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Catalytic and Plasma-Catalytic Processing of Nitrous Oxide

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The gliding discharge (Glid-Arc) is a specific form of the electrical discharge with a simple electrical feeding system and the ability to operate under high gas flow rates. In the presence of the gliding discharge non-equilibrium plasma the average of electron energy is higher than the gas temperature. In that kind of plasma a number of reactions may be conducted, whereas the mean temperature of the gases does not exceed several hundred Kelvins.

Both oxidation of nitrous oxide to NO and decomposition of N_2O to nitrogen and oxygen are known to be very slow processes, even at high temperature. The catalytic decomposition of nitrous oxide to elements has been carried out in the presence of metals, metal oxides, spinel or perovskites catalysts, and zeolites [1–8]. Catalysts with potential commercial application include Pd/Al_2O_3, NiO and CoO on a zirconia, binary metal oxide catalysts, and zeolites [9–10]. It was found that in the gliding discharge plasma nitrogen, oxygen and NO are the products of nitrous oxide processing [11,12]. This way is the most favourable one, because the NO obtained can be used for nitric acid production. It should be added that, in the experiments in which air was used as carrier gas, NO was produced from nitrogen and oxygen [11]. However, nitric oxide is unstable and according to the chemical equilibrium it decomposes to nitrogen and oxygen. The scheme of plasma processing of nitrous oxide is as follows:

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

This paper shows that the Cu-ZSM-5 catalyst exhibits sufficient activity and stability for the decomposition of nitrous oxide. The reaction rate obtained on this catalyst was higher than that obtained in early studies. Cu-ZSM-5 in the reaction space of the gliding discharge increases the overall conversion rate of nitrous oxide. However, no significant effect of the catalyst used on the conversion rate of nitrous oxide to NO was observed.

Two types of the reactor were used: one with a catalyst for measurement of the overall conversion rate of nitrous oxide to elements (CR) and gliding reactor (GR, Fig. 1) with a pair of electrodes and catalyst [11,12].

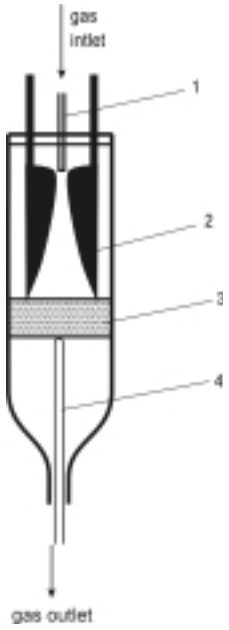

Figure1. Reactor for nitrous oxide conversion. 1 – gas inlet nozzle, 2 – electrodes, 3 – catalyst, 4 – thermocouple.

The activity of the zeolite catalysts was tested in a reactor (CR) (18.5 mm in diameter). The temperature was measured by means of the thermocouple placed inside the quartz reactor. The tests of the catalyst in N_2O decomposition were performed at the temperature up to 600°C using N_2O-O_2 or N_2O-air mixtures.

In the experiments the mass of catalyst was 3 g. The height of the catalyst bed was 3 cm. At the end of each of the series of measurements we repeated the measurement at a temperature close to that applied in the first experiment. No deactivation of any catalyst was found during the series of measurements.

The plasma-catalytic experiments were carried out in the gliding discharge reactor (GR) with a pair of electrodes connected to a high-voltage power supply (50 Hz). The temperature of the gas mixture was measured by a thermocouple below the catalyst bed. 11 g of the Cu-ZSM-5 catalyst was used. The height of the bed was 15 mm. The content of nitrous oxide in the gas mixtures was analysed by gas chromatography (Porapak Q column). Energy counter was used for measurements of the discharge power.

Three types of the catalysts were examined: (A) – CuO on alumina – CuO/γ-Al_2O_3, (B) – CuO on zeolite Na-ZSM-5 – CuO/ZSM-5, (C) – Cu-ZSM-5 (from powder and extrusions).

The CuO/γ-Al_2O_3 catalysts were prepared by impregnation of γ-Al_2O_3 (S_{BET} = 298.5 m^2/g) with cupric nitrate, followed by calcination 5 h in air at 300°C to convert cupric nitrate into oxide. Three catalysts were prepared with 17, 23 and 28wt.%Cu.

The CuO/ZSM-5 catalyst was obtained by impregnation of Na-ZSM-5 (Si/Al = 17.5) (ICRI) with cupric nitrate and calcination at 140°C for 3 h and then at 300°C for 5 h to convert cupric nitrate into cupric oxide. Finally, the material was pressed, ground and sieved to obtain a 2–3.15 mm fraction.

The Cu-ZSM-5 samples were prepared from three kinds of zeolites (Süd Chemie) with Si/Al = 70 (powder), 35 and 70 (extrusions 1.6 mm in diameter with 30% alumina). The Cu-ZSM-5 catalyst was prepared by Cu^{+2} exchange of a Na-ZSM-5 zeolite [3]. The Cu-ZSM-5 samples were filtered and dried and then pressed, ground and shifted. Finally, the material was heated in air for 2 h at 120°C, 1 h at 250°C, 1 h at 350°C and 3 h at 500°C. A fraction of catalyst 2–3.15 mm was used for the study. The properties of the catalysts are presented in Table 1.

Table 1. Specific area and content of cupric of the catalysts for nitrous oxide conversion.

Catalyst	Content of copper [wt. %]	Specific area (BET), [m^2/g]
CuO/γ-Al_2O_3	17	168
CuO/γ-Al_2O_3	23	140
CuO/γ-Al_2O_3	28	126
CuO/ZSM-5	17	–
Cu-ZSM-5, Si/Al = 17.5	2.38	–
Cu-ZSM-5, Si/Al = 70	1.21	369
Cu-ZSM-5, Si/Al = 35, extrusions	1.65	291
Cu-ZSM-5, Si/Al = 70, extrusions	1.41	336

The results (with CR reactor) of the experiments with N_2O-air and N_2O-O_2 mixtures of 5% by vol. N_2O for the gas flow rate 200 Nl/h are presented (Table 2–3, Fig. 2) using the following quantities:

W – flow rate of O_2 + N_2O or air-N_2O mixtures [mol/h]; W [N_2O] – flow rate of N_2O [mol/h]; X – overall conversion of nitrous oxide; X_{NO} – conversion of nitrous oxide to NO.

Overall nitrous oxide conversion rate:

$$r = X\, W\, [N_2O] \qquad [mol/h]$$

Nitrous oxide conversion rate to NO:

$$r_{NO} = X_{NO}\, W\, [N_2O] \quad [mol/h]$$

Table 2. Overall conversion rate of nitrous oxide in air and oxygen performed in CR reactor.

Catalyst	Conversion rate of N_2O in oxygen, mol/h			Conversion rate of N_2O in air, mol/h		
	500°C	550°C	600°C	500°C	550°C	600°C
CuO/γ-Al_2O_3 (28% Cu)	0.03	0.05	0.09	0.02	0.04	0.09
Cu-ZSM-5, Si/Al = 70 powder	0.31	0.36	0.39	0.29	0.36	0.38
Cu-ZSM-5, Si/Al = 70 extrusions	0.13	0.23	0.34	0.11	0.22	0.32

Table 3. Overall conversion rate of nitrous oxide in oxygen performed in CR reactor.

Catalyst	Conversion rate of nitrous oxide, mol/h		
	500°C	550°C	600°C
Cu/Al_2O_3 17%Cu	0.02	0.04	0.08
Cu/Al_2O_3 23%Cu	0.02	0.05	0.10
Cu/Al_2O_3 28%Cu	0.03	0.05	0.09
CuO/ZSM-5, Si/Al = 17.5	0.04	0.09	0.17
Cu-ZSM-5, Si/Al = 35, extrusions	0.05	0.09	0.19
Cu-ZSM-5, Si/Al = 70, extrusions	0.13	0.23	0.34
Cu-ZSM-5, Si/Al = 17.5	0.30	0.38	0.42
Cu-ZSM-5, Si/Al = 70	0.31	0.36	0.39

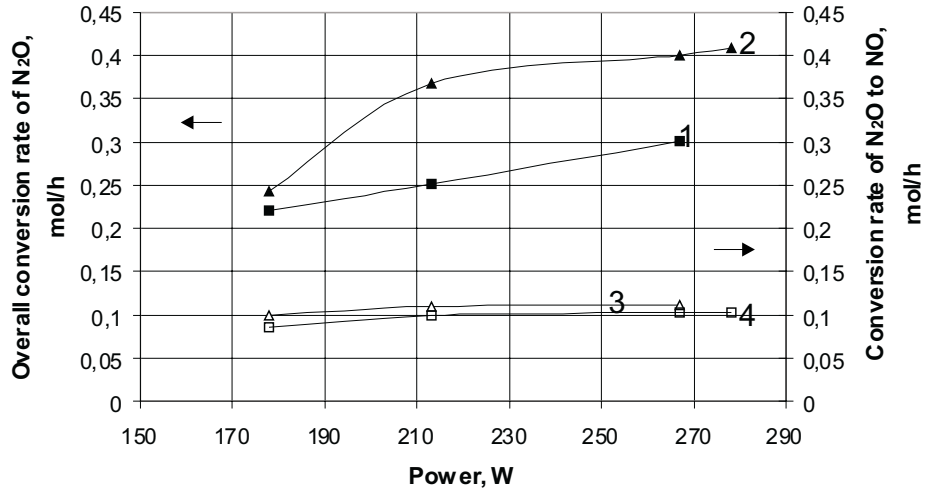

Figure 2. Effect of electric power on overall conversion rate of nitrous oxide to elements and conversion of N_2O to NO in plasma-catalytic processing of nitrous oxide. Gas flow rate 200 Nl/h. Initial concentration of nitrous oxide 5% by vol. Overall conversion rate of N_2O: 1 – without catalyst, 2 – with catalyst (zeolite Cu-ZSM-5 from extrusions). Conversion rate of N_2O to NO: 3 – without catalyst, 4 – with catalyst.

The overall conversion rate of the nitrous oxide obtained on copper-based catalyst in N_2O-O_2 mixture was slightly larger than that in the N_2O-air mixture (Table 2). The overall conversion rate of nitrous oxide in oxygen with CuO/γ-Al_2O_3 catalysts (17% Cu) is very low (Table 3). Increasing the content of copper from 17 to 28% an

increase in the overall conversion rate was observed (Table 3). A higher activity was obtained on CuO/ZSM-5 catalyst (Si/Al = 17.5) (Table 3). The overall conversion rate of N_2O was the highest with Cu-ZSM-5 (Si/Al = 17.5). Over the Cu-ZSM-5 catalyst (Si/Al = 70) prepared from powder of Cu-ZSM-5, the conversion rate of nitrous oxide was smaller (Table 3).

The overall conversion rate of nitrous oxide over the zeolite catalyst from extrusion (Si/Al = 70 and 35) at 600°C was lower, than that obtained over Cu-ZSM-5 from powder (Table 3). On the other hand, the catalyst from powder has a smaller mechanical strength. For this reason, the Cu-ZSM-5 catalyst (Si/Al = 70, from extrusions) was used for the study of the combined plasma-catalytic process of nitrous oxide. However, it should be added, that all the zeolite catalysts exhibited a very high activity.

It may be concluded that zeolite catalysts may be used for conversion of nitrous oxide to oxygen and nitrogen in plasma-catalytic processing. The zeolite catalyst increased the overall conversion rate of nitrous oxide to elements (Fig. 2). It should be added at the end, that only a slight influence of the Cu-ZSM-5 catalyst on the conversion rate of N_2O to NO was observed.

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