

Study of Ozone Generation in the Bed of Heterogeneous Catalysts of Various Geometry

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Abstract

An urgent worldwide problem in the field of environment protection is the development of energy saving and highly efficient technologies for removal of volatile organic compounds (VOCs) from gas emissions of large volume and emitted at rather low temperatures, such as low concentrated ventilation exhausts at room temperatures.

From the other side, the efficiency of ozone-catalytic process significantly decreases due to the parallel reaction of ozone recombination to molecular oxygen.

For this reason, the development of devices providing direct generation of ozone in the heterogeneous catalyst bed attracts particular interest. The application this kind of devices leads to combination of the processes of formation of highly reactive O₃ molecule and oxidation of undesirable organic admixtures.

In this paper the results on the development of the devices for the ozone generation directly in the bed of the catalysts of different geometry (spherical and honeycomb monolith) are presented. The experiments upon variation the electric signal frequency, flow rate have been carried out. It was shown, that developed device provides effective ozone generation within frequency range 500-1000 Hz and allow effectively combine the catalytic and electric properties and can be considered as the prototype for different appliance in environment protection.

Introduction

An urgent worldwide problem in the field of environment protection is the development of energy saving and highly efficient technologies for removal of volatile organic compounds (VOCs) from gas emissions of large volume and emitted at rather low temperatures, such as low concentrated ventilation exhausts at room temperatures.

The application of conventional thermal and thermocatalytic methods requires preliminary heating of exhaust gases up to 400-500°C and more, resulting in very high energy consumption for the process.

The use of ozone induced catalytic oxidation allows complete removal of pollutants at 50-60°C, providing the minimum energy consumption, operating and capital costs [1]. As was shown by calculations the self-cost of the process of the ozone-catalytic purification is 1.5 time lower than that for the conventional thermocatalytic process [2].

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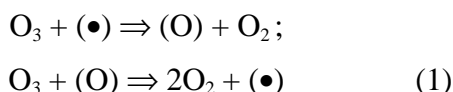
Ozone-catalytic oxidation of hydrocarbons and other VOCs attracts considerable attention during last decades due to its evident advantages [3].

The oxidation of different organic compounds such as alcohols, ketones, aromatic compounds and chlorinated hydrocarbons was studied [4]. It was found that the ozone introduced into the initial gas mixture provides effective oxidation of these compounds at low temperature. Recently Ismagilov et al. described catalytic oxidation of the vapors of toluene, benzene and iso-propanol in a temperature range 25-80°C at a gas humidity of 20 Pa over catalysts 5% MnO₂/γ-Al₂O₃, 10% MnO₂/γ-Al₂O₃, γ-Al₂O₃, copper oxide containing catalyst ICT-12-9 and Pt catalysts supported on aluminosilicate monoliths with a Pt content 0.1-0.3 wt.%. [5]. Upon oxidation of toluene vapor over 10% MnO₂/γ-Al₂O catalyst at T = 60-70°C, initial concentrations of toluene 360 mg/m³ and ozone 5.3 g/m³, P_{H₂O} = 20 Pa and space velocity = 10000 h⁻¹ a maximum toluene removal efficiency close to 100% was achieved and was stable during 30 h. The ozone decomposition efficiency was

95-98%. However, the introduction of ozone in a case of saturated hydrocarbons *e.g.* methane [6] and butane [7] does not lead to substantial increasing of conversion.

The ozone-catalytic method is of particular interest because of his suitability for solving of “cold start” problem for automotive emissions control when the system of catalytic purification is not heated to optimal operation temperature.

From the other side, the efficiency of ozone-catalytic process significantly decreases due to the parallel reaction of ozone recombination to molecular oxygen:



At the first step, an ozone molecule is activated on the catalyst surface and dissociated to atomic oxygen (in the adsorbed state) and molecular oxygen released into the gas phase. At the second step, the adsorbed atomic oxygen interacts with ozone from the gas phase to produce molecular oxygen.

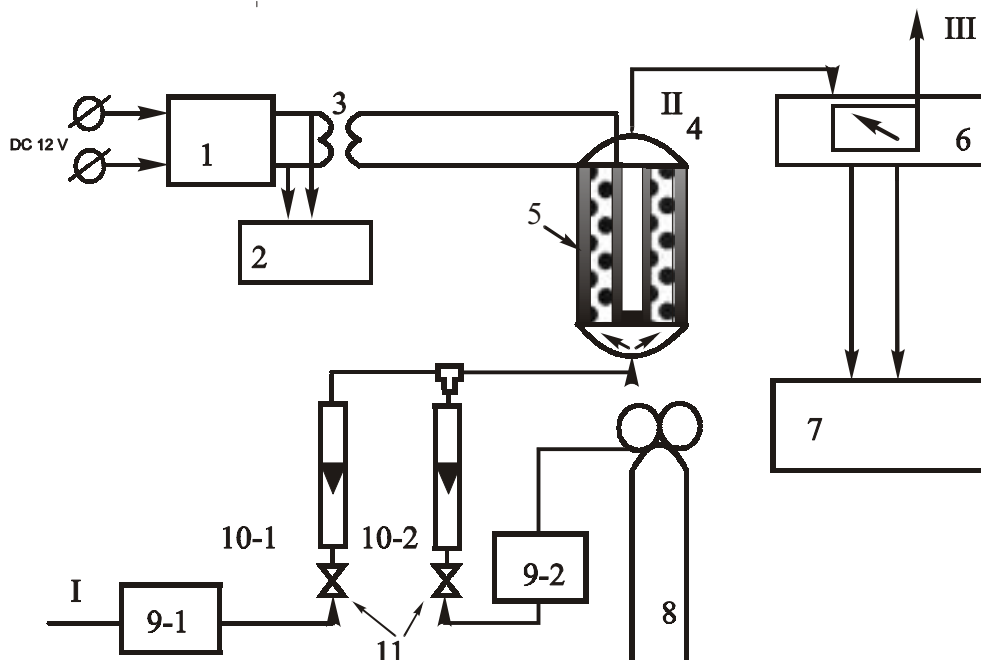
The catalysts for ozone decomposition based on different materials are subject of a considerable attention [8-9]. Such a catalyst is prepared from pow-

der activated carbon ($S_{\text{BET}} = 700\text{-}2000 \text{ m}^2/\text{g}$), which is precipitated with an aqueous manganese solution [10], or activated carbon with a binding agent (acrylamide, urea, kaolin, bentonite) as described in [11], or granular and dust-like activated carbon and zeolite, which is calcined in the inert gas medium at 623-873 K [12]. The activated carbon based catalyst can reduce the concentration of ozone in the initial gas from 800-3000 ppm to the level less than 0.14 ppm at the room temperature. The catalysts based on transition metals are also effective systems for decomposition of ozone. Thus, the manganese oxide loaded on various support were successfully used for purification of cabin air in Boeing's aircrafts [13].

For this reason, the development of devices providing direct generation of ozone in the heterogeneous catalyst bed attracts particular interest. The application this kind of devices leads to combination of the processes of formation of highly reactive atomic oxygen and total oxidation of undesirable organic admixtures to the carbon dioxide and water.

Experimental

The process of ozone generation was studied on the laboratory setup schematically is shown in Fig. 1.



Units: 1 – multivibrator, 2 - Oscillograph CI-112, 3 - inductance coil, 4 - plastic reactor, 5 - ozone generator filled with spherical granules, 6 - on-line ozone analyzer Cyclon-5-2, 7 - XY recorder, 8 - Oxygen cylinder, 9-1, 9-2 - gas drying units, 10-1, 10-2 - Gas flow controllers, 11 - Gas regulators.

Flows: I – compressed air, II – air/ozone gas mixture to analyzer, III – to stack.

Fig. 1. Scheme of laboratory set-up for studying the process of ozone generation directly in the bed of spherical catalysts.

Description of the laboratory setup

Electric equipment/installation/circuit

Direct current (12 V) is applied to a multivibrator where the electric signal is subjected to high-frequency transformation.

At the multivibrator outlet, a CI-112 oscillograph is placed to control frequency of output signal. Afterwards the signal is directed to an inductance coil to be transformed to 18 kV. A high-frequency signal (up to 3 KHz) is supplied to the ozone-generator electrodes, which are fixed on the plastic case

Gas circuit

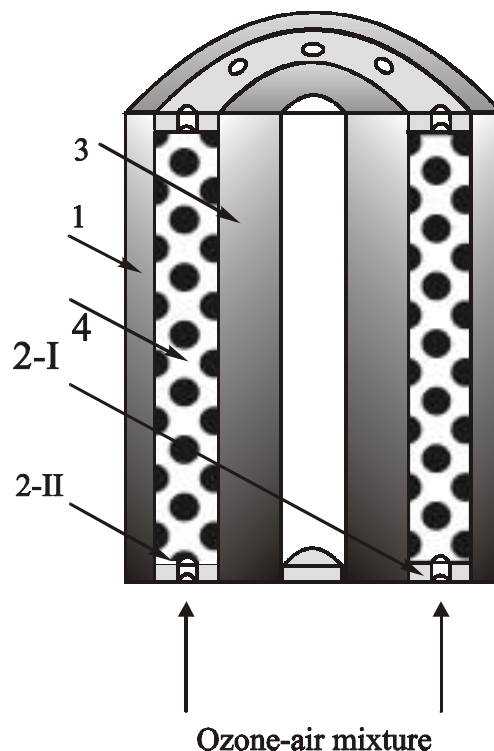
Initial compressed air is passed through a drying module filled with silica gel and a system of gas regulators and controllers to the lower part of the plastic reactor into a gap of the ozone-generator. Air/ozone mixture leaving the reactor is supplied to an analytical cell of a "Cyclone-5-2" on-line ozone analyzer. The analyzer operates on the principle that ozone absorbs light in the ultraviolet region at a frequency of 254 nm. The analyzer readings are registered on the dial of the milliamperimeter, located on the front face, and registered by a XY automatic recorder. The analyzer is equipped with a scale switch and measures concentration of ozone at the following ranges: 0-100 mg/m³, 0-200 mg/m³, 0-400 mg/m³, and 0-6 g/m³. Accuracy of the measurements is 1 mg/m³.

Ozone-generators

Ozone-generator Type I (Fig. 2) assembled as two metallic hollow co-axially mounted cylinders (electrodes) is manufactured from stainless steel. The electrodes are fixed between themselves with the help of corrugated teflon rings. A samples of spherical catalyst is loaded into the annular gap. The volume of loaded catalyst is 50 cm³.

Loaded sample	Fraction, mm
γ -Al ₂ O ₃	1.2 – 1.6
α - Al ₂ O ₃	0.8 – 1.0

Ozone-generator Type II is manufactured on the base of honeycomb monolith with iron and chromium oxide as active component (IC-12-30). The electrodes of different polarities are placed into the channels. The monolith is placed into the metallic case. The length of monolith piece is 100 mm.



1 – external stainless steel electrode; 2-I, 2-II – teflon insulating seal; 3 – internal stainless steel electrode; 4- spherical catalyst.

Fig. 2. Laboratory device for study of ozone generation in a bed of spherical catalysts.

Results and Discussion

Generation of ozone in an generator not filled with spherical catalysts ("blank" experiment)

The goal of the primary experiments was studying of ozone formation in the developed device upon variation the frequency of electric signal in order to determine the conditions of stable ozone formation.

In the frequency range is 500-1000 Hz and the air flow rate within range from 9 to 22.5 l/h over the entire surface of electrodes, stable discharges is forming. The concentration of ozone in the outlet gas mixture is > 6 g/m³ (the upper-range value). The results are summarized below in a Table 1.

Study of ozone decomposition

Ozone decomposition was performed using an external generator producing an ozone-air mixture.

The experimental conditions are as follows:

Sample – γ - Al ₂ O ₃ (preliminary dried at 120°C, 3 h)	
Loading	50 cm ³
Air/ozone flow rate	22.5 l/h

Table 1

Ozone formation upon variation electric signal frequency

Frequency, Hz	Flow rate, l/h	The concentration of ozone in exit gases, mg/m ³
300	9	40
500	9	> 6000
700	9	> 6000
900	9	> 6000
1000	9	> 6000
1200	9	10-15
4000	9	10-20

Concentration of ozone in the initial air flow rate - 5 g/m³

According to the analysis of exit gases, due to the interaction of ozone with the catalyst surface, its concentration sharply decays to 130 mg/m³, which corresponds to the ozone recombination degree >97%.

Study of ozone generation and recombination of on the catalysts of different geometry

Study of the process of ozone generation in the generator filled with spherical gamma-alumina (Generator Type -I)

As air was supplied to the device filled with gamma alumina without preliminary drying, the stable discharge between electrodes was not initially observed. The catalyst bed resistance was about 200 k Ω , and short circuit takes place. As the catalyst layer becomes dry (condensation of moisture is visually observed on the top reactor walls), a stable discharge comes about. It was registered that exit gases contain ozone whose concentration in outlet gas increases as the flow rate increases. Apparently, with increasing of the flow rate the (low residence time range) the efficiency of ozone recombination drops down and O₃ molecules are released into the gas phase (Fig. 3).

It should be noted that if preliminary dried at 120°C α -Al₂O₃ is loaded into the annular generator gap, the above phenomenon is not observed and ozone was not detected in off-gases (on the level of analyzer accuracy).

Study of the process of ozone generation in the

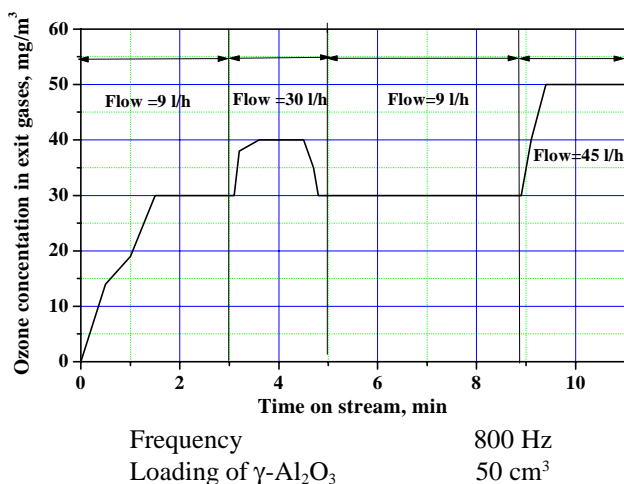
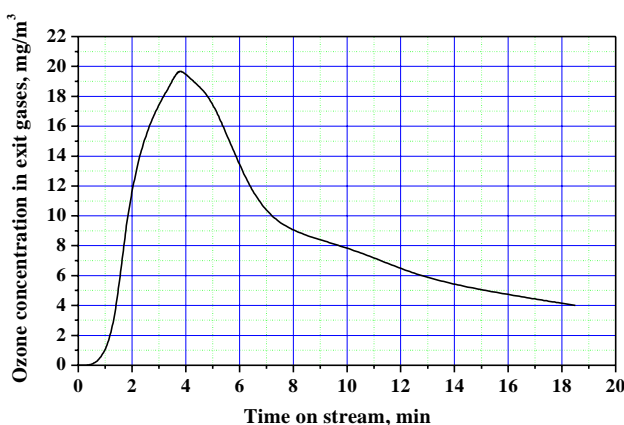


Fig. 3. Ozone concentration in exit gases vs device time on stream (spherical alumina sample).

generator filled with a honeycomb monolith catalyst (Generator Type-II)

As was shown the ozone is detected in negligible amounts only in presence of oxygen (Fig. 4). This fact can be explained taking into account high efficiency of ozone recombination over the oxides of transition metals. Thus ozone molecules are completely decomposing without releasing to the gas phase.



Catalyst IC-12-30 (honeycomb monolith catalyst)
 Fragment length 100 mm
 Frequency 500 Hz
 Initial mixture oxygen (2 l/h) + air (12 l/h)

Fig. 4. Ozone concentration in exit gases vs device time on stream (honeycomb monolith sample).

Conclusions

The developed device provides effective ozone generation within frequency range 500-1000 Hz

The developed generators allows effectively combine the catalytic and electromechanical properties and can be considered as the prototype for different appliance of environment protection *e.g.* for solution of the “cold start” problem.

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