COMPARATIVE STUDIES OF CELLULAR PERMEABLE SOLIDS AS CATALYST SUPPORTS

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Abstract. Metallic and ceramic foam catalyst supports and catalysts were manufactured. Comparative studies of the foam-structure catalyst supports and straight-channel catalysts supports were performed. Affect of the catalyst support pore structure upon the catalyst operational performance was analyzed.

1. Introduction

Cellular permeable solids have been extensively used during the last decade due to their excellent strength-to-weight and surface-to-volume ratios, mechanical stiffness, extremely low density, high gas permeability [1]. Manufacture of monolithic catalyst supports is one of the most advantageous applications of the cellular permeable materials.

The use of common pellet bed catalysts can be objectionable in processes running under the high flow rates or external dynamic loads because of the intensive abrasion wear and unacceptable hydraulic losses. In this case, the state-o-the-art solution is to use catalysts deposited onto a permeable monolithic support. Nowadays, typical applications of the monolith supported catalysts include the automotive or industrial exhaust control, selective oxidation of hydrocarbons, steam reforming of natural gas, solar energy driven processes, etc. [2-6].

A monolith supported catalyst comprises a macroporous permeable monolith (metallic or ceramic) with a catalytic active compound deposited all along its internal structural elements [7,8]. Pore structure, porosity and material of the monolithic support define the mechanical, hydraulic and thermal properties of the catalyst as a whole.

Cellular monoliths with the straight channel structure (ceramic honeycombs, corrugated steel sheets) are the best commercialized monolithic supports for the automotive and some other gaseous exhaust neutralizers [5, 9]. Such pore structure ensures the laminar flow under very high linear gas velocities and, therefore, the minimized hydraulic losses. Foam-structure catalyst supports are less commercialized but has the advantageous heat and mass transfer parameters [9] and the proven ability to operate under the higher flow rates [10]. However, their industrial use is considered to be limited because of the poorer mechanical strength and higher hydraulic losses under the fast gas flow.

The task of this study was to analyze how the catalyst support pore structure affects the monolithic catalyst operational performance.

2. Materials and methods

2.1. Materials

Metallic and ceramic cellular materials were prepared at PMI as described in [8]. Ceramic foams (70% Al_2O_3 – 30% SiO_2) were manufactured by impregnating the 15 ppi reticulated polyurethane foam with a ceramic slurry, porosity of the foams varied within 0.78-0.90. Nickel foams were manufactured by electroplating of the 10, 20 and 30 ppi polyurethane foams, porosity of the foams

was 0.94-0.96. A part of the Ni foams (20 ppi) was subjected to the pack aluminization as described in [11], the resulting Al content was 4.5 wt. %. Samples were fabricated to cylinders of different dimensions depending on the testing procedure.

Two types of the straight-channel monolithic catalyst supports were received from outside suppliers. Metallic honeycomb made from a corrugated stainless steel sheet was received from Enco Tuning GmbH, Germany (cell density - 300 cpsi). The cordierite honeycomb monoliths were manufactured by extruding the plastic mass extrusion at BIC (cell density – 400 cpsi). The (0,8% Pt + 0,4% Pd) / γ-Al$_2$O$_3$ pellet-type catalyst was prepared at BIC as well.

Catalytic coatings (Pt-Pd/γ-Al$_2$O$_3$ and Pd/γ-Al$_2$O$_3$) were deposited to the cellular supports by the multiple washcoating. procedure followed by calcination at 400°C in the hydrogen atmosphere.

2.2. Methods

Compressive strength was determined using Instron 1195 mechanical testing machine. Cylindrical samples ($\varnothing$20x20 mm) were loaded with a cross head speed of 1 mm/min.

Gas permeability was determined by passing the air flow through porous cylindrical samples ($\varnothing$10x200 mm). Long cylinders were assembled from short nickel foam samples ($\varnothing$10x20 mm) inserted tightly into the steel tube of the corresponding diameter. The overpressure was measured in the tube at the entrance to the porous cylindrical samples with the measurement accuracy of ±2 Pa. Testing installation was made at PMI.

Catalytic activity in the buthane oxidation process was studied at BIC. The flow-through reactor was designed and made at BIC. Ni-Al foams with the (0,64%Pt + 0,32 % Pd) / γ-Al$_2$O$_3$ catalytic coating (10 % wt.) were tested jointly with the pellet bed catalyst of similar composition. Cylindrical samples ($\varnothing$15x40 mm) were studied.

Catalytic activity in the Diesel exhaust combustion process were performed at Diesel Engine Institute, St.-Petersburg, Russia. Pollutions were produced by the 5 kW Diesel engine at 1500 rpm. The Pd / γ-Al$_2$O$_3$ catalytic coatings (9-10 wt.%) were deposited to the cordierite honeycomb and Ni-Al foam supports. The content of Pd and γ-Al$_2$O$_3$ was the same in both cases (4 g/l and 100 g/l correspondingly).. Dimensions of both supports were $\varnothing$45x100 mm.

3. Results and discussions

3.1. Mechanical properties

The comparative strength *vs* porosity data for different porous solids can be quantified, in the general case, by Eq. 1 [10].
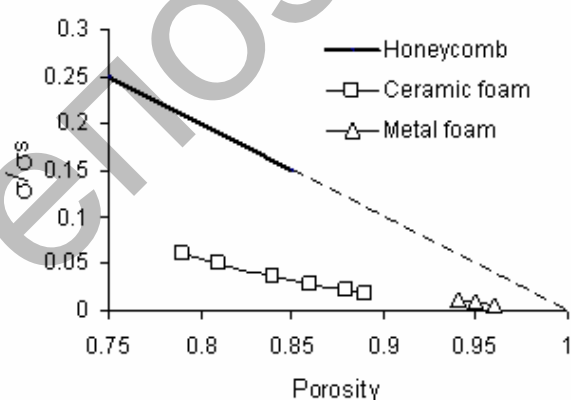
Fig. 1. Relative compressive strength *vs* porosity of different cellular solids

$$\frac{\sigma}{\sigma_s} = \left(\frac{\rho}{\rho_s} \right)^n = (1 - \varepsilon)^n \qquad (1)$$

where σ and σ_s are the strength parameters of a porous body and a solid material; ρ and ρ_s are densities of a porous body and the solid material; ε is the body porosity; n is the factor depending on the pore structure, its geometry, etc.

Fig. 1 demonstrates the $\sigma/\sigma_s = f(\varepsilon)$ compressive loading data for Ni-Al foam (yield strength), Al$_2$O$_3$–SiO$_2$ foam (ultimate compressive strength) and cordierite honeycomb (ultimate compressive strength for axial loading, calculated by assuming n=1 [8]). The data for both ceramic and metallic foams were well fit

to Eq. 1 with n≈1.8, which indicates that lower mechanical strength of the foam-structure catalyst supports compared to the honeycomb ones is determined by the nature of their pore structure. Another issue is the area of the material real existence. Porosity of commercial honeycombs is usually below 0.85 whereas typical porosities of the ceramic and metal foams are 0.8-0.9 and 0.94-0.96, respectively. In the case of static loading, the higher mechanical strength of honeycombs is not of great importance. Hydraulic pressure drops under common exploitation conditions usually should not exceed 3-5 kPa while the measured mechanical strength of the open-cell foams was 0.5-0.8 MPa for metallic foams and 0.9-2.5 MPa for ceramic foams. However, this brings a great advantage to the honeycomb catalyst supports in the case of significant dynamic loading (vehicle applications).
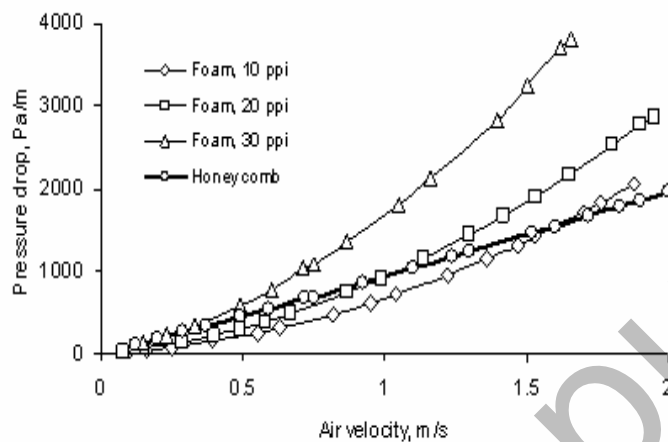
3.2. Hydraulic properties

The pressure drop in a homogeneous and rigid porous solid *vs* superficial velocity data is traditionally described by the Forscheimer equation:

Fig. 2. Hydraulic losses in 300 cpsi metallic honeycomb and open-cell Ni foams

$$\frac{\Delta P}{L} = \frac{\mu}{k_1} \cdot v + \frac{\rho}{k_2} \cdot v^2 \qquad (2)$$

where ΔP is the pressure drop; L is the porous medium thickness; μ and ρ are the gas viscosity and density respectively; v is the superficial flow velocity; k_1 and k_2 are the Darcian and non-Darcian permeability.

Depending on the gas flow mode (laminar or turbulent) the contribution of linear and quadratic members in Eq. 2 changes, which affects the shape of the $\Delta P/L = f(v)$ curve.

It was stated that the curve was close to linear for the honeycomb and close to quadratic for all the Ni foam samples (.Fig. 2) within the studied velocity range. The foams ensured lower hydraulic losses at low air velocities and evidently higher losses at the increased velocities. In the case of vehicle applications with the arrangement limitations, the catalytic reactor is usually performed as an elongated cylinder and the $\Delta P/L$ value becomes the limiting factor. The honeycomb catalyst supports ensure the lowest hydraulic losses due to the laminar (linear) flow mode at air velocities >10-15 m/s [6]. However, the following consideration must be taken into account. The catalyst capacity is defined by the permissible volumetric velocity which is understood as a volume of gas that passes through the catalyst unit volume per one hour and which is only dependant on the catalyst volume only. So, when the reactor structure allows re-shaping the monolithic element of the same volume to much lower thickness-to-filtration area ratio, the foam-structure catalyst supports will be advantageous. Firstly, they ensure similar or lower hydraulic losses. Secondly, the turbulent gas flow in the pore structure results in the enhanced heat and mass transfer, which can affect the monolithic catalyst activity [9, 10].

3.3. Catalytic activity

Fig. 3 demonstrates catalytic activities of the (Pt-Pd)/γ-Al$_2$O$_3$ catalyst shaped to pellets and deposited to the Ni-Al foam support in the buthane oxidation process. At low gas velocity (1000 h^{-1}) and high buthane concentration (1 % vol.) the pellet-type catalyst demonstrated evidently higher activity: the 50% buthane conversion was achieved at 200°C on pellet bed catalyst and at 265°C on the foam supported catalyst. When the air velocity increased to 18000 h^{-1} and the concentration decreased to 300 ppm the pellet-type catalyst lost its benefits despite the content of noble

metals was 7.5 times lower in the case of the foam-supported catalyst (0.016 and 0.12 % wt., respectively). This must result from diffusion limitations in the catalyst micropores, which impedes the delivery of reactants to catalytic active centers in the depth of a pellet. As a result, the pellet catalyst activity benefits are diminished while the hydraulic disadvantages become evident.

Fig. 4 shows activities of honeycomb and foam supported $Pd/\gamma-Al_2O_3$ catalysts in the process of the Diesel exhaust conversion of at different volumetric velocities. Both catalysts demonstrated similar catalytic activities until 30000 h^{-1}. Further gas velocity growth resulted in the decrease of activity of honeycomb catalyst, which demonstrates the limited mass transfer in the straight-channel pore structure compared to the open-cell foam one.
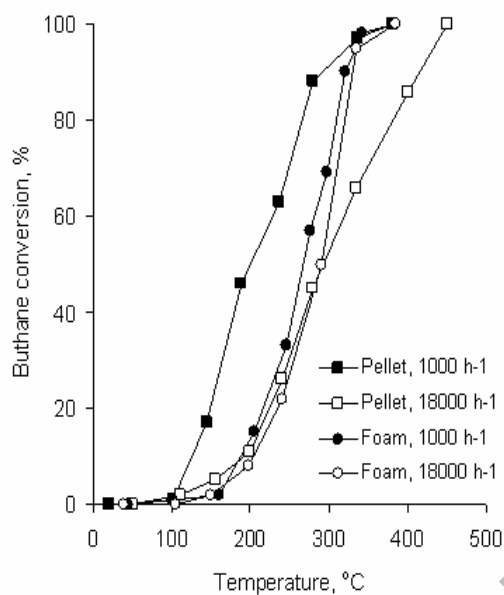

Fig. 3. Buthan conversion on pellet and foam supported (Pt-Pd)/γ-Al$_2$O$_3$ catalysts
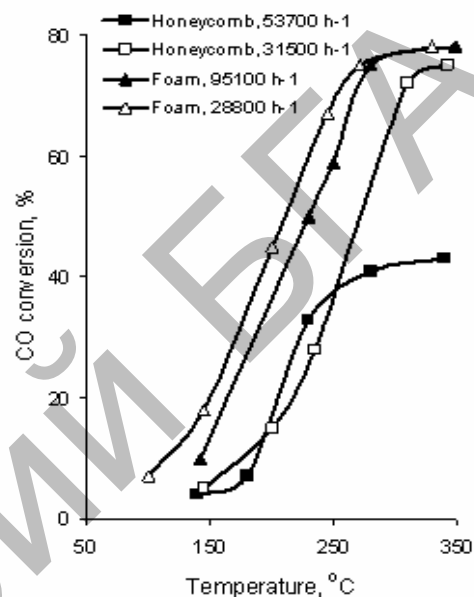
Fig. 4. Diesel exhaust CO conversion honeycomb and foam supported Pd/γ-Al$_2$O$_3$ catalysts

4. Summary

Pore structure of the monolithic catalyst support affects the catalyst operational performance: its ability to withstand mechanical loading, hydraulic losses, activity. Open-cell foam-structure catalyst supports are advantageous in processes running under high volumetric flow velocities. Limiting factors can be high superficial linear flow velocity and dynamic mechanical loading.

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