Study of Supported Catalysts Synthesized by the Use of Plasma Technique

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Abstract

Some prospects of application of plasma spraying technique for the synthesis of supported catalysts are demonstrated. It was shown that Mn-containing catalysts deposited on γ-Al_2O_3 by means of plasma spraying demonstrate superior activity in methane oxidation reaction compared with those of reference catalysts prepared via standard conventional route. Gradient alumina layer sprayed on the surface of metal supports of different geometry improves the performance characteristics of combustion catalysts on metal supports during long term operation at high temperatures. A catalytic heat-exchanging (HEX) tubular reactor for combining exothermic combustion and endothermic methane steam reforming has been developed. The methane combustion and steam reforming catalysts were synthesized on the heat-conducting metal foam support materials by application of preliminary plasma spraying in order to increase adhesive properties of the active layer. The HEX reactor with perovskite or Pt supported catalyst on Ni–Cr foam material on the external surface of the HEX tube and with Ni containing reforming catalyst on the internal Ni foam was successfully tested in methane combustion reaction combined with methane steam reforming.

INTRODUCTION

Last years works on the synthesis of catalysts with substantially improved or new unique properties by the use of plasma techniques have been intensively carried out. Although most of the papers are devoted to the preparation of bulk catalysts, some efforts are undertaken to manufacture supported catalysts for different applications, *i. e.* selective hydrogenation, combustion processes, *etc.*

This paper focuses on the development of supported catalysts by the use of plasma spraying technique. Direct current plasma torch [1] with interelectrode insert and diffusive attachment of arc on anode surface was used for synthesis of Mn-containing catalysts supported on alumina as well as alumina coatings on metal surfaces of different geometry (plates, foams) with subsequent deposition of combustion catalysts.

EXPERIMENTAL

Operating modes of plasma torch with the interelectrode insert were provided by the variation of the plasma-forming gas (air) flow rate over a wide range (from 0.5 up to 2.5 g/s) [2]. The main regimes of the plasma torch operation and outflowing jets are presented in Table 1.

Powders of pure γ-alumina or γ-alumina impregnated by $Mn(NO_3)_2$ were injected into the plasma jet outflow and quenched in water. Influence of powder size (90–1000 μm), regime of plasma jet outflow (laminar or turbulent) and Mn content (5 or 17 % mass) on the

TABLE 1

Main regimes of the plasma torch operating and outflowing jets

Flow rate of plasma-forming gas (air), G_g, g s^{-1}	0.5	0.75	1.0	1.25	2.0	2.5
Arc current, I, A	255	250	245	240	220	210
Arc voltage, U, V	180	200	210	220	250	270
Efficiency of electric energy utilization, η, %	45	50	60	65	70	72.5
Effective thermal power of outflowing plasma jet, kW	20.6	25.0	30.8	34.3	38.5	41.1
Regime of the plasma jet outflow and approximate length of powder thermal treatment zone in axial direction, L_r, m	Laminar, 0.15	Laminar-transient, 0.09	Transient, 0.075	Transient, 0.06	Turbulent, 0.05	Turbulent, 0.05
Mean-mass velocity of plasma prior to powder injection section, m s^{-1}	460	570	720	815	1020	1160

properties of catalysts synthesized in a plasma jet outflow (plasma catalysts) was studied. Reference catalysts having identical chemical composition were prepared using standard conventional route, *i. e.* the calcination of γ-alumina impregnated by $Mn(NO_3)_2$ at 550 °C for 4 h.

Alumina powders differing in phase composition and particle size (α-Al_2O_3 20–80 and γ-Al_2O_3 90–500 μm) were used to spray an intermediate (gradient) layer on titanium plates and Ni, Ni–Cr foam materials under laminar, transient and turbulent regimes of the plasma jet outflow [3]. Various combustion catalysts ($LaCoO_3$, Pt, Pd, $LaMnAl_{11}O_{19}$) were deposited on Ni–Cr foams covered by plasma sprayed alumina layer by means of impregnation or suspension techniques [2, 4].

Phase composition of the catalysts was studied by XRD analysis, specific surface area of the samples was measured by BET method, pore volume of the sprayed layers was calculated using water capacity technique. The morphology of the catalysts was studied by SEM. Active component distribution in alumina was defined by X-ray microprobe analysis, whereas catalyst surface was examined by XPS. Catalysts were tested in methane oxidation reaction in a flow set-up; the reaction mixture was 1 % CH_4 in air with a space velocity 1000 h^{-1}.

RESULTS AND DISCUSSION

γ-Al_2O_3

Study of the influence of the regimes of jet outflow on the properties of alumina powders treated in plasma and quenched in water has been performed. The results for γ-Al_2O_3 powder are presented in Table 2.

A comparison of cross section views of initial and plasma treated particles of γ-Al_2O_3 showed that in the latter case the pellet consists of a core and a shell (Fig. 1). Densities of these two basic areas are different. Analysis of scanning electron micrograph and XRD data (see Table 2) allows the assumption that the particle core consists of γ-Al_2O_3 phase, while the particle shell is formed by α-Al_2O_3. It seems that the use of large particles for spraying and high quenching velocities lead to the formation of a cold core and a hot melted shell.

Mn–γ-Al_2O_3

XRD analysis showed the presence of β-Mn_2O_3 and γ-Al_2O_3 phases in all Mn-containing reference catalysts, independent on the content of Mn and particle size of the samples. Phase composition of the plasma catalysts is more com-

TABLE 2

Properties of γ-Al_2O_3 after plasma treatment and quenching in water

Particle size, μm	Flow rate, g s^{-1}	Regime	Specific surface area, $m^2 g^{-1}$	Phase composition	I_α/I_γ^*
90–200	0.5	Laminar	2.2	α-Al_2O_3, γ-Al_2O_3	30
90–200	1.0	Transient	22	α-Al_2O_3, γ-Al_2O_3	13
200–300	0.5	Laminar	19	α-Al_2O_3, γ-Al_2O_3	25
200–300	1.0	Transient	76	α-Al_2O_3, γ-Al_2O_3	11
300–400	0.5	Laminar	67	α-Al_2O_3, γ-Al_2O_3	8
300–400	1.0	Transient	104	α-Al_2O_3, γ-Al_2O_3	6
400–500	0.5	Laminar	119	α-Al_2O_3, γ-Al_2O_3	

*I_α/I_γ – ratio of intensities of line d/n = 2.085 (α-Al_2O_3) and d/n = 1.990 (γ-Al_2O_3).

plicated. It depends on the Mn content, particle size as well as the regime of plasma jet outflow. The Mn-containing phases are registered in plasma catalysts with particle size equal to 100–200 μm. It was found that Mn is present in solid solutions of Mn–Al–O composition based on spinel structure and having different cell sizes (a = 7.940–8.242 Å).

X-ray microprobe analysis revealed that the active component in reference catalysts is uniformly distributed inside the particle (Fig. 2, *a*). Discrepancy between K_αMn and K_αAl profiles is observed. This fact correlates with XRD data showing the formation of crystalline β-Mn_2O_3 phase in reference catalysts. Analysis of K_αMn and K_αAl profiles of plasma catalyst allows us to conclude that Mn is transferred to the catalyst surface (see Fig. 2. *b*). XPS confirmed that Mn concentration on the surface of the plasma catalyst exceeds the ones of the reference catalyst by 50 %. The XPS spectra of plasma and reference catalysts present one O 1*s* photoline at 531 eV corresponding to the lattice oxygen of alumina. Meantime, the chemical states of manganese in plasma and reference catalysts are different: binding energy of Mn $2p_{3/2}$ photoline of plasma catalysts is 641.6 eV, whereas that of reference catalysts is 640 eV.

Plasma catalysts demonstrate superior activity in methane oxidation reaction (Fig. 3). Temperature of 50 % methane conversion for plasma catalyst with the content of active component 5 % mass is lower than the temperature of 50 % methane conversion for reference catalyst by 90 °C, whereas for catalysts with content of active component 17 % mass by 120 °C. This fact can be probably explained by increased concentration of manganese on the surface of plasma catalyst as well as by formation of active Mn-containing surface phases invisible for XRD analysis.

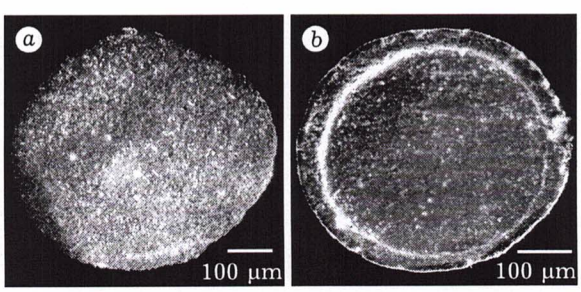

Fig. 1. Micrographs of a cross-section view of initial (*a*) and plasma-treated γ-Al_2O_3 particles (*b*).

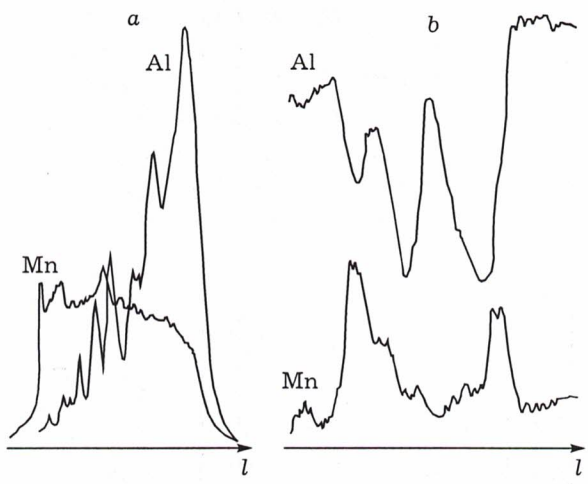

Fig. 2. X-ray microprobe spectra (K_αMn, K_αAl) of cross section of particles of catalyst 17 % Mn_2O_3/γ-Al_2O_3, 100–200 μm: *a* – reference catalyst, *b* – plasma catalyst (laminar regime of plasma jet outflow).

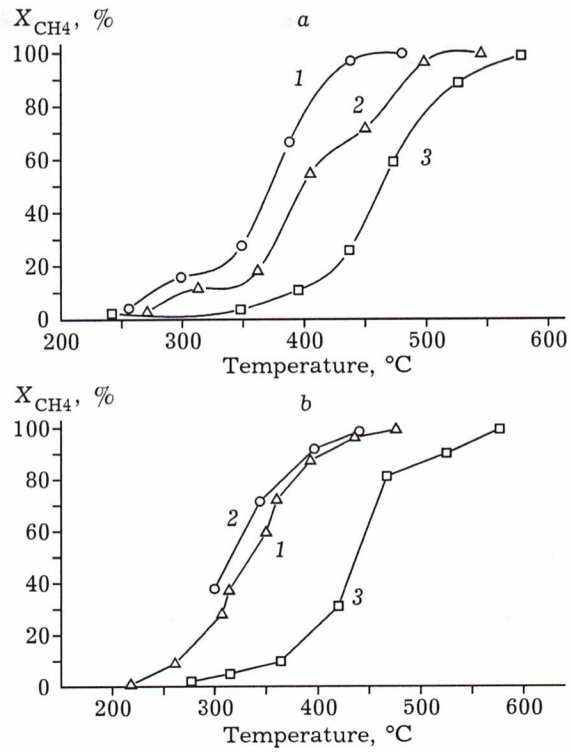

Fig. 3. Temperature dependencies of methane conversion (1 % CH_4 in air, 1000 h^{-1}) on catalysts: *a* – 5 % Mn_2O_3/γ-Al_2O_3, *b* – 17 % Mn_2O_3/γ-Al_2O_3 synthesized using turbulent (*1*) or laminar (*2*) regime of jet outflow and conventional (*3*) route.

Thus, plasma technique allows the synthesis of Mn-containing catalysts deposited on γ-Al_2O_3 with substantially improved properties compared with those of reference catalysts prepared via conventional route.

Alumina-metal supports

Experiments on the plasma spraying of alumina of different phase composition and particle size on titanium plates have shown that

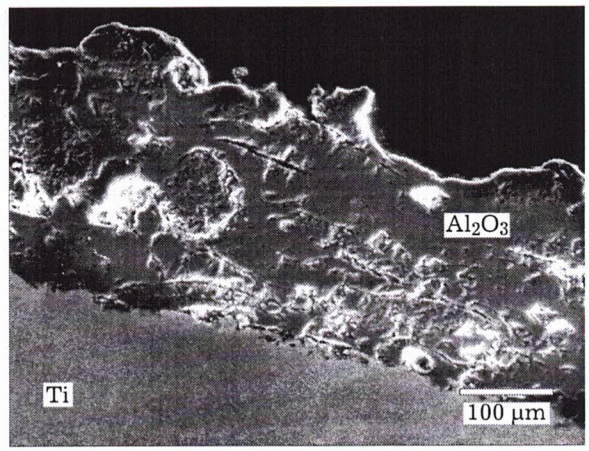

Fig. 4. Micrograph of cross section view of Al_2O_3 plasma sprayed on metal surface.

the properties of plasma sprayed layers are quite similar and do not depend on the jet outflow regime used (Table 3).

When α-Al_2O_3 is sprayed on titanium plates, the coatings are characterized by a low specific surface area and their pore volume increases when the spraying regime is changed from a laminar to a turbulent one. It has been established that the dependence of the regime on the coating properties is the same when γ-Al_2O_3 is sprayed. Moreover, in the latter case the spraying regime influences the quantitative proportions of α-Al_2O_3 and θ-Al_2O_3 phases of the coatings and their specific surface area. The maximum porosity and minimum α-Al_2O_3 phase content were found when a transient jet outflow regime was used.

The formation of dense layers when γ-Al_2O_3 was sprayed on titanium plates was shown by scanning electron microscopy (Fig. 4). It is obvious that the contact between alumina and the metal surface is rather strong and uniform. The

TABLE 3

Properties of alumina sprayed on titanium plates

Particle size, μm	Type of alumina sprayed	Flow rate, g s^{-1}	Regime of plasma jet outflow	Specific surface area, m^2 g^{-1}	Phase composition	Pore volume, cm^3 g^{-1}
40	α-Al_2O_3	0.75	Laminar-tansient	0.2	α-Al_2O_3	0.052
40	α-Al_2O_3	1.25	Transient	0.2	α-Al_2O_3	0.065
40	α-Al_2O_3	1.75	Turbulent	0.2	α-Al_2O_3	0.167
90–200	γ-Al_2O_3	0.5	Laminar	0.2	α,θ-Al_2O_3	0.068
90–200	γ-Al_2O_3	0.75	Laminar-transient	0.4	α,θ-Al_2O_3	0.075
90–200	γ-Al_2O_3	1.0	Transient	0.6	α,θ-Al_2O_3	0.166

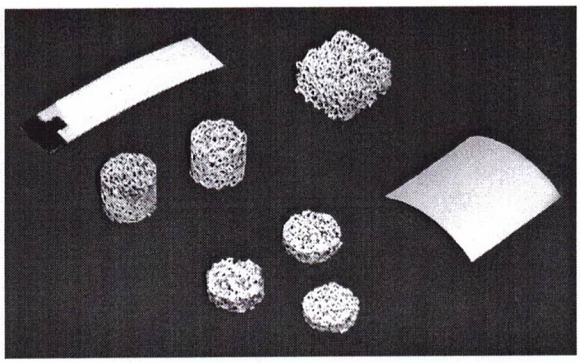

Fig. 5. Plasma sprayed samples of different surface geometry.

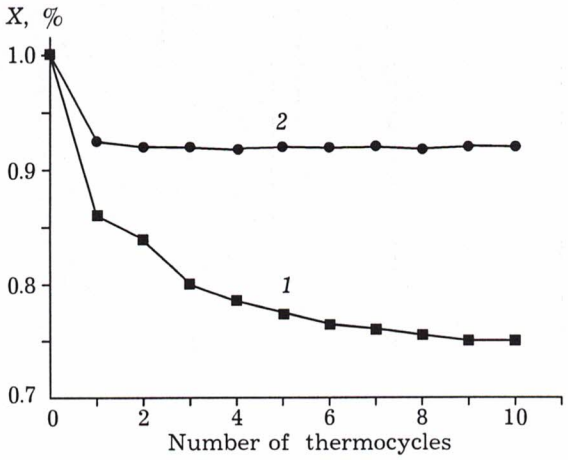

Fig. 6. Dependence of the catalyst mass loss on number of thermocycles, X, % = m_n/m_0 (m_0 – initial mass, m_n – mass after n thermocycles): *1* – $LaCoO_3/La-\gamma-Al_2O_3$/Ni–Cr foam; *2* – $LaCoO_3/La-\gamma-Al_2O_3/\alpha-Al_2O_3$/Ni–Cr, plasma sprayed $\alpha-Al_2O_3$ layer.

sprayed layer has a complicated structure consisting of dense areas and macropores of different forms and sizes.

Taking into account that phase composition and BET area of plasma sprayed alumina do not depend significantly on the properties of alumina powders used for spraying, α-alumina with particle size 40 μm was sprayed on metal supports of different geometry (Fig. 5).

Combustion catalysts on metal foams

It was shown in [2] that the genesis of an active component in the combustion catalyst is not affected by the presence of the plasma sprayed α-alumina on the metal foam. Meanwhile, the experiments on thermal cycling have revealed that the presence of the plasma sprayed alumina layer on the metal surface allows to improve the adhesive properties of the active layer (Fig. 6). It was found that in the catalyst prepared by a pure chemical method the substantial destruction of the active layer continuously proceeds during each of 10 thermocycles performed, whereas in the catalyst with the plasma sprayed alumina the loss of the active layer is observed only after the first thermocycle.

Different types of combustion catalysts were synthesized on Ni–Cr foam supports covered by dense α-alumina gradient layer using plasma spraying technique. Comparative analysis of the initial activity of metal foamed catalysts calcined at 1000 °C and having different types of active components allowed finding the best compositions for methane combustion at high temperatures: $Pd/CeO_2-\gamma-Al_2O_3$ > $LaMnAl_{11}O_{19}/La-Al_2O_3$~$Pd-LaCoO_3$ > $LaCoO_3/La-\gamma-Al_2O_3$. Thermal stability of these catalysts was studied during long time catalyst operation at the following conditions: 8.6 % CH_4 in air, GHSV = 10 000 h^{-1}, T = 1000 °C. The activity of catalysts was measured after 3, 6, 10, 20 and 50 h of operation. The catalysts tested for 50 h can be arranged into the following sequence according to their activity: $LaMnAl_{11}O_{19}/La-Al_2O_3$ > $Pd/CeO_2-\gamma-Al_2O_3$ >> $Pd-LaCoO_3$ > $LaCoO_3/La-\gamma-Al_2O_3$.

Thus, gradient alumina layer sprayed on the surface of a metal support successfully serves as a washcoat on which active component can be deposited and improves thermal stability of the catalysts.

Heat-exchanging reactors

A catalytic heat-exchanging (HEX) tubular reactor for combining exothermic combustion and endothermic methane steam reforming has been developed [4]. The methane combustion and steam reforming catalysts were synthesized on the heat-conducting metal foam support materials by application of preliminary plasma spraying in order to increase adhesive properties of the active layer. The HEX reactor with perovskite or Pt supported catalyst on Ni–Cr foam material on the external surface

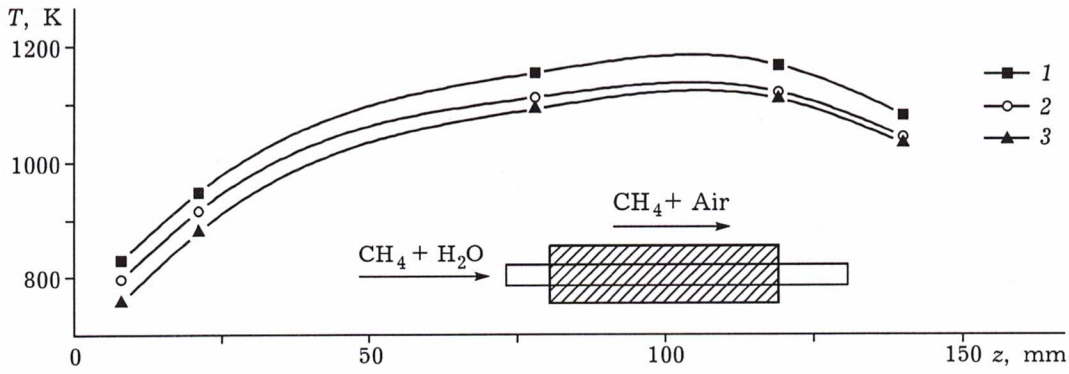

Fig. 7. Temperature profile in the combustion catalyst bed. Combustion of methane-hydrogen mixture with simultaneous steam reforming in heat-exchanging reactor: $C_0(CH_4)$, %: 27.5 (*1*), 38.5 (*2*), 47.8 (*3*); X_{CH_4}, %: 75 (*1*), 63.5 (*2*), 34 (*3*); V, $h^{-1} \cdot 10^{-3}$: 60 (*1*), 7.1 (*2*), 8.3 (*3*).

of the HEX tube and with Ni containing reforming catalyst on the internal Ni foam was successfully tested in methane combustion reaction combined with methane steam reforming (Fig. 7).

CONCLUSION

Some prospects of application of plasma spraying technique for the synthesis of supported catalysts are demonstrated. Plasma spraying technique successfully allows to synthesise the supported catalysts with enhanced catalytic activity properties and to improve the performance characteristics of combustion catalysts on metal supports during long term operation at high temperatures.

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