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TRANSFER PROCESSES IN A LOW-TEMPERATURE PLASMA

DECOMPOSITION OF VOLATILE ORGANIC COMPOUNDS IN A PLASMA-CATALYTIC REACTOR

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A combined plasma-catalytic reactor was used for purification of air. The air was circulated through a grained catalyst, in which a pulsed-discharge plasma was excited at one time at atmospheric pressure. Acetone, ethyl lactate, and propylene glycol monomethylethyl acetate were used as impurities. The dry air and saturated humid air were purified. Results on the decomposition of the impurities with the use of a heated catalyst and a plasma in an inert filling material were also obtained. The combined reactor showed points in its favor for the purification conditions realized at a relatively small specific power consumption of ~100 J/liter.

Keywords: *volatile organic compound, plasma-catalytic reactor, pulsed barrier discharge, atmospheric-pressure plasma, degree of decomposition of impurities.*

Introduction. At present, different plasma-catalytic systems based on a barrier discharge are actively used for purification of air from volatile organic compounds (VOC) [1–4].

The decomposition of a VOC in a barrier discharge is a power-intensive process [2]. For example, at a power consumption of 1 kJ/liter and an initial concentration of acetone of 130 ppm in an air, the degree of the air purification was ~70%. It is necessary that the power supplied be ~50 J/liter to provide the 99% purification of an air from propylene glycol monomethylethyl acetate (PGMEA) in the case where the initial concentration of the latter is equal to 50 ppm. Close energies are required for the decomposition of ethyl lactate.

In a combined reactor of serial type, air is passed through the discharge-plasma zone and is fed into the catalyst for the afterpurification [3]. In this reactor, the discharge is excited directly in the bulk of the material with a porous catalyst, which allows one to create a compact and effective purification system [4]. To prevent the plasma pinching in the porous material, a supply-voltage discharge with a steep edge is used [5].

The aim of the present work is to investigate the efficiency of decomposition of VOC impurities in a combined plasma-catalytic reactor, in which a plasma is excited by a pulsed barrier discharge at atmospheric pressure.

Experimental Procedure. The reactor includes barrier-discharge electrodes of coaxial geometry (Fig. 1). Electrode 1 is fitted to a quartz tube 3 of diameter 20 mm with a wall of thickness 1.5 mm, serving as a dielectric barrier. The inner electrode 2 has a diameter of 10 mm. The interelectrode volume is filled with a catalytic or an inert material 4. The heat released in the discharge is partially recuperated by preheating of the incoming air by the exhaust-gas heat. A heat insulator of kaolin cotton is installed outside the reactor.

A series of experiments with dry air having a dew point lower than -60°C and air saturated with water vapor of relative humidity 80–100% was carried out. The dry air was obtained by mixing oxygen with nitrogen extracted from balloons (Fig. 2), and the humid air was obtained by admixing with water vapor.

A portion of the gas being investigated was bubbled through a vessel, placed in thermostat 5, with a definite liquid VOC and carried water vapor into reactor 1. The composition of the initial mixture upstream of the reactor and of the products downstream of it was determined by sampling into a liquid absorbent. Samplers 12 were installed in

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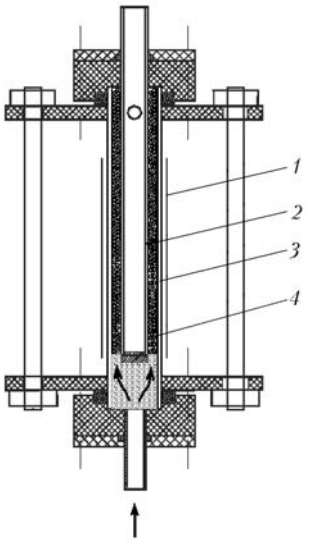

Fig. 1. Plasma-catalytic reactor of coaxial design: 1) outer electrode; 2) inner electrode; 3) dielectric barrier, (quartz tube); 4) catalytic filling material.

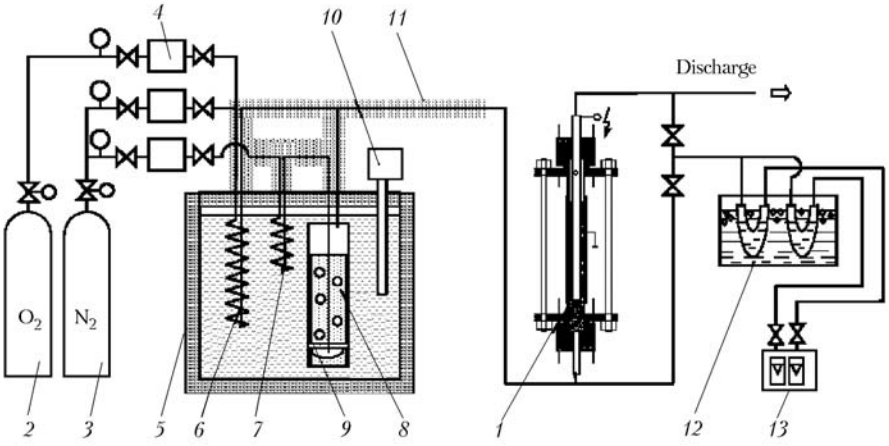

Fig. 2. Scheme of the experimental setup: 1) coaxial barrier-discharge reactor with a filling material; 2) balloon with oxygen; 3) balloon with nitrogen; 4) regulator of mass flow rate of the gas; 5) thermostat; 6, 7) heat exchangers; 8) vessel with a certain volatile organic compound; 9) dispersant; 10) temperature controller; 11) heat insulator; 12) samplers-absorbers in the tank with a thawing ice; 13) aspirator.

a tank with ice and, depending on the measurement method, were duplicated or connected in series. The initial concentration of a VOC was varied from 50 to 200 ppm. As the VOC impurities, acetone C_3H_6O, ethyl lactate $C_5H_{10}O_3$, and PGMÉA $C_6H_{12}O_3$ were used.

A large amount of ozone O_3 was released in the process of operation of the reactor. For the purpose of investigating its influence on the decomposition of a VOC in a sample we investigated model samples with a different initial content of impurities. It was established that the concentration of the impurities in these sample changes insignificantly under the action of ozone and comprises 0.5–1 ppm.

The decomposition of the volatile organic compounds was conducted under different conditions: under the action of a discharge excited in catalytic or inert materials and in a thermally heated catalyst without a discharge. The energy consumed for a pulse was measured by a Tektronix-644A oscillograph; it was equal to ~7–8 mJ. The average power supplied to the plasma was varied by a corresponding change in the pulse repetition rate within the range 100–1500 Hz. In the case where a catalytic filling material was used, the temperature in the reactor was controlled by an

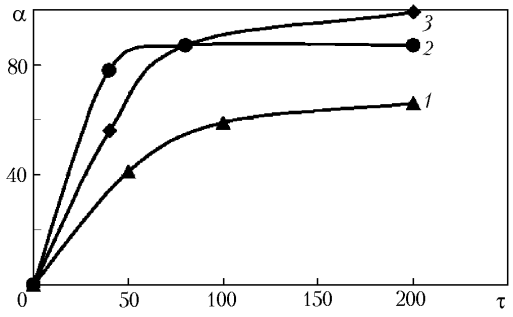

Fig. 3. Dependence of the degree of purification of an air contaminated with different impurities on the time of treatment of the gas in the plasma-catalytic reactor (specific power consumption is ~100 J/liter): 1) acetone; 2) PGMÉA; 3) ethyl lactate. α, %; τ, msec.

external resistance heater. The graphic dependences were constructed using the data on the temperature recalculated into the energy necessary for the heating of air to a definite temperature.

The serial catalyst 1.5%Pt/γ–Al_2O_3 in the form of ceramic γ–Al_2O_3 grains of size 1.5–2 mm was used. The inert filling material represented glass spheres of diameter 1 mm. As a result of the treatment of the air in the reactor, a gas mixture of the undecomposed residues of the VOC impurity, the CO_2 and H_2O products, and some other compounds of the type of nitrogen oxides not investigated in our experiments, was obtained at its output.

The degree of decomposition of the volatile organic compounds increased with increase in the time of treatment of the air in the reactor (Fig. 3). As is seen, at an acceptable power consumption of ~100 J/liter the process of air purification saturates for ~200 msec. In our experiment this condition was met at an air-flow rate of ~2 liters/min; this quantity was selected as the main parameter.

The grained catalyst had a developed surface; therefore, the adsorption of impurities was significant for it. The character of the transient process proceeding under the action of a discharge depends on the concentration of the impurity remaining in the filling material after the previous experiment. The preliminary investigations showed that, in the case where the rate of the air flow is equal to 2 liters/min, a stationary regime is established for 8 min. Therefore, to obviate the errors caused by the adsorption, a sample was taken not earlier than within 10 min after the beginning of the operation of the reactor.

Results and Discussion. The effect of purification of air in a combined reactor subjected to the action of a catalyst and a plasma is realized due to exchange and surface processes. The VOC impurities found in the gas volume are decomposed by the discharge plasma. Classical catalysis and a corresponding chemical destruction of the impurities proceed on the surface of the heated catalyst.

It was established that the humidity of the air treated in a combined reactor significantly influences the degree of its purification. In the process of circulation of humid air in this reactor, in it there arise a large number of processes, including adsorption in the filling material, evaporation under the action of the discharge heat, decomposition of the water in the plasma, discharge pinching, and so on, which leads to a scatter of the experimental data. At the same time, the influence of the humidity of the air on its purification by a catalyst is not so significant. The results of investigations on the decomposition of the acetone, ethyl lactate, and PGMEA impurities with the use of a thermally heated catalyst and in the plasma-catalytic reactor are presented in Fig. 4 (the vertical lines reflect the data spread). The dependences obtained allow one to estimate the degree of decomposition of a VOC by the catalyst and the plasma.

The degree of decomposition of a VOC with the use of a catalyst increases with increasing temperature, beginning with a certain temperature threshold for the surface chemical reactions. For example, in the case of purification of an air from acetone with the use of the 1.5%Pt/γ–Al_2O_3 catalyst, acetone begins to decompose at ~120°C, which is realized at a power supply to the gas of ~100 J/liter (Fig. 4a, curve 5). The decomposition of ethyl lactate and PGMÉA is initiated when the catalyst is heated to ~50–70°C.

The purification of the air by the plasma was carried out with the use of an inert filling material. It was established, with acetone, as an example, that the quantity α increases smoothly and saturates (Fig. 4a, curve 3), which

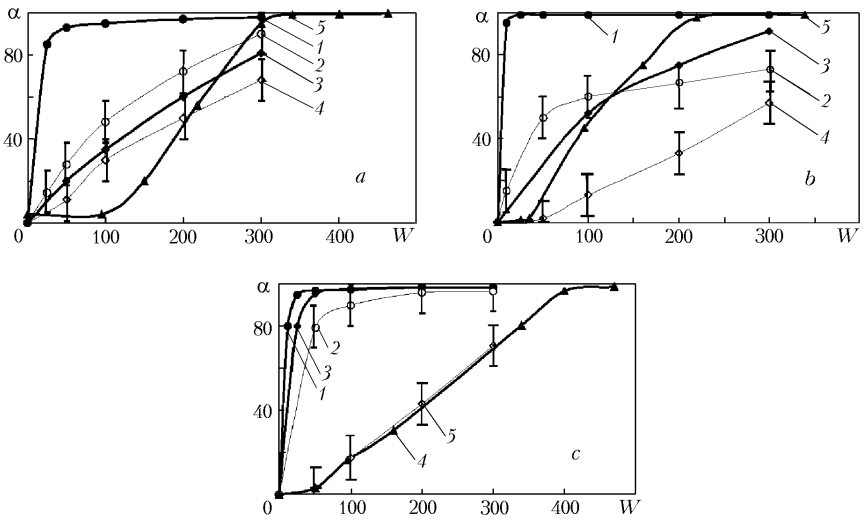

Fig. 4. Dependence of the degree of purification of the air with an impurity of acetone (a), ethyl lactate (b), and PGMÉA (c) on the specific power consumption for different methods of air purification: 1) plasma + catalyst, dry air; 2) plasma + catalyst, humid air; 3) plasma + inert filling material, dry air; 4) plasma + inert filling material, humid air; 5) catalyst. α. %; *W*, J/liter.

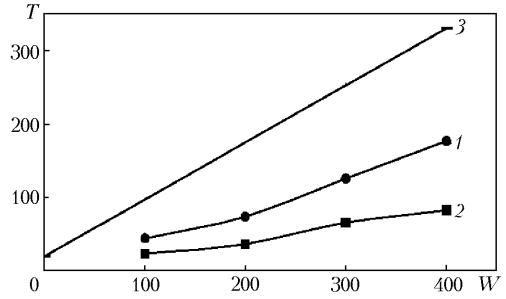

Fig. 5. Dependence of the temperature in the combined reactor on the specific power consumption. The time of treatment of the air under the operating conditions with a discharge is 10 min: 1) body of the reactor; 2) outward air flow; 3) adiabatic limit of heating of the air. *T*, ^{o}C; *W*, J/liter.

points to the fact that active particles effecting the decomposition of the impurity appear in the plasma. An analogous dependence is characteristic of the production of ozone O_3, representing an active oxidizer, in a barrier discharge. A smaller amount of active particles and ozone are produced in humid air, and, correspondingly, the degree of its purification is lower as compared to dry air (Fig. 4a, curve 4). In the case where an inert filling material is used, the efficiencies of purification of dry air and humid air from more complex substances, such as ethyl lactate and PGMEA, differ even more significantly (Fig. 4b and c).

It was established that the purification of air from a VOC impurity in the combined reactor is not only due to the simple combination of the catalyst and plasma actions. For example, at a power consumption of ~100 J/liter, the degree of purification of air from acetone in a plasma reaches ~40% (Fig. 4a, curve 3). The average power required for this process is equal to ~4 W, which is insufficient for the heating of the catalyst to the temperature necessary for its activation (Fig. 4a, curve 5). At the same time, the combined action of the catalyst and the plasma on the dry air provides approximately 95% purification of it from the impurities being considered (Fig. 4a, curve 1).

It may be suggested that the catalyst is locally heated and activated due to the contraction of the discharge and the appearance of a filtration heat wave [6]. However, the measurements of the temperature of the gas at the output of the reactor did not reveal its superadiabatic overheating (Fig. 5). Therefore, the purification of air under the combined action of a plasma and a catalyst is probably due to the decomposition of a VOC impurity by the nonequili-

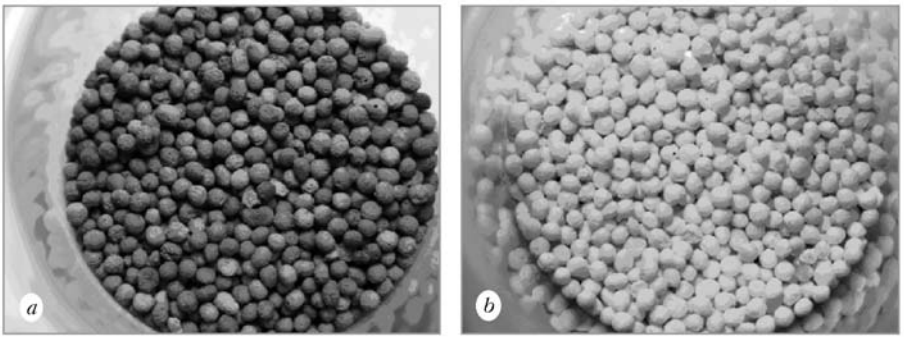

Fig. 6. Catalyst after the work under the thermal-heating conditions (a) and after the work in the plasma reactor (b).

TABLE 1. Comparison of the Efficiencies of the Decomposition of VOC Impurities in the Plasma-Catalytic Reactor and in the Commercial Catalytic-Thermal Aketon Thermo Clean 650 Setup

VOC Impurity	Degree of purification, %	Aketon Thermo Clean 650, power consumption, J/liter.	Plasma-Catalytic Reactor, power consumption, J/liter.
Acetone	95	400	100
	98	450	300
Ethyl lactate	99	60	25

brium plasma in the gas volume and the short-run heating of the catalytic surface by the plasma pulse. For the time of the succeeding pause between the pulses, the heat is scattered and the catalyst ceases to work; the cycle is repeated under the action of the next discharge pulse.

The quality of purification of a humid air in the combined reactor is worse (Fig. 4a, curve 2), which points to the fact that a part of the catalyst surface does not work, most likely due to the pinching of the discharge on the surface of the grains.

In the process of purification of an air by a thermally heated catalyst, the color of the grains changes as a rule, which indicates that their surface is contaminated (Fig. 6a). Under the discharge conditions, the surface of the catalyst is continuously cleaned by the plasma, which is evidenced by the unchanged color of the surface of the grains and its purity (Fig. 6b). A plasma and a catalyst arranged in series does not provide this effect.

A comparison of the efficiencies of the decomposition of VOC impurities in the plasma-catalytic reactor and in the commercial catalytic-thermal Aketon Thermo Clean 650 Setup [7] showed that the combined system of purification offers an advantage over the indicated setup (see Table 1).

Conclusions. The high efficiency of purification of dry air from VOC impurities in a combined reactor is attained due to the combined action of the plasma and the catalyst on these impurities. The mechanism of decomposition of the VOC impurities in the indicated reactor may be the decomposition of these impurities in the gas volume by the nonequilibrium plasma is supplemented by the classical catalysis arising on the surface of the catalyst as a result of its periodic heating by the discharge-plasma pulses. The humidity of the air decreases the efficiency of the volume purification, in particular because of the decrease in the production of ozone, and the pinching of the plasma on the surface of the catalyst results in a part of it ceasing to work. The plasma-catalytic purification of air offers a marked advantage over the catalytic-thermal purification process for systems with a relatively small power consumption of ~100 J/liter. The use of a barrier discharge allows one to rapidly actuate the reactor and establish required conditions of its operation. In the process of operation of the reactor, the plasma removes organic impurities from the surface of the catalyst, which increases the service life of the setup.

NOTATION

T, temperature, ^{o}C; W, specific power supply, J/liter; α, degree of purification, %; τ, time of treatment of a gas in the reactor, msec.

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