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Foam-metal catalysts for purification of waste gases and neutralization of automotive emissions

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Abstract

Catalysts of a new structural type — foam metals — have been tested in the process of neutralization of exhaust gases of automotive engines. Foam catalysts have physico-chemical, gas-dynamic and catalytic characteristics exceeding the indices of the traditional granular and honeycomb catalysts.

Keywords: Foam metal catalysts; NO reduction

1. Introduction

Catalysts based on foam metals indicated high efficiency in the processes of deep oxidation of hydrocarbons [1–4]. Some previous studies suggested the possibility of the foam catalyst application for neutralization of automotive emissions as well [4,5]. Traditional honeycomb neutralizers ensure a high degree of emission purification (80%–90%). However, good mechanical and gas-dynamic properties of foam metals promise to make them an efficient alternative for the conventional catalysts.

The purpose of the present study is to continue the investigation of the catalysts based on foam metals with a supported active cover in the processes of exhaust gas removal from toxic compounds: CO, hydrocarbons and nitrogen oxides.

2. Experimental

The catalysts were prepared by thermal or chemical deposition of active cover based on Pt, Pd or complex oxides of transition metals on the foam-metal support. The foam metal (Nichrome or steel) was coated with a layer of γ-Al_2O_3 intermediate support in order to increase the catalyst surface area. The content of Pt or Pd in the neutralizers accounted for 0.5 wt.-%, concentration of the transition metal oxides amounted to 10–12 wt.-%.

The laboratory experiments were carried out in a flow-circulating catalytic system under the following conditions: temperature = 150–350°C; concentration of the oxidized substance (CO, C_3H_8) in gas–air mixture = 1.0 vol.-%; flow rate = 0.5 l/min.

The foam neutralizers (1.5 l) were also tested on a bench carburettor engine at oxygen/(oxidized substance) ratio = 1. For comparison, the commercial Pt-containing hon-

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eycomb neutralizer was tested under the same conditions.

3. Results and discussion

Foam metals — high-porous block materials — have uniform cellular structure with an anisotropy of mechanical and gas-dynamic properties. The elementary cell of the foam metal cage has a dodecahedron form (Fig. 1). Geometrical parameters of the elementary cell are set by the preparation conditions and can be varied within 0.5–5.0 mm diameter. Properties of the whole block change depending on the cell average diameter: porosity (hollow volume) = 80%–98%, volume density (specific weight of the foam-metal block) = 0.1–0.5 g/cm^3. Foam metals are easily formed into blocks of any configuration that is rather convenient for preparation of catalytic neutralizers.

As Fig. 2 demonstrates, the foam catalyst strength depends on the sample porosity that is explained by changing the density and gauge of lintels between nodes of the cells. Foam catalysts have high gas permeability close to that of honeycomb neutralizers but far beyond the index of granular sample (Fig. 3).

Any corrosion-resisting metal or alloy — Cu, Ni, Fe, Cu–Ni, Ni–Cr, steel — can be a foam support stock. Although all these metals have intrinsic catalytic activity in the processes of deep oxidation, the efficiency of pure foam metals is not high because of their low surface area — 0.05–0.1 m^2/g [1]. Therefore, in order to increase the surface area the method of applying the Al_2O_3 intermediate support has been worked out [1]. The use of the intermediate support complicates the catalyst preparation process somewhat but it permits to raise the surface area up to 20–50 m^2/g and, accordingly, the catalytic activity. The previous studies showed that Al_2O_3 layer changes strength and permeability of the samples [1,3]. So for specific conditions, it is necessary to select the optimal Al_2O_3 percentage. On the foam support with the intermediate layer, the active cover of

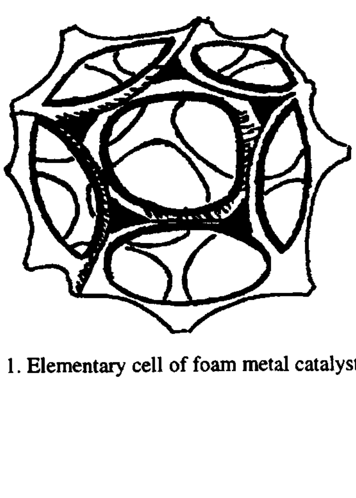

Fig. 1. Elementary cell of foam metal catalyst [4].

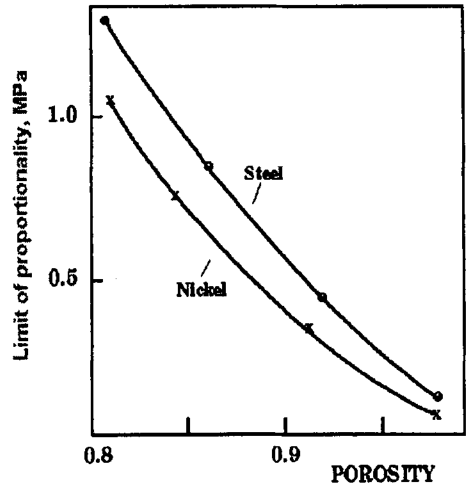

Fig. 2. Strength in compression of the foam metals.

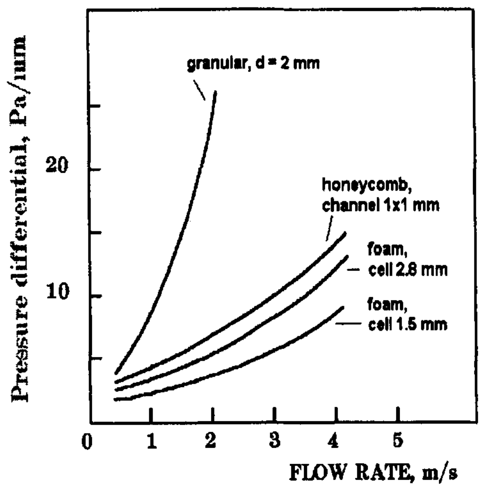

Fig. 3. Gas permeability of the catalysts.

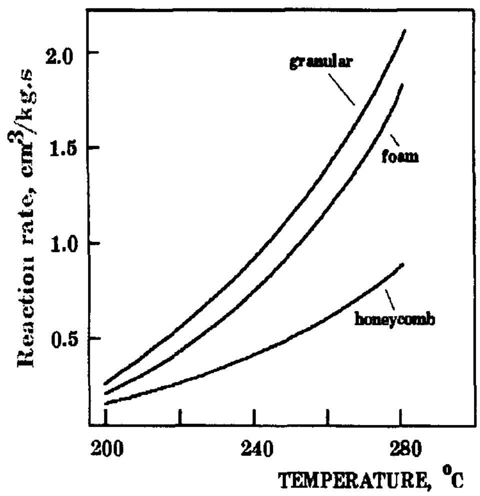

Fig. 4. Catalytic activity in propane oxidation of the catalysts with Cu/Cr_2O_4 active cover.

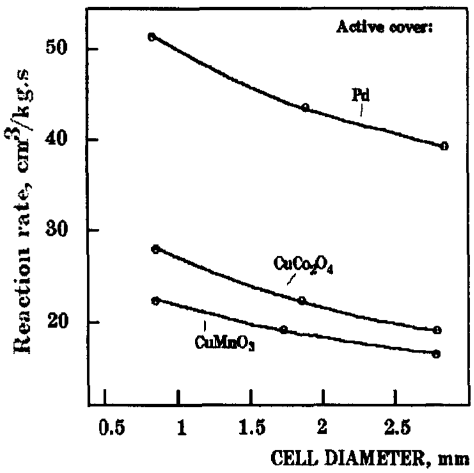

Fig. 5. Catalytic activity in CO oxidation of the foam catalysts (200°C).

any composition can be deposited (both oxide and Pt- or Pd-containing).

Tests of the catalysts in the process of propane deep oxidation in kinetic temperature range revealed that activity of the foam catalyst is higher than that of the honeycomb sample with the same composition of active cover (Cu/Cr_2O_4) (Fig. 4). This is explained by the distinctions of the foam metal structure. Cellular structure of the foam metal gives rise to high turbulency of the gas flow that affords better contact of the reacting gas with the catalyst surface and accordingly higher extent of the use of active surface as compared with the honeycomb sample where part of the organic molecules short-circuits in laminar flow without contact with the catalyst. The activities of foam and granular catalysts are similar but mechanical and gas-dynamic properties of the block catalysts are much higher.

Activity of the foam catalysts depends strongly on the cell size (Fig. 5). This is also concerned with better use of the catalyst surface in fine-cellular samples. However, the fine-cellular catalysts have worse strength and permeability (Figs. 2 and 3). As neutralizers suffer great mechanical and gas-dynamic in-service load, it is necessary to optimize catalytic, geometric and strength characteristics of the foam catalysts. On our data the foam metals of 1.5–2.2

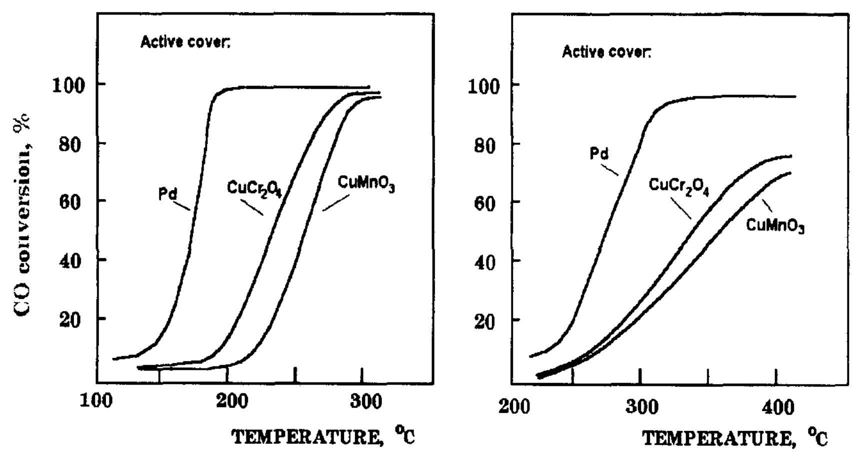

Fig. 6. Conversion of CO on the foam catalysts before (A) and after (B) treatment with SO_2.

mm cell diameter (with regard to Al_2O_3 layer) are optimal for catalytic neutralizers.

Resistance to SO_2 is a very important characteristic of neutralizers, especially in cars with Diesel engines. The experiments indicated that after treatment with SO_2 (1 vol.-% in air flow) for 10 h the activity of the samples with oxide active cover falls abruptly (Fig. 6). Pt,Pd-containing catalysts are more resistant to SO_2. It is essential to note that in SO_2 and at high temperature in air the stock of foam support corrodes. So, such metals and alloys as Cu, Ni and Cu–Ni do not fit for preparation of foam neutralizers. Foam ceramics is the most corrosion-resistant, but neutralizers based on foam ceramics are too friable and fail when using. So, foam supports on the base of steel or Nichrome are optimal in this case.

The neutralizer tests in the bench carburettor engine revealed that under the same conditions (catalyst volume, active cover composition, temperature and load rating) the Pt-containing foam neutralizer performs better than commercial honeycomb sample (Table 1). Moderate extent of NO_x conversion is caused by the fact that the tested samples do not contain rhodium — the best catalyst for the $NO_x + CO = N_2 + CO_2$ process.

Neutralizers based on complex oxides of transition metals are not able to afford a necessary extent of automotive emission removal and a prolonged service life. However, in Russia, where neutralizers are not used entirely, production of inexpensive oxide catalysts of 60%–70% efficiency may be economically justified.

Table 1
Efficiency of the catalytic neutralizers

Neutralizer	Average conversion (%)		
	CO	CH	NO_x
Honeycomb, Pt-doped	84.3	85.2	57.7
Foam, Pt-doped	88.8	91.7	66.5
Foam, oxide	62.3	67.9	–

4. Conclusion

The investigations have demonstrated that the catalysts based on foam metals have high catalytic, mechanical and gas-dynamic properties that recommend them for application in the processes of exhaust gas purification including neutralization of automotive emissions.

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