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Decomposition of CO_2 in a barrier discharge in the presence of cerium oxide catalysts

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A number of catalysts based on cerium oxide have been synthesized to study the process of plasma-catalytic decomposition of CO_2 in a barrier discharge. For the first time, an oxide catalyst MgCe−Al has been compared with samples containing in the composition only cerium oxide or magnesium oxide. It has been established that, in the presence of the MgCe−Al sample, the highest degree of the CO_2 decomposition and highest energy efficiency get achieved.

Keywords: barrier discharge, cerium oxide, low temperature plasma, catalyst, CO_2 decomposition.

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Rapidly expanding consumption of fossil fuels results in a continuous increase in carbon dioxide emission which is regarded as one of the main factors causing the Earth global warming. At present, various strategies are being developed, which are aimed at disposing waste CO_2 instead of releasing it into the atmosphere. One of the possible ways of solving this problem is utilizing CO_2 as a feedstock for producing useful products, for instance, for commercial production of synthetic fuels and chemicals [1–5].

Low-temperature plasma possesses a number of advantages for the processes of CO_2 decomposition: nonequilibrium character, low energy consumption, and unique ability to induce chemical reactions at low temperatures [6,7]. The use of the barrier discharge in the CO_2 decomposition also has a number of advantages, such as a simple design, possibility of working at the atmospheric pressure, and possibility of using dielectric (catalytic) reactor packing to improve energy efficiency of the process [8].

The method of plasma-catalytic CO_2 decomposition is based on using electrical discharges and catalytic materials and allows combining the advantages of the catalytic and plasma methods for CO_2 decomposition [9,10]. Interaction between the electric field and pellets filling the reactor results in that, depending on the pellet shape, porosity and dielectric constant, the local electric field becomes nonuniform and higher than the applied external field [9]. It is known from literature that promising components of heterogeneous catalytic systems for the plasma-catalytic process are oxides of alkaline-earth metals (CaO, MgO), as well as oxides of metals containing oxygen vacancies (CeO_2) [11]. By now, no publications have described simultaneous use of oxides of both types in one catalyst. Introducing such materials into the plasma-chemical reactor enables an essential enhancement in the CO_2 conversion and increase in energy efficiency of the plasma process [8,11].

In this work we studied the CO_2 decomposition in the barrier discharge at the atmospheric pressure in the presence of catalysts. Catalyst pellets and ceramic beads were used as a reactor filler for studying their effect on the decomposition degree and energy efficiency of the process of CO_2 decomposition.

The experimental setup (Fig. 1) consists of a reactor, high-voltage power supply, gas inlet system, chromatograph, and two-channel oscilloscope. The CO_2 flow rate was controlled by mass flowmeter RRG-20 („Eltochpribor", Russia) and was equal to 17 cm^3/min. As a power supply, a source of 23−kHz sinusoidal high voltage was used. The electrical signal was fed to digital oscilloscope Tekronix TDS 2021, the discharge power was determined by calculating the Lissajous figure areas in real time (the power measurement error was ±20%). Reaction product gases (CO_2, CO, O_2) were identified with a portable gas backflush chromatograph PIA (NPF MEMS, Russia) equipped with a thermal-conductivity detector and having two chromatographic columns with absorbents Hayesep N and molecular sieves 13F. As a carrier gas, highest-quality argon 99.993% was used. The measurement error of gaseous product concentrations was ±5%.

The reactor consisted in a quartz tube with the outer diameter of 16 mm and wall thickness of 2 mm. As an inner electrode of the reactor, a steel rod 8 mm in diameter with screw thread M8 was used. As an outer earthed electrode, a steel grid arranged on the tube outer surface was used (the electrode length was 8 cm). The inter-electrode gap was 4 mm.The catalysts were placed in the discharge space and fixed with mineral cotton located beyond the discharge region.

To study the process of CO_2 decomposition in the presence of catalysts, there were synthesized samples

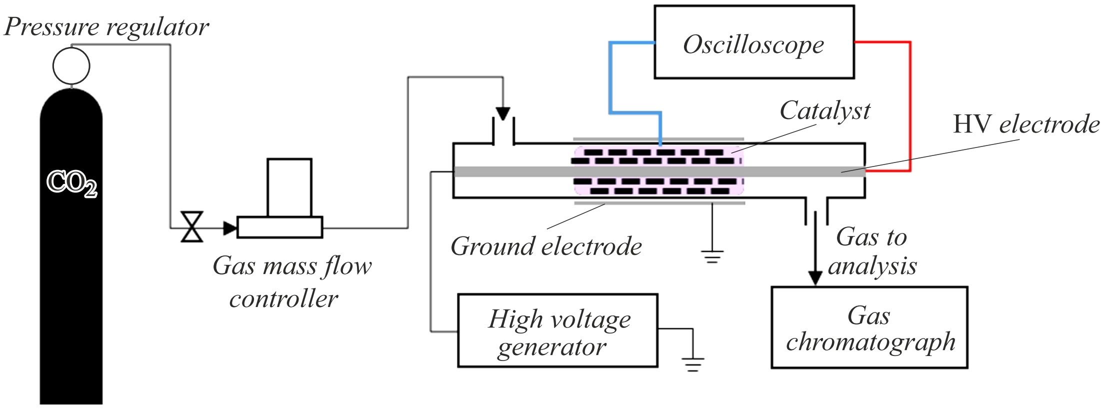

Figure 1. Experimental setup layout.

Physical-chemical characteristics of the synthesized catalysts

Sample designation	Surface characteristics			Content of oxides, mass%			
	S_{BET}, m^2/g	V_{pore}, m^3/g	d_{pore}, nm	Al_2O_3	MgO	CeO_2	SiO_2
Al_2O_3	202	0.50	8.6	99.0	–	–	1.0
Ce–Al	190	0.43	8.5	88.7	–	10.5	0.8
Mg–Al	181	0.43	8.1	87.2	12	–	0.8
MgCe–Al	161	0.33	7.6	75.7	11.8	11.7	0.8

Note. S_{BET} is the specific surface area measured via the BET (Brunauer-Emmett-Teller) model, V_{pore} is the pore volume, d_{pore} is the pore diameter.

containing MgO and CeO_2 applied on inert carrier Al_2O_3 (fraction 0.63–1.00 mm). The samples were synthesized by impregnating the carrier with salts $Mg(CH_3COO)_2 \cdot 4H_2O$ (Vecton, chemically pure) and $Ce(NO_3)_3 \cdot 6H_2O$ (OJSC „Technology Center Lantan“, chemically pure) with subsequent annealing at 400°C during 3 h; as a result, appropriate metal oxides were formed. The synthesized catalysts were characterized by a large specific surface area (see the Table); application of metal oxides led to reduction of the surface characteristics, which was caused by partial blockage of the carrier pores.

The absorbed power was calculated as

$$P = fW = f \int_{t_0-\frac{T}{2}}^{t_0+\frac{T}{2}} u(t)i(t)dt$$

$$= fC_n \int_{t_0-\frac{T}{2}}^{t_0+\frac{T}{2}} u(t)du_c(t) = fC_nA, \quad (1)$$

where $u(t)$ is the applied voltage, $i(t)$ is the current flowing through the reactor, $u_c(t)$ is the voltage at both ends of the external capacitor, T is the applied voltage period, f is the applied voltage frequency, C_n is the external capacitance, A is the Lissagous figure area. The power absorbed in the discharge was 5–10 W. The discharge voltage and discharge current were measured by using capacitance dividers.

Gas contents prior to and after the reaction were determined with a gas chromatograph. The decomposition degree α [%] CO_2 was calculated via the CO percent in the products. Energy efficiency η [%] of the reaction process was calculated as

$$\eta = \frac{\alpha G_{in}^{CO_2} \Delta H_{298\,\text{K}}^0}{P} \cdot 100\%, \quad (2)$$

where $G_{in}^{CO_2}$ is the inlet CO_2 flow rate ([mol/s]), $\Delta H_{298\,\text{K}}^0$ is the C=O bond breaking enthalpy equal to 283 kJ/mol [11].

Fig. 2 presents the dependence of the CO_2 decomposition degree on the reactor filling status.

Experiments with all the reactor fillers were performed at the voltage of 5 kV. Fig. 3 demonstrates the dependences of absorbed power and energy efficiency on the reactor filling status.

As the obtained results show, the best process characteristics can be achieved by using catalyst MgCe–Al. For instance, placing the given sample into the plasma-chemical reactor leads to an increase in the CO_2 decomposition degree from 11 to18.6%. Using inert ceramic beads as the packing material provides only slight increase in the CO_2 decomposition degree; more significant effect on the CO_2 dissociation comes from cerium-containing catalysts based on aluminum oxide. This may be explained by the presence of oxygen vacancies in the cerium-oxide phase; those vacancies promote the CO_2 adsorption on the catalyst

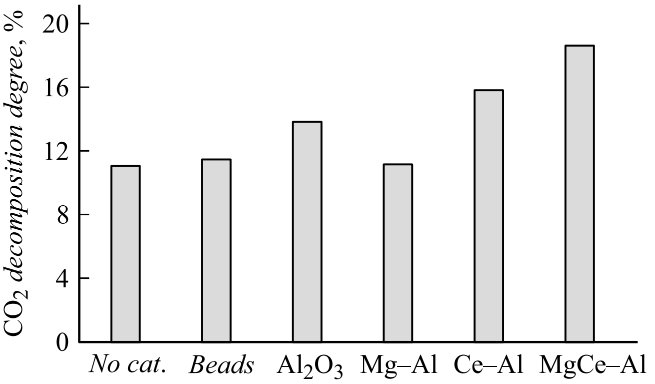

Figure 2. The degree of CO_2 decomposition in a barrier discharge depending on the reactor filling status. *No cat.* — empty reactor, *Beads* — reactor packed with catalyst-free beads.

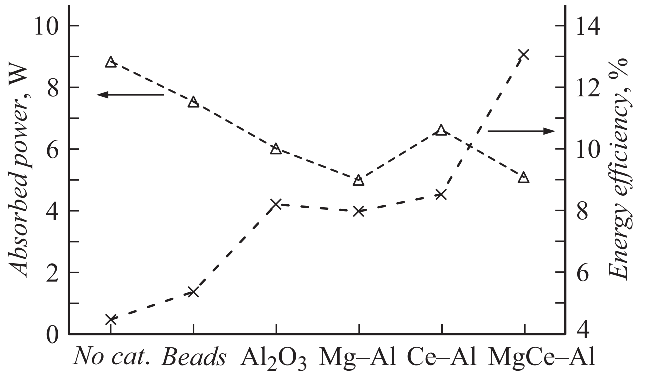

Figure 3. Power absorption and energy efficiency depending on the reactor filling status.

surface followed by breaking of the C=O bond under the action of high-energy plasma electrons.

This paper is the first that has presented the comparison of the role of double oxide catalysts MgCe–Al with that of the samples containing magnesium or cerium oxides applied on Al_2O_3 in the process of the CO_2 decomposition in the barrier discharge. In the presence of the MgCe–Al sample, the CO_2 decomposition degree increases from 11 to 18.6%, and the process energy efficiency rises drastically. These facts reveal the promise of using catalysts based on double oxide systems. These systems are of interest for further research.

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Conflict of interests

The authors declare that they have no conflict of interests.

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