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Short communication

A catalytic heat-exchanging tubular reactor for combining of high temperature exothermic and endothermic reactions

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Abstract

A multifunctional catalytic heat-exchanging (HEX) tubular reactor for combining exothermic and endothermic reactions has been developed and tested for catalytic methane oxidation and methane steam reforming. The methane combustion and steam reforming catalysts were synthesized on the heat-conducting metal foam support materials by application of preliminary plasma spraying of alumina in order to increase adhesive properties of the active layer. The HEX rector with perovskite-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.

Keywords: Catalytic heat exchanging reactor; Methane combustion; Methane steam reforming

1. Introduction

Many of industrial chemical processes, such as methane steam reforming and methane pyrolysis are endothermic and consequently consume heat. The natural gas flame combustion is one of the main sources of thermal energy supply for these processes. The temperature of methane combustion flame is higher than 1500°C and it leads to substantial heat loss and high thermal NO_x emission. The promising way to solve problems of heat consumption efficiency and NO_x abatement is use of the catalytic heat exchangers. The catalytic heat exchanger composed with a combustion catalyst supported on the metallic foam on one side of the reactor wall provides a good heat transfer for another endothermic reaction proceeding on the other side of the wall; thus, preventing energy loss and giving low NO_x emission due to low temperature catalytic combustion.

Metal foam materials having unique structure are very attractive to be used as a catalyst support in the catalytic combustion. In this case, the problem of the preparation of catalytic coatings on metal surface with high adhesive and strong mechanical properties for durable exploitation at high temperatures appears, therefore, the new ways of synthesis are required. Plasma spray technique gives a good possibility to support oxide coatings on metal surfaces exhibiting high adhesive and mechanical characteristics. The application of plasma spray methods makes it possible to support both preliminary inert washcoats as well as catalytically active coatings.

Plasma spraying of washcoatings of alumina, titania, zirconia, etc. will allow one to solve successfully the problem of the adhesion of the active component to the metal surface and to protect the metal support substrates from aggressive medium and improve their durability for high temperature use. Moreover, the plasma spray method will give an opportunity to design composite materials consisting of various combinations of plasma-sprayed catalytic and protective layers.

Although plasma spray technique is well developed and in common use today, information on the application of these methods in catalysis is rather scarce. Traditionally, plasma spraying is used for development of dense, non-porous protective layers and it should be modified for application of this method in catalyst synthesis.

A number of papers have shown that the porous structure of sprayed coatings depends significantly on the jet outflow regime (laminar, transient or turbulent): the chemical composition and flow rate of the plasma-forming gas, the plasma torch power, the spraying distance, etc. For example, an

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increase of the plasma-forming gas flow rate and spraying distance leads to a growth of the porosity of the coating and this is accompanied by lower adhesion [1–3]. Changing the particle size of the powder sprayed also allows regulation of the physicochemical characteristics of the layers deposited: the phase composition, the porosity, the specific surface area and the thermal conductivity properties [4,5].

Therefore, successful application of the plasma spraying techniques for the synthesis of catalysts requires a comprehensive study of the influence of the various parameters of the plasma spraying and properties of the spraying materials on the coatings obtained.

The technique of plasma spraying of alumina on the metal foams was developed [6,7]. The prospects of the application of the plasma spraying technique for the preparation of the combustion catalysts on the metal foams were shown on the example of the synthesis of the perovskite containing catalyst. Intermediate alumina layer was formed by plasma spraying. The plasma sprayed alumina was then modified by La-containing γ-alumina, and La-Co perovskite catalyst was supported by an impregnation procedure.

The subject of this paper is the development of combustion catalyst on metal foams by plasma spraying to be used in catalytic heat exchangers for methane steam reforming and determination of its optimal operation parameters.

2. Experimental

Alumina powders differing in phase composition and particle size (α-Al_2O_3 20–80 mkm and γ-Al_2O_3 90–200 mkm) were used to spray an intermediate layer on titanium plates and Ni, Ni-Cr foam materials under laminar, transient and turbulent regimes of the plasma jet outflow (Fig. 1). The modification of the plasma-sprayed layer was provided by the deposition of lanthanum-containing γ-Al_2O_3 to increase the specific surface area of the intermediate layer. For comparison, the same catalyst on Ni foam support was prepared by direct deposition of a γ-Al_2O_3-containing washcoat on the metal surface by a chemical method without deposition of preliminary plasma-sprayed layer [8].

The X-ray analysis of the samples was carried out using a HZG-4 diffractometer with copper radiation in the 2θ range of 20–55°. To specify the parameters of the solid solutions and of the perovskite composition, the data were obtained in the range of 2θ of 62–72°. The specific surface areas of the samples were measured by the BET method and the pore volumes of the sprayed layers were calculated using the water capacity technique. The morphology of the catalysts was characterized by SEM (REM-100U, Russia).

A thermal cycling technique was used for investigation of the adhesion of the catalytic coating on the surface of the metal foam support. The experiments were performed as follows. First, a catalyst was heated to 900°C; then, it was dipped into water and dried in air. After drying, the operation was repeated. The number of thermal cycles needed for achievement of a stationary figure on the weight loss curve was used as criteria.

A metal foam heat-exchanging (HEX) reactor has been manufactured by placing the thermally stable high-permeable metal foam on both internal and external surfaces of the stainless steel metal tube: o.d. = 20 mm, i.d. = 18 mm (Fig. 2). The metal foams were prepared by duplication of a foamed polymer matrix, impregnated by metal salts with subsequent thermal treatment and reduction. The alumina was sprayed on external metal foam and perovskite (La-Co) combustion catalyst was deposited on this oxide layer by an impregnation or suspension technique. The methane reforming Ni-based catalyst was loaded from its slurry directly on the internal foam.

A laboratory set-up has been built for catalytic heat exchangers testing. A catalytic metal foam HEX tubular reactor was axially placed into a quartz tube (Fig. 3) insulated with rock wool to reduce heat loss. The mixture of fuel gas (methane and/or hydrogen) with air was injected into the external combustion catalyst of heat exchanger. A preheated steam–methane mixture with temperature 100–300°C was fed into the internal Ni-containing reforming catalyst.

The spatial temperature distribution in the reactor, in the combustion catalyst and the gas phase above it was measured with the aid of 10 chromel–alumel thermocouples, and two thermocouples were used to measure the inlet and outlet temperature of the reforming reactor. The H_2, CO, CH_4 and CO_2

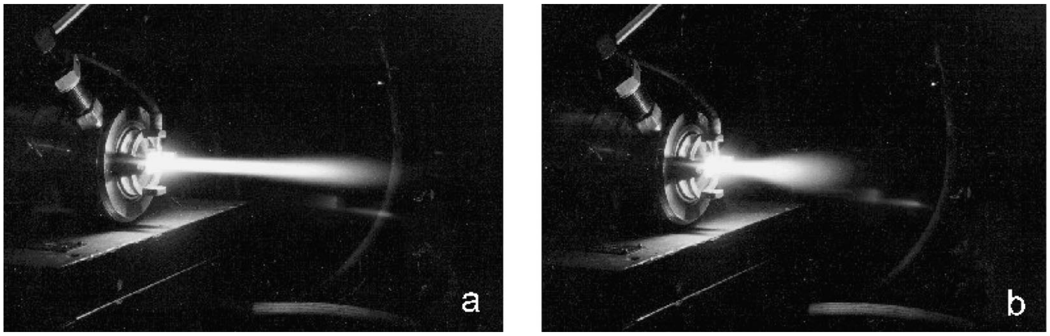

Fig. 1. Laminar (a) and turbulent (b) plasma jet outflow.

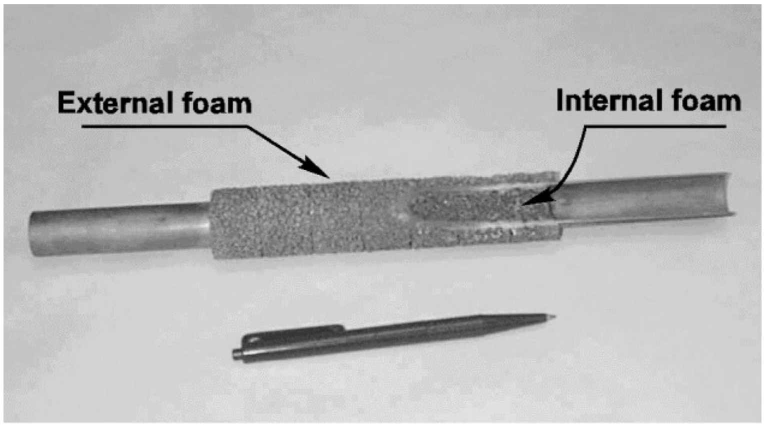

Fig. 2. Catalytic heat-exchanging reactor with metal foam deposited on the internal and external surfaces of a metal tube.

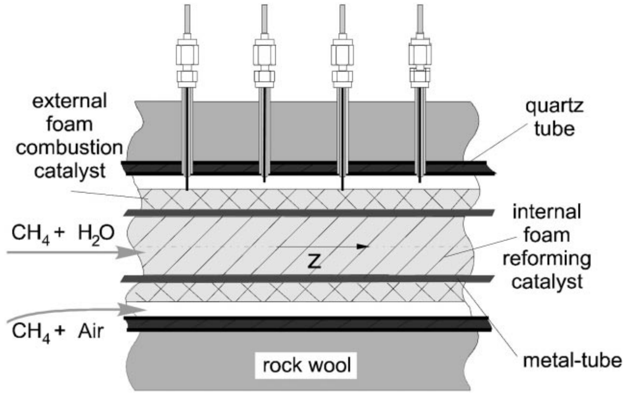

Fig. 3. Longitudinal section of the catalytic metal foam heat-exchanging reactor.

concentrations were measured with a gas-chromatograph equipped with TCD and column with activated carbon.

On the external surface of the catalytic heat-exchanger, the exothermic catalytic combustion of H_2 and/or CH_4 took place

$$CH_4 + 2O_2 = CO_2 + 2H_2O, \quad \Delta H = -802.28\,\mathrm{kJ\,mol^{-1}}$$

$$H_2 + \tfrac{1}{2}O_2 = H_2O, \quad \Delta H = -241.81\,\mathrm{kJ\,mol^{-1}}$$

Heat released in the above reactions transferred through the metal wall of the heat exchanger into the internal chamber, where it was consumed in the endothermic methane steam reforming process

$$CH_4 + H_2O = CO + 3H_2O, \quad \Delta H = 206.4\,\mathrm{kJ\,mol^{-1}}$$

3. Results and discussion

3.1. Study of the combustion catalyst on metal support synthesized by the application of plasma spraying of the intermediate layer

Experiments on the plasma spraying of alumina of different phase composition and particle size on titanium plates showed that the properties of plasma sprayed layers are quite similar and do not depend significantly on the jet outflow regime used (Table 1). When α-Al_2O_3 was sprayed on titanium plates, the coatings were characterized by a low specific surface area; meanwhile, their pore volume increased when the spraying regime was changed from laminar to turbulent. It was established that the dependence of the regime on the coating properties was the same when γ-Al_2O_3 was sprayed. Moreover, in the latter case, the spraying regime influenced the quantitative proportions of the α-Al_2O_3 and θ-Al_2O_3 phases of the coatings and their specific surface areas. The maximum porosity and minimum α-Al_2O_3 phase content were registered when a transient jet outflow regime was used. The low rates of hardening when

Table 1
Properties of alumina sprayed on Ti plates

Sprayed alumina	Particle size (mkm)	Regime	Specific surface area (m^2/g)	Phase composition	Pore volume (cm^3/g)
α-Al_2O_3	30	Laminar	0.2	α-Al_2O_3	0.052
α-Al_2O_3	30	Transient	0.2	α-Al_2O_3	0.065
α-Al_2O_3	30	Turbulent	0.2	α-Al_2O_3	0.167
γ-Al_2O_3	90–200	Laminar	0.2	α,θ-Al_2O_3	0.068
γ-Al_2O_3	90–200	Transient	0.4	α,θ-Al_2O_3	0.075
γ-Al_2O_3	90–200	Turbulent	0.6	α,θ-Al_2O_3	0.166

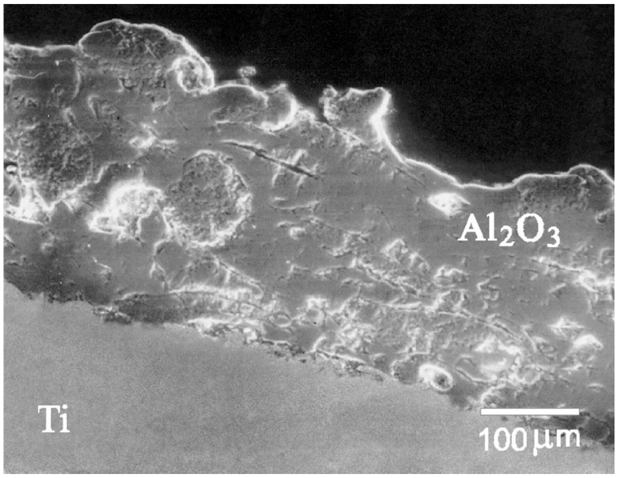

Fig. 4. Micrograph of cross-section view of Al_2O_3 plasma sprayed on metal surface.

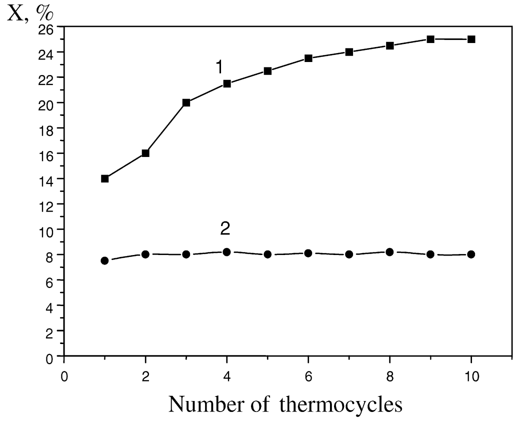

Fig. 5. Dependence of the catalyst weight loss on number of thermocycles, $X(\%) = (m_0 - m_n)/m_0$, where m_0 is initial catalyst weight, m_n the catalyst weight after n thermocycles: (1) $LaCoO_3$/La-γ-Al_2O_3/Ni-Cr foam; 2) $LaCoO_3$/La-γ-Al_2O_3/α-Al_2O_3/Ni-Cr foam, plasma sprayed α-Al_2O_3.

alumina was sprayed on metal surface lead to the transformation of γ-Al_2O_3 predominantly to the α-Al_2O_3 and θ-Al_2O_3 phases. When both γ-Al_2O_3 and α-Al_2O_3 were sprayed on Ti plates, the coatings were characterized by strong adhesive properties and had a complicated structure consisting of dense areas and macropores of different forms and sizes (Fig. 4). It is obvious that the contact between the alumina and the metal surface was rather strong and uniform.

The direct deposition of the active La-Co component on these supports led to the formation of $LaCoO_3$ and Co_3O_4 phases, as shown by XRD. The quantities of the supported active component did not exceed 2 wt.% because of the low porosity of the sprayed alumina layer. A modification of the sprayed layer by La-containing γ-Al_2O_3 allowed to increase this value by one order of magnitude. The phase composition of the modified catalyst after the deposition of the active La-Co component was more complex. Besides the presence of the $LaCoO_3$ and Co_3O_4 phases, minor quantities of $LaAlO_3$ perovskite and solid solutions based on γ-Al_2O_3 were registered. Increasing of La content in the modifying layer led to the decrease of the relative content of $LaAlO_3$ and the solid solution based on γ-alumina phases. Phase composition of the catalyst synthesized without preliminary spraying of intermediate alumina layer was identical to that described above. Thus, it can be concluded that presence of the plasma spayed alumina layer does not affect the genesis of the formation of the perovskite active component, catalyst phase composition depend only on the composition of the modifying layer. Meanwhile, the experiments on thermal cycling (Fig. 5) have revealed that the presence of the plasma sprayed alumina layer on the metal surface allows to improve substantially the adhesive properties of the active layer. It was found that in the catalyst prepared by a 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 minor loss of the active layer is observed only after the first thermocycle.

3.2. Testing of the metal foam catalytic heat exchanger in the steam reforming combined with catalytic combustion of methane and methane–hydrogen mixture

Experiments in the catalytic HEX reactor have been performed to determine the effectiveness of heat transfer and the parametric sensitivity of conditions of stable performance of catalytic combustion with simultaneous heat transfer to steam reforming. The following parameters were varied in the experiments: gas hour space velocity (GHSV), fuel concentration in gas, steam–methane mixture flow rate. The following values were obtained under observed steady state operation modes: the temperature profile along the combustion catalyst bed and the gas phase above it, inlet and outlet steam–methane mixture temperature, fuel conversion and composition of the outlet gases. Methane and methane–hydrogen mixture were used as a fuel. Before each experiment, the HEX reactor was preheated by introducing of air–methane–hydrogen mixture (5.5% CH_4, 10% H_2, 25,000 h^{-1}). When reactor temperature was reached the value of 750°C, the desired operational parameters were set.

3.2.1. The influence of the combustion catalyst layer thickness

The thickness of metal foam with a combustion catalyst on it is an important factor to stable operation of combustion reactor. The thickness of catalytic foam was varied in a range 2–5 mm in the experiments with the combustion of methane and methane–hydrogen mixtures. As it has been found, the thickness of catalytic foam <2.5 mm was

Table 2
Steam reforming of methane supported by catalytic combustion of methane in catalytic heat-exchanging reactor

Combustion zone of heat-exchanger	
Maximum catalyst temperature, T_{max} (°C)	1007
GHSV (20°C, 1 bar, h^{-1})	10000
CH_4 concentration, Co_{CH_4} (%)	6.0
CH_4 conversion, X_{CH_4} (%)	99.9
Adiabatic temperature rise, T_{ad} (K)	1400
Steam reforming zone	
GHSV (20°C, 1 bar, h^{-1})	7100
CH_4 concentration, Co_{CH_4} (%)	38.5
H_2O/CH_4 mole ratio	1.6
$T_{gas,in}$ (°C)	101
$T_{gas,out}$ (°C)	543
CH_4 conversion, X_{CH_4} (%)	50

Table 3
Steam reforming of methane supported by catalytic combustion of methane–hydrogen mixture in catalytic heat-exchanging reactor[a]

Combustion zone of heat-exchanger	
Maximum catalyst temperature, T_{max} (°C)	865
GHSV (20°C, 1 bar, h^{-1})	19200
CH_4 concentration, Co_{CH_4} (%)	6.1
H_2 concentration, Co_{H_2} (%)	9.7
CH_4 conversion, X_{CH_4} (%)	74.9
H_2 conversion, X_{H_2} (%)	97.6
Adiabatic temperature rise, T_{ad} (K)	1720
Steam reforming zone	
GHSV (20°C, 1 bar, h^{-1})	7100
CH_4 concentration, Co_{CH_4} (%)	38.5
H_2O/CH_4 mole ratio	1.6
$T_{gas,in}$ (°C)	265
$T_{gas,out}$ (°C)	723
CH_4 conversion, X_{CH_4} (%)	63.5

[a] Range of operation parameters.

insufficient for effective methane combustion in our experimental conditions, after preheating the temperature of catalytic layer dropped fast to the ambient temperature. As was found the optimal thickness of combustion catalyst layer is 4–5 mm.

3.2.2. The influence of composition of combustion gas

When methane was used for combustion the methane conversion in combustion reaction in the HEX reactors was close to 100% (Table 2). The temperature profile along HEX reactor was not uniform with a maximum 1037°C on the combustion catalyst. The efficiency of steam reforming was close to thermodynamic figure (conversion CH_4 50%) for the temperature profile attained in the internal reforming catalyst.

From literature survey it's known [9] that selectivity of the endothermic methane steam reforming reaction

$$CH_4 + H_2O = CO + 3H_2,$$
$$\Delta H = -206.4\,\mathrm{kJ\,mol^{-1}}\ \text{(main reaction)}$$

$$CO + H_2O = CO_2 + H_2,$$
$$\Delta H = 41.0\,\mathrm{kJ\,mol^{-1}}\ \text{(side reaction)}$$

is maximal at the temperature range 750–900°C and H_2O/CH_4 ratio equal 1.2–4. Therefore, in our experiments, we tried to maintain the temperature profile in combustion catalyst layer in this range.

Addition of certain amount of hydrogen to combustion mixture has a positive effect on to the steam reforming catalyst performance. The temperature profile in the combustion catalyst layer becomes more uniform in the range of 850–900°C (Fig. 6). Methane conversion in reforming

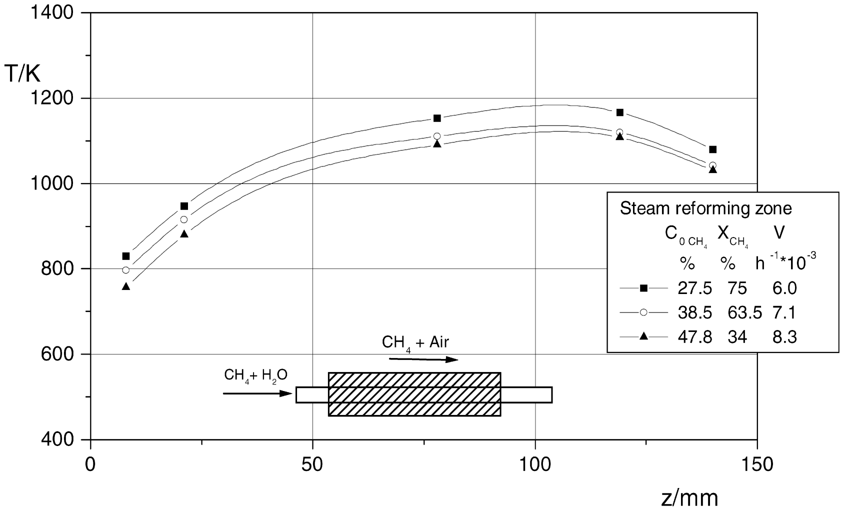

Fig. 6. Temperature profile in the combustion catalyst bed. Combustion of methane–hydrogen mixture with simultaneous steam reforming in heat-exchanging reactor.

section increases to 65% (Table 3) due to better uniformity of the temperature profile in the reforming catalyst as well.

4. Conclusion

The methane combustion catalyst of perovskite structure was synthesized on the heat-conducting Ni-Cr foam support materials by means of preliminary plasma spraying of alumina in order to increase adhesive properties of the active layer. It was shown that plasma sprayed alumina does not change the genesis of the formation of the perovskite active component but allows to improve substantially the adhesive properties of the active layer at high temperature.

This technique of catalyst preparation was used for development of tubular catalytic heat exchangers for combination: catalytic combustion of CH_4 and steam reforming of CH_4. The optimum stable operation of catalytic heat exchangers was obtained by the varification of the composition of the combustion mixture and thickness of the combustion catalyst layer.

Acknowledgements

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