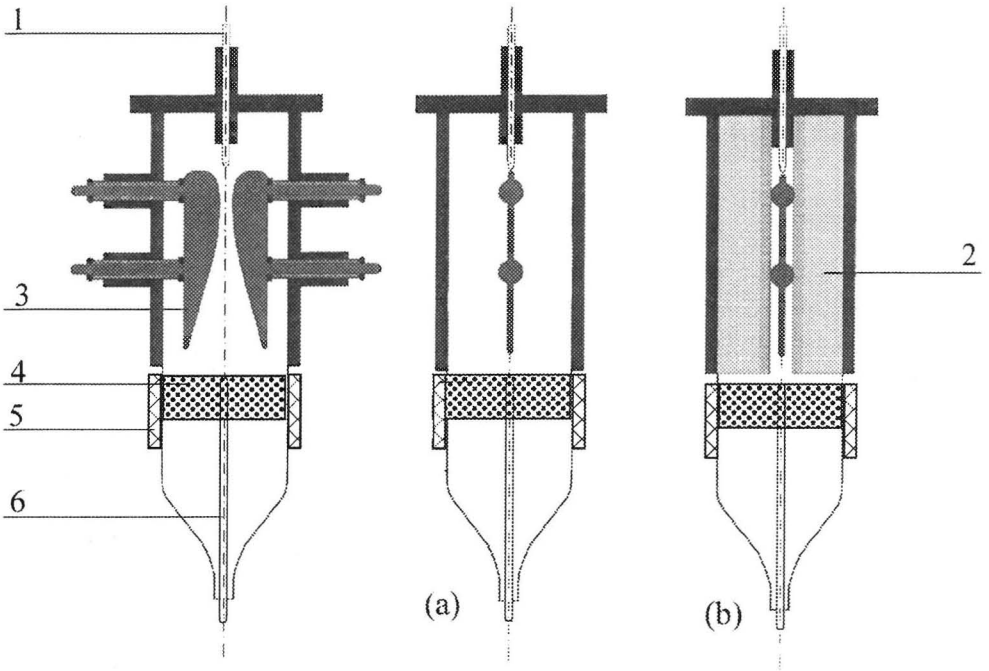

Fig.1. Reactors for nitrous oxide conversion: (a) - unmodified reactor, (b) – reactor after modification. 1 – gas inlet nozzle, 2 – ceramic filling, 3 - electrodes, 4 – packing bed, 5 – heating jacket, 6 – thermocouple.

RESULTS AND DISCUSSION

The studies on conversion of nitrous oxide in gliding discharge plasma coupled with the action of the CuO/Al_2O_3 catalyst have shown that the catalyst has a bearing on the overall conversion of nitrous oxide. In a reactor (a) without catalyst and the nozzle 0.75mm the overall conversion of nitrous oxide was maximum 66%. In the presence of a catalyst at constant temperature of 480 or 600°C the overall conversion of nitrous oxide reached 79% and 97%, respectively (Fig. 2a). No effect of the catalyst on the conversion of nitrous oxide conversion to NO was observed in the experiments with the 0.75mm nozzle. The highest values obtained for the highest power applied were about 20% (Fig. 2b, Table 1).

In the experiments with lower gas flow velocity ($45ms^{-1}$) at the nozzle outlet (nozzle diameter 1.25mm) the overall conversion of nitrous oxide was lower than that obtained with the nozzle 0.75mm. Also the conversion of nitrous oxide to NO was lower by about 2-6 % (see Table 1).

The conversion of nitrous oxide to NO was by about 5% lower in experiments with the reactor (b) with reduced reaction space (Fig. 1b) than that observed in the unmodified reactor (a) (Figs. 3b, 4b, Table 1). No clear effect of organisation of the reaction space on the overall conversion of nitrous oxide was observed in cases where the 0.75mm nozzle was applied (Table 1). The effect of construction of the reaction space was evident, however, in experiments involving the use of the 1.25mm nozzle (Figs. 3a, 4a). In the system with plasma and catalyst (at 600°C) conversion of nitrous oxide increased by more than 30% (Table 1).

Table 1. Results of nitrous oxide conversion to NO, nitrogen and oxygen at the discharge power of 230 W.

Nozzle diameter mm	Gliding reactor	Overall conversion of nitrous oxide, %		Conversion of nitrous oxide to NO, %	
		Unmodified reactor, (a)	Reactor after modification, (b)	Unmodified reactor, (a)	Reactor after modification, (b)
0.75	Without catalyst	54	49	19	16
	With catalyst T_{kat} 480°C	71	78	20	16
	With catalyst T_{kat} 600°C	97	95	19	16
1.75	Without catalyst	50	51	18	15
	With catalyst T_{kat} 480°C	62	77	16	14
	With catalyst T_{kat} 600°C	64	96	14	13

The decrease of the reaction space volume resulted in a change of hydrodynamic conditions of gas flow through the plasma and catalyst reaction zone. The conversion of nitrous oxide to NO was lower than that in the experiments with original reaction space volume. The fact may be due to the higher temperature in the reactor with modified reaction space, owing to the increase of power density within the reactor. The increase of temperature can accelerate the decomposition of the NO formed (reaction 4).

The results of the experiments performed have shown that in decomposition of nitrous oxide, with and without the catalyst, maximum amounts of NO are obtained when the process is carried out in a reactor with higher cross-section area. When high linear gas flow velocities were applied, the maximum conversion of N_2O to NO was about 20%. The conversion of N_2O to NO decreased by about 2-4% when the volume of the reaction space was reduced.

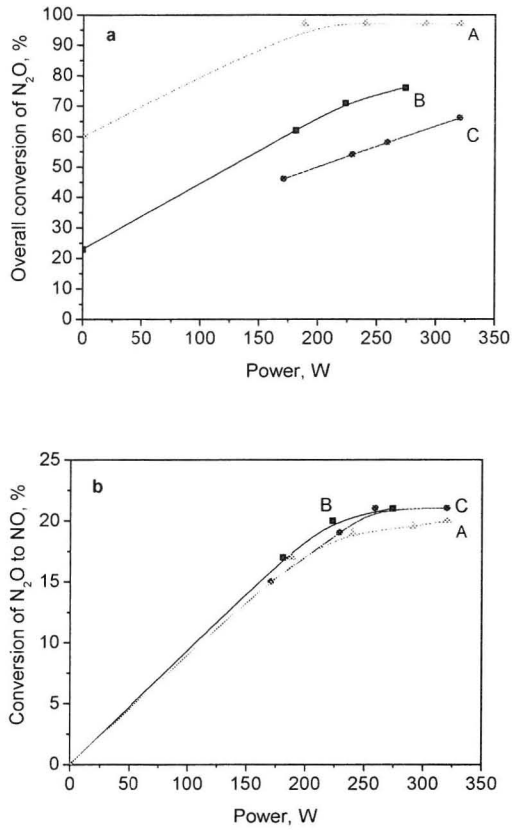

Fig. 2. Effect of discharge power on overall conversion of nitrous oxide (a) and conversion of nitrous oxide to NO (b). Interelectrode gape width 1 mm, initial nitrous oxide concentration 5% by vol. Nozzle with inner diameter 0.75mm. A - reactor without catalyst, B - reactor with catalyst (T=480°C), C - reactor with catalyst (T=600°C).

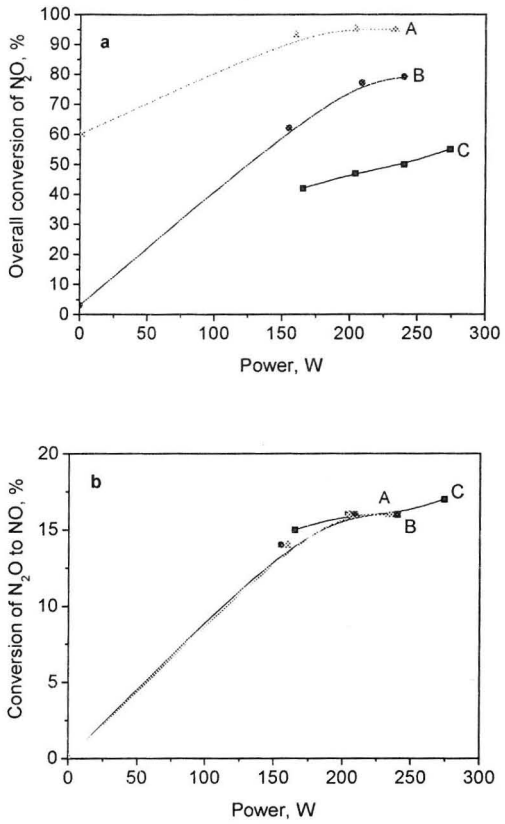

Fig. 3. Effect of discharge power on overall conversion of nitrous oxide (a) and conversion of nitrous oxide to NO (b). Interelectrode gape width 1 mm, initial nitrous oxide concentration 5% by vol. Nozzle with inner diameter 1.75mm. A - reactor without catalyst, B - reactor with catalyst (T=480°C), C - reactor with catalyst (T=600°C).

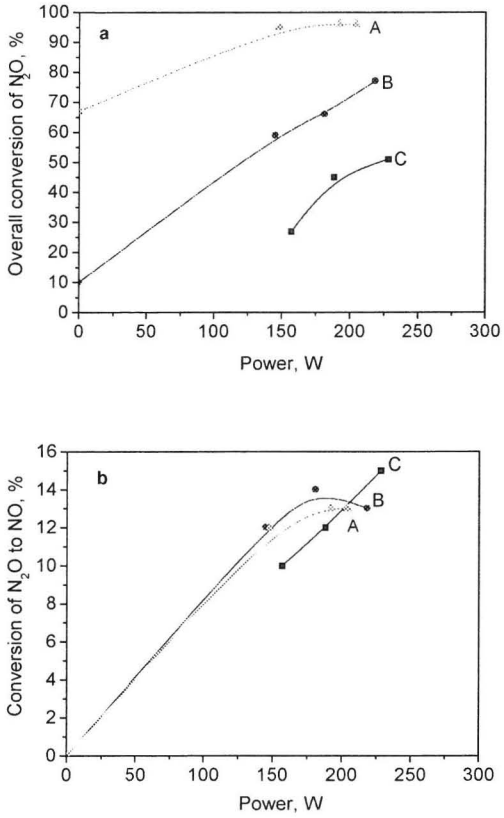

Fig. 4. Effect of discharge power on overall conversion of nitrous oxide (a) and conversion of nitrous oxide to NO (b). Interelectrode gape width 1 mm, initial nitrous oxide concentration 5% by vol. Nozzle with inner diameter 0.75mm. Reactor with modified reaction space. A - reactor without catalyst, B - reactor with catalyst (T=480°C), C - reactor with catalyst (T=600°C).

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UTLENIANIE PODTLENKU AZOTU DO TLENKU AZOTU W ŚLIZGOWYM WYŁADOWANIU ŁUKOWYM

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S t r e s z c z e n i e. Celem pracy było badanie zależności między kształtem reaktora a przemianą N_2O w NO, azot i tlen w wyładowaniu ślizgowym. Wyładowanie połączono z zastosowaniem złoża katalizatora o temperaturze 480°C i 600°C. Całkowity stopień przemiany N_2O w tym procesie zależy od temperatury katalizatora, natomiast przemiana w kierunku NO od kształtu przestrzeni wyładowczej.

S ł o w a k l u c z o w e : wyładowania ślizgowe, plazma, podtlenek azotu, kataliza heterofazowa.