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Nitrous oxide processing by a combination of gliding and microwave discharges

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Abstract

Non-thermal plasma of microwave discharge coupled with gliding discharge was applied to convert nitrous oxide. The experiments were carried out using air or oxygen as carrier gases for N_2O (5%). The overall rates of nitrous oxide conversion determined for the N_2O + air mixture were slightly higher than those for N_2O + oxygen. No significant effect of the carrier gas (air or oxygen) on the rate of $N_2O \rightarrow NO$ conversion was observed. The effect of the power of the microwave discharge and gas flow rate (air) on the overall rate of nitrous oxide conversion and rate of N_2O conversion to NO was studied. The increase of the gas flow rate from 200 to 400 N l/h resulted in an increase of the N_2O conversion rates both overall (r) and to NO (r_{NO}). For 400 N l/h, both rates were higher by about 80–100% than those determined in the experiments performed with 200 N l/h.

Keywords: Gliding discharge; Microwave discharge; Nitrous oxide; Nitric oxide

1. Introduction

The investigations aiming at reducing nitrous oxide emission are carried out in three ways: (1) catalytic decomposition of nitrous oxide; (2) thermal decomposition of nitrous oxide; (3) oxidation of nitrous oxide to NO.

Studies of the catalytic decomposition have been carried out in the presence of unsupported metals (gausses), metals deposited on aluminia or zirconia as well as in the presence of metal oxide catalysts, including binary oxides, spinel and perovskites or zeolites [1–4]. Thermal decomposition (at 1500 °C) of nitrous oxide to nitrogen and oxygen is a very attractive way of N_2O emission reducing but, according to the chemical equilibrium, NO is one of the reaction products [5–6].

The most advantageous process consist in N_2O oxidation to NO:

$$N_2O + 0.5O_2 \rightarrow 2NO$$

It was found that in the non-equilibrium plasma of gliding and microwave discharges, nitrogen, oxygen and NO are the products of nitrous oxide conversion [7–11]. Additionally, in the experiments in which air was used as carrier gas, NO was produced from nitrogen and oxygen. However, nitric oxide, according to the chemical equilibrium, decomposes to nitrogen and oxygen. The overall scheme of plasma processing of nitrous oxide is as follows:

$$N_2O \rightarrow N_2 + O_2$$
$$\searrow NO \nearrow$$

The catalysts placed in the reaction zone of the gliding discharge increase the rate of overall N_2O conversion [4,7]. However, no significant effect of those catalysts on the rate of nitrous oxide conversion to NO was observed.

The microwave radiation generators (magnetrons) belong to the most efficient sources of electromagnetic radiation. Their energetic efficiencies are very high. Nowadays, two ways of conducting chemical reactions in microwave discharge are well known.

1. Excitation of reacting species in electrodeless plasma contained in a dielectric tube. The electric field strength must be sufficient to maintain a stable discharge due to the process of cumulative ionisation. Electrodeless plasma, sometimes called MIP (microwave induced plasma) is more frequently obtained at reduced gas pressures.

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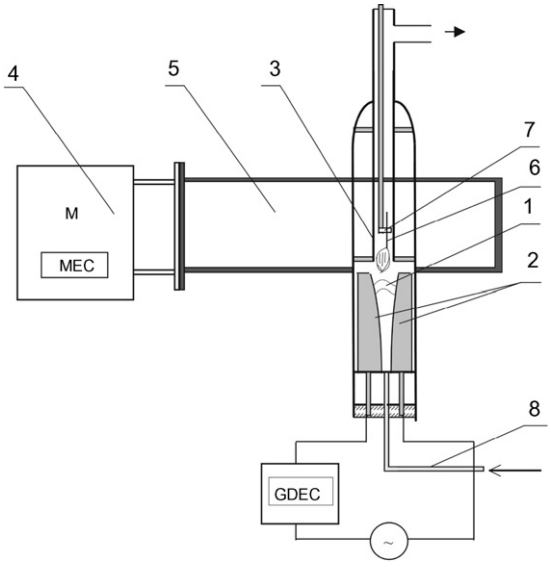

Fig. 1. Reactors for nitrous oxide conversion: (1) discharge zone, (2) metal electrodes, (3) quartz-glass tube (13 mm in diameter), (4) generators of microwave, (5) wave-guide cavity, (6) microwave initiation electrode, (7) ceramics and (8) gas inlet. MEC, microwave energy counter; GDEC, gliding discharge energy counter.

2. Excitation of reacting species with the aid of a single electrode capacitively coupled plasma called CMP (capacitive microwave plasma). The positive role of a single metal electrode as a plasma stabilising means for the first time has been implemented in the design of the microwave plasma torch (MPT). Concentration of the electric field at the electrode tip enables easy discharge ignition and plasma maintenance, even if the discharge remains practically not contaminated with the electrode material.

The preliminary gas ionisation by gliding discharge [12] enables the initiation of microwave discharge at atmospheric pressure in oxygen and air.

The aim of this work was to study the conversion of N_2O to NO and overall conversion (to nitrogen, oxygen and NO) in plasma of microwave discharge coupled with gliding discharge. More specifically, the effect of the discharge power and that of the gas flow rate (air or oxygen) on the rates of N_2O conversion (overall and to NO) were examined.

2. Experimental

The reactor (Fig. 1) consists of two parts. One of them is responsible for the gliding discharge generation and the other one is responsible for the microwave discharge generation [12]. In the central part of the reactor zone (1), the gliding discharge overlaps the microwave discharge. Two stainless steel electrodes (2) are used to generate the gliding discharge. The internal diameter of the reaction zone is 36 mm. The microwave discharge is generated in a quartz tube (3) (a diameter of 13 mm), installed axially inside the upper part of the reactor. The magnetron (4) generates microwaves (2.45 GHz) which are transported to the reactor through the wave-guide (5). The initiation of microwave plasma is possible due to the initiating electrode (6) mounted in a ceramic sifter (7).

The process of nitrous oxide conversion was studied for the 5% N_2O/air (O_2) mixtures at flow rates 200, 300 or 400 N l/h. The experiments were carried out under atmospheric pressure. The contents of nitrous oxide in the inlet and outlet streams were determined by gas chromatography using a column filled with Porapak Q. The concentration of NO in the outlet gas was determined by the volumetric–gravimetric method [7]. The microwave plasma was initiated by means of tungsten with 2% ThO_2 or platinum–rhodium rod.

The overall nitrous oxide conversion (X_1) was calculated from the formula:

$$X_1 = \frac{A - B}{A}$$

where A is the stream of nitrous oxide (mol/h) in the inlet gas and B is the stream of nitrous oxide (mol/h) in the outlet gas.

The conversion of nitrous oxide to nitric oxide (X_2) was calculated as:

$$X_2 = \frac{C}{2A}$$

where C is the stream of moles of NO (mol/h) in the outlet gas.

The overall rate of nitrous oxide conversion (r) and rate of conversion to NO (r_{NO}) were calculated from the following equations:

$$r = X_1 A\ (\mathrm{mol/h}), \qquad r_{NO} = X_2 A\ (\mathrm{mol/h})$$

Table 1
Conversion of nitrous oxide in coupled gliding and microwave discharges

Gas flow rate (N l/h)	Gliding power (W)	Microwave power (W)	Overall power (W)	Overall conversion of N_2O (X_1) (%)	Conversion of N_2O to NO (X_2) (%)
Carrier gas: air					
200	138.6	68	209.9	31	18.1
200	131.1	106	237.1	33	14.7
300	166.8	73	239.8	36	14.2
400	178.1	86	264.1	34	13.0
Carrier gas: oxygen					
200	121.5	90	211.5	25	13.8
300	152.9	120	272.9	25	17.6
400	184.6	100	284.6	24.2	15.5

The W + ThO_2 electrode initiated and maintained the microwave discharge.

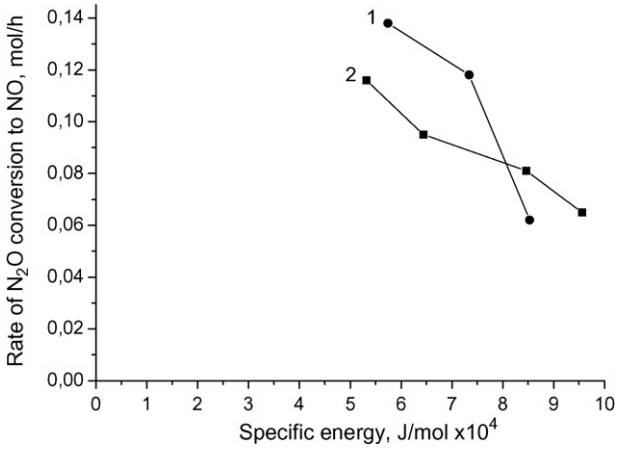

Fig. 2. Effect of specific energy (per mol of the gas mixture) on the rate of N_2O conversion to NO in coupled discharges. The W (2% ThO_2) electrode initiated microwave discharge. Carrier gas: (1) oxygen and (2) air.

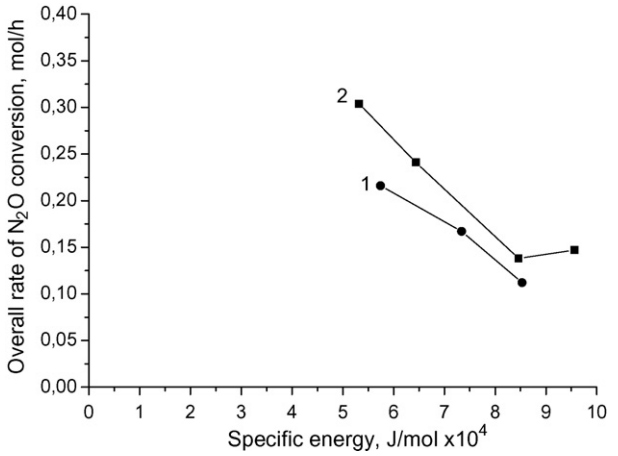

Fig. 3. Effect of specific energy (per mol of the gas mixture) on the overall rate of N_2O conversion in coupled discharges. The W (2% ThO_2) electrode initiated microwave discharge. Carrier gas: (1) oxygen and (2) air.

3. Results and discussion

Two series of experiments (5% N_2O) were performed using oxygen or air as a carrier gas. A tungsten or platinum–rhodium rod was used as an electrode for initiating and maintaining the microwave discharge.

3.1. Nitrous oxide conversion with tungsten electrode

The studies demonstrate (see Table 1) the effect of the discharge power to be rather small both on the overall conversion and conversion to NO. The effect of the flow rate on the two parameters (X_1, X_2) proved to be minor too. Two-fold increase in the gas flow rate does not produce noticeable changes: the difference in overall conversions as well as that in conversions to NO is lower than 5% (see Table 1). In contrast to the above, the effect of the carrier gas on the overall conversion of N_2O was observed. In the case of N_2O (5%) – air mixture, the conversions were 31–36%, whereas for the N_2O–O_2 mixtures – the overall conversion was about 25%. However, no effect of the carrier gas on the conversion of nitrous oxide to NO was observed.

On the basis of the results presented in Table 1, the overall rate of nitrous oxide conversion (r) and rate of conversion to NO (r_{NO}) were calculated. It was found that both r and r_{NO} decrease with an increase in the specific energy (Figs. 2 and 3) independent of the carrier gas (O_2, air). For small specific energies the r_{NO} parameter corresponding to the N_2O–O_2 mixture (Fig. 2) is higher than that obtained for N_2O–air. For large specific energies, however, the rates of conversion to NO are higher when air is used as a carrier gas (Fig. 2). A disadvantageous effect of oxygen in the region of large specific energy might be ascribed to intensive oxidation of a tungsten electrode where operating. The overall rates of N_2O conversion

Table 2
Conversions of nitrous oxide in coupled gliding and microwave discharges

Gas flow rate, N l/h	Gliding power (W)	Microwave power (W)	Overall power (W)	Overall conversion of N_2O, X_1 (%)	Conversion of N_2O to NO, X_2 (%)
200	150	0	150	24	13
	158.7	80	238.7	40	18.1
	158.7	126	284.7	44	18.6
	176.1	155	331.1	48	21.1
	177.8	222	399.8	53	23.0
300	211	0	211	31	16.1
	193.9	83	276.9	37	16.7
	193.9	120	313.9	40	17
	195.9	150	345.9	40	17.5
	195.9	185	380.9	40	18.3
	195.9	302	497.9	48	20.6
400	204.3	0	204.3	26	12.6
	197.9	102	299.9	33	17.6
	195.9	160	355.9	40	17.1
	200	221	421.0	39	18.4

Electrode initiating the microwave discharge—PtRh.

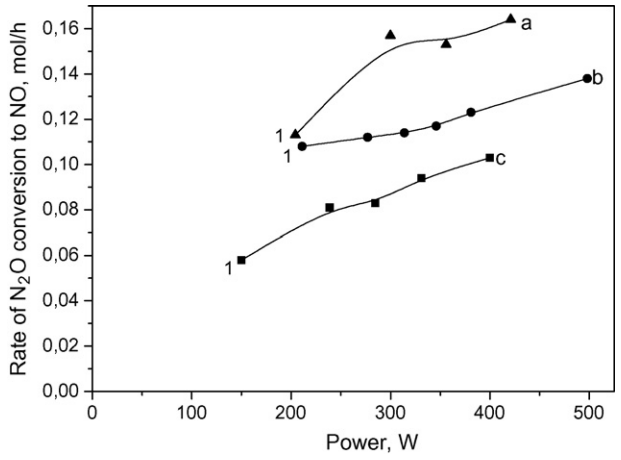

Fig. 4. Effect of electric power on rate of nitrous oxide conversion to NO in gliding discharge (points denotes as 1) and in coupled discharges. Gas flow rate: (a) 400 N l/h; (b) 300 N l/h; (c) 200 N l/h.

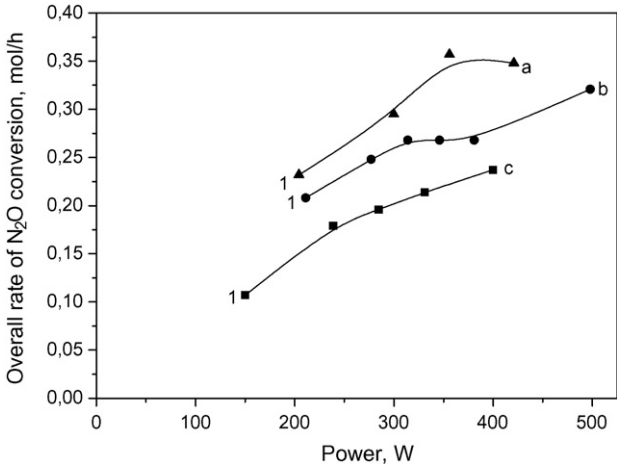

Fig. 5. Effect of electric power on overall rate of N_2O conversion in gliding discharge (points denotes as 1) and in coupled discharges. Gas flow rate: (a) 400 N l/h; (b) 300 N l/h; (c) 200 N l/h.

obtained for the N_2O–oxygen mixture were slightly smaller than those for the N_2O–air mixture (Fig. 3).

3.2. Nitrous oxide conversion with platinum–rhodium electrode

The advantage of the platinum–rhodium rod electrode is that much higher powers of the microwave discharge could be applied. The studies performed with the PtRh electrode have shown that the gas flow rate influences strongly both the overall N_2O conversion and conversion to NO (see Table 2).

It was found that in coupled discharges, the gas flow rate and discharge power affect considerably the rates of nitrous oxide conversion (Figs. 4 and 5). The r and r_{NO} rates increase strongly with an increase in the gas flow rate as well as with increase in the power of the microwave discharge. For 400 N l/h, both rates of N_2O conversion (r, r_{NO}) were higher by about 80–100% than those determined in the experiments performed with 200 N l/h.

4. Conclusions

The experiments have revealed that the microwave discharge coupled with the gliding discharge is a very attractive combination for the conversion of nitrous oxide to NO. The rates of $N_2O \rightarrow NO$ conversion obtained in coupled discharges were higher than those determined for the gliding discharge alone. Clear correlations between the microwave discharge power and conversion rates in coupled discharges were found. Furthermore, both nitrous oxide conversion rates (r, r_{NO}) depend on the kind of the carrier gas (O_2 or air): the conversion rates of nitrous oxide obtained for N_2O–air were slightly higher than those for N_2O–oxygen. However, no significant effect of the carrier gas on the conversion rate of nitrous oxide to NO in coupled discharges was observed.

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