

Thermostable Polyoxide Catalysts of Complete Combustion of Methane or Biogas in the Catalytic Heat Generators

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It is known that environmentally friendly flameless combustion of hydrocarbons without formation of nitrogen oxides is an important way to dispose of natural gas. In this regard, the development of energy-saving and environmentally friendly catalytic combustion technologies of light hydrocarbons for heating of greenhouses and using of formed CO₂ for additional fertilizing of plants is the aim of the present work. Polyoxide thermally stable (up to 1,473 K) highly efficient Ni-Cu-Cr and Mn-containing catalysts for complete oxidation of methane and propane-butane in vapour-air mixture have been developed. Prototype of catalytic heat generator was created for ecologically clean burning of methane and propane-butane. Pilot testing of catalytic heat generator for heating of greenhouses was conducted. Carbon dioxide fertilizing of plants was carried out.

1. Introduction

Methane is the main component of natural gas and biogas. Conversion of methane to more expensive fuels, useful chemicals and heat have been proposed to convert methane into hydrogen-rich gases on Ni-containing catalyst in membrane reactor (Kyriakides et al., 2013) or flow reactor (Corbo et al., 2009), olefins (Patcharavorachot et al., 2013), oxygenates (Yoon et al., 2012), and products of catalytic combustion (Buchneva et al., 2009). Flameless catalytic combustion of natural and oil gases without formation of nitrogen oxides is one of the most promising ways for utilization of methane and other alkanes to produce heat and carbon dioxide (Bhavsar et al., 2014). Catalytic combustion differs essentially from thermal combustion, as occurs selectively to CO₂ on the surface of solid catalysts without flame at significantly lower temperatures which avoids the formation of nitrogen oxides and other harmful substances.

Analysis of technical and patent literature indicates the use of several types of catalysts in oxidation of CH₄: noble metals (Pt, Pd) on carriers, spinels (Chenakin et al., 2014), oxide manganese-based catalysts on hexa-aluminate composites (Machida et al., 1995) or manganese catalyst with oxides of rare earth and alkaline-earth elements (Dossunov et al., 2009), as well as honeycomb catalysts (Landi et al., 2010).

Creation of energy-saving and environmentally friendly catalytic technologies for combustion of gaseous hydrocarbon fuel for heating of greenhouses and use of produced CO₂ for fertilizing of plants is the aim of work.

2. Experimental

New approaches to the synthesis of thermally stable multicomponent oxide catalysts were used for the development of catalysts for combustion of methane and propane-butane in heat generators. The rare earth elements (REE - La, Ce) and alkaline earth elements (AEE - Ba, Sr) were entered into the composition of supported polyoxide catalysts based on 3d metals (Ni, Cu, Cr, Mn) for the formation of perovskite-like structures and spinels on the surface. The granulated θ -Al₂O₃ (S = 100 m²/g) modified with cerium, which forms resistant surface CeAlO₃ perovskite up to 1,373 K was used as a carrier. The oxide

catalysts have been promoted with platinum and palladium (0.05 %) to improve the activity and thermal stability.

Catalysts were prepared by capillary impregnation of alumina by mixed aqueous solution of nitrates by incipient wetness, followed by drying at 453 - 473 K (4 - 5 h) and calcination at 873 K (1 - 1.5 h) in air. Activity of catalysts was determined at oxidation of methane by air in flow installation at 673-973 K. Investigation of deep oxidation of CH₄ (0.5-4 %) on catalysts was carried out by varying the space velocity from 10×10³ h⁻¹ to 20×10³ h⁻¹ and the O₂ concentration from 2 % to 20 %.

The layering method of prepared catalyst using aluminum oxynitrate as a binding agent (15-20 % by weight relative to the deposited catalyst) was used at preparation of MnREEAEE/Ce/θ-Al₂O₃ catalyst for combustion of methane and propane-butane mixture. Blocks from the α-Al₂O₃ (diameter = 15 mm, height = 20 mm, the number of holes per 1 cm² = 30) were used as the primary carrier.

3. Results and Discussion

3.1 Oxidation of 0.5% CH₄ on the Ni-Cu-Cr and MnREEAEE catalysts supported on 2 % Ce/θ-Al₂O₃

Table 1 presents the data obtained at the oxidation of 0.5 % CH₄ in air at GHSV = 10×10³ h⁻¹ on the synthesized catalysts after heating at 873 K and 1,473 K. It can be seen, the initial contacts allow to obtain 85-99 % conversion at 973 K after heating of catalysts at 873 K for 1 h. Catalysts heated at 873 K for 1 h can be arranged in series according to the degree of oxidation at 973 K: AP-56 (100 %), NiCuCr + Pd (99 %), NiCuCr + Pt (96 %), MnREEAEE/2 % Ce/θ-Al₂O₃ (92 %), NiCuCr/2 % Ce/θ-Al₂O₃ (91 %), MnREEAEE + Pd (90 %), MnREEAEE + Pt (85 %). Contact based on Ni-Cu-Cr/2 % Ce/θ-Al₂O₃ is the most effective catalyst for oxidation of methane at 973 K. This catalyst is similar to the known industrial Pt contact AP-56 (0.56 % Pt).

Table 1: Oxidation of 0.5 % CH₄ at GHSV = 10×10³ h⁻¹ in air at 773 K and 973 K after heating at 873 K and 1,473 K

Catalyst	Active phase (wt%)	α _{CH₄} after heating at 873 K / 1,473 K (%)		S (m ² /g) before and after heating
		773 K	973 K	
MnREEAEE	7.0	39 / 14	92 / 88	62.9 / 3.1
MnREEAEE + Pd	7.5	31 / 16	90 / 81	56.4 / 3.6
MnREEAEE + Pt	7.6	40 / 17	85 / 86	51.1 / 2.8
AP-56 (0.56 % Pt)	0.6	54 / 10	100 / 60	119.6 / 2.9
NiCuCr	9.0	38 / 0	91 / 63	61.3 / 2.2
NiCuCr + Pd	9.5	45 / 0	99 / 58	60.0 / 2.1
NiCuCr + Pt	9.5	50 / 12	96 / 62	53.5 / 2.2

Synthesized contacts were heated in air at 873 K for 1 h, then sequentially at 1,073 K, 1,273 K, 1,373 K and 1,473 K for 5 h at each temperature due to the fact that catalysts may be subjected to significant overheating (1,473 K) and lose activity during combustion of CH₄.

Heating at high temperatures affects in different ways on the degree of oxidation of CH₄ on different catalysts. The Table 1 shows that heating of catalysts at 1,473 K resulted in a significant decrease in the surface of catalysts. High temperature heating had no negative effect on the degree of oxidation of CH₄ on MnREEAEE catalysts up to 1,373 K. Slight decrease in the degree of conversion of CH₄ (not more than 10 %) was observed only in the case of heating at 1,473 K in contrast to Pt/Al₂O₃ (AP-56) catalyst the efficiency of which dramatically decreased after 1,373 K. As a result, α_{CH₄} reached 60 % at 973 K and only 10 % - at 773 K. The activity of MnREEAEE catalyst decreased slightly for the initial and heated samples at 973 K (not more than 2-7 %). A sharp decrease in the degree of conversion of methane occurred after heating starting from 1,373 K and especially at 1,473 K for Ni-Cu-Cr catalyst. It reached 63 % at 973 K and decreased to "zero" at 773 K. Specific oxidation rate of methane remains constant for MnREEAEE catalyst even as result of heating at 1373-1473 K in contrast to Ni-Cu-Cr catalyst (Figure 1).

It has been shown that MnREEAEE/2 % Ce/θ-Al₂O₃ catalyst is the most thermally stable up to 1,473 K in comparative studies of oxide catalysts for the combustion of methane to CO₂. It provided 88-92 % methane oxidation at 973 K and a GHSV of 10×10³ h⁻¹.

Investigation the changes in phase and surface composition of the MnREEAEE/2 % Ce/θ-Al₂O₃ catalyst during heating, and analysis of the adsorption properties towards oxygen using XRD (Grigoriyeva et al., 2002), TEM (Komashko et al., 2002), BET, ESDR (Popova et al., 2000), TPD, TPR, TPO (Popova et al., 2001) were conducted to determine the causes of thermal stability.

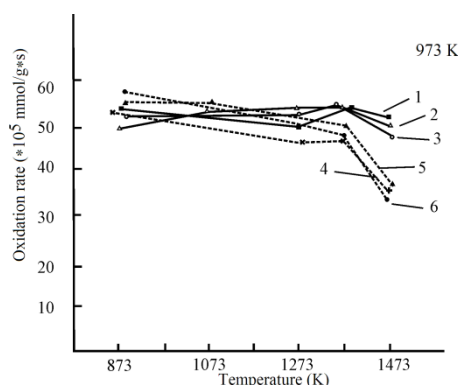


Figure 1: Effect of the heating temperature on oxidation rate of methane in air on catalysts supported on 2% Ce/ θ -Al₂O₃ (1 - MnREEAEE, 2 - MnREEAEE + Pt, 3 - MnREEAEE + Pd, 4 - NiCuCr, 5 - NiCuCr + Pt, 6 - NiCuCr + Pd)

3.2 Oxidation of methane and propane-butane on the granulated MnREEAEE/2 % Ce/ θ -Al₂O₃ catalyst

Identification of technological process conditions (space velocity, concentration of reactants, temperature of the heating of catalyst), which affect on performance of process at different temperatures, have great importance in deep oxidation of CH₄ to CO₂ for industrial purposes (receiving of heat, cleaning of ventilation gases of coal mines from CH₄, creating an atmosphere for storage of agricultural products, using of CO₂ for fertilizing of plants). Effect of the CH₄ and O₂ concentrations to completeness conversion of CH₄ to CO₂ on the 7 % MnREEAEE/2 % Ce/ θ -Al₂O₃ catalyst at GHSV = $10 \times 10^3 \text{ h}^{-1}$ is shown in Figure 2. 90-92 % conversion of methane is provided at 973 K at methane concentrations from 0.5 % to 4 %, and oxygen concentrations from 2 % to 20 %. Change in the concentration of CH₄ in initial mixture in the range of 0.5-4 % have a little effect to completeness of CH₄ oxidation into carbon dioxide at 873-973 K (α_{CH_4} is changed to 4-7 %, and at 823 K - to 5-12 %). The observed degrees of CH₄ conversion are close to reported in the work (Chimino et al., 2000) on the LaMnO₃/La- γ -Al₂O₃ catalyst at 773-823 K at varying of reagents concentrations.

Thus, the study of influence of process parameters on degree of CH₄ conversion on the most thermally stable 7 % MnREEAEE catalyst supported on 2 % Ce/ θ -Al₂O₃ has shown that contact provides 90-92 % oxidation by varying the oxygen concentration from 2.0 % to 20.0 %, CH₄ - from 0.5 % to 4.0 % at space velocity $10 \times 10^3 \text{ h}^{-1}$ at a temperature of 973 K.

Comparison of data on the activity of granulated Mn catalyst on θ -Al₂O₃ in oxidation of CH₄ (Table 2) and hydrocarbon mixtures (Table 3) indicates on a more light oxidation of propane-butane in comparison with methane: reduction of temperatures of the beginning of oxidation and $\alpha = 90 \%$ on 160 and (180) - 270 (300) K are observed.

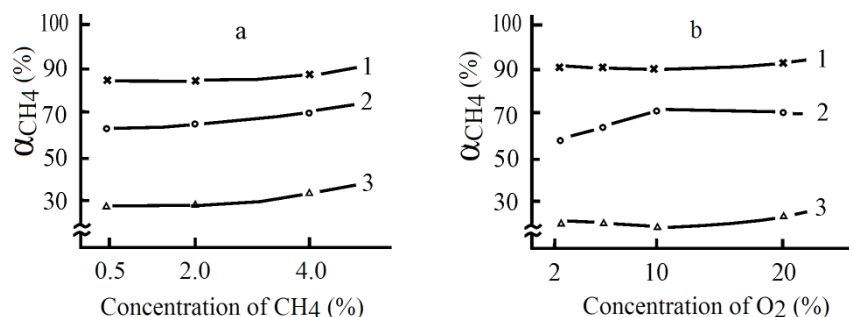


Figure 2: Influence of the concentration of methane (a) and oxygen (b) on degree of CH₄ conversion to CO₂ on the MnREEAEE/2 % Ce/ θ -Al₂O₃ at GHSV = $10 \times 10^3 \text{ h}^{-1}$ (1 - 973 K, 2 - 923 K, 3 - 873 K)

Table 2: Oxidation of methane in air

Catalyst	The degree of conversion (%)	Temperature (K)
MnREEAEE/2 % Ce/ θ -Al ₂ O ₃	20-30	733
	90	943
MnREEAEE/2 % Ce/ θ -Al ₂ O ₃ +Pt (0.1 %)	20-30	753
	90	973

Table 3: Oxidation of propane-butane mixture in air

Catalyst	The degree of conversion (%)	Temperature (K)
MnREEAEE/2 % Ce/ θ -Al ₂ O ₃	20-30	< 573
	90	673
MnREEAEE/2 % Ce/ θ -Al ₂ O ₃ +Pt (0.1 %)	20-30	573
	90	673

3.3 Oxidation of methane and propane-butane on the MnREEAEE/2 % Ce/ θ -Al₂O₃ on porous blocks from the α -Al₂O₃

The degree of oxidation of methane in air on all catalysts increases with increasing concentration of CH₄ from 0.5 % to 1.0 % and temperatures from 623 K to 873 K. The degree of CH₄ oxidation is increased to 97-100 % at 773-873 K and variation of methane concentration from 0.5 % to 1.0 % on supported MnREEAEE/2 % Ce/ θ -Al₂O₃ catalyst (from 7.5 % to 20.0 %) on the blocks. 7.5 % Mn catalysts supported on granular carriers provide 97-100 % oxidation of CH₄ (0.5-2.0 %) at T = 943-973 K. However, a similar degree of oxidation is achieved at 873 K after supporting of catalyst on block from α -Al₂O₃, which is lower by 100-130 K despite the reduction of the total concentration of catalyst. α_{CH_4} = 97-100 % is achieved on the 7.5 % Mn-catalyst supported on the granular carrier at a deep oxidation of 0.5-2.0 % propane-butane mixture at 773-873 K as well as on the 7.5 % Mn-catalyst supported on the block from α -Al₂O₃ (Table 4).

Table 4: Oxidation of 1 % CH₄ in air on MnREEAEE/2 % Ce/ θ -Al₂O₃ supported on the block from α -Al₂O₃ at GHSV = 10×10³ h⁻¹

Concentration of MnREEAEE/2 % Ce/ θ -Al ₂ O ₃ (%)	The degree of CH ₄ oxidation (%) at various temperatures (K)				
	573	623	673	773	873
7.0	0	43	90	93	100
15.0	10	54	94	97	100
20.0	15	54	95	98	97

The obtained results indicate on more rational application of 15-20 % MnREEAEE/2 % Ce/ θ -Al₂O₃ catalyst after supporting it on porous block in the amount of 15.9-16.8 % during combustion of methane or propane-butane mixture. At the same time 97-100 % oxidation of hydrocarbons is provided at lower temperature (on the 100 K) than on the granules at reduction of catalyst consumption approximately 6 times. This is due to the greater development of the catalyst surface in the form of a film on the block from α -Al₂O₃, than when fully impregnating of Al₂O₃ granules (Table 5 and Table 6).

Table 5: Oxidation of CH₄ and propane-butane mixture by air at GHSV = 10×10³ h⁻¹ on granulated MnREEAEE/2 % Ce/ θ -Al₂O₃ catalyst

Oxide content in catalyst (%)	Concentration (%)		Temperature (K)
	CH ₄	C ₃ H ₈ + C ₄ H ₁₀	
7.5	0.5 – 2.0	-	943 - 973
7.5	-	0.5 – 2.0	773 - 873

Mn-containing catalysts supported on a metal block carriers have been tested in the combustion of propane-butane mixture. The catalysts supported on block metal supports were made from heat-resistant steel such as "federal" with a thickness of 40 μ m. Density of the longitudinal channels - 45 cells per 1 cm². Open cross sections of carrier - (90 \pm 2) %, height the corrugations - (1.7 \pm 0.2) mm. The secondary carrier on the base of aluminum oxide with heat stabilizing additives is supported on the surface of each side of the foil of metal frame with a thickness of 10 μ m. The active phase is supported from aqueous-salt solutions by impregnating of blocks with subsequent drying and calcination. The content of metal oxides supported on block metal support is ~ 5 wt%.

Table 6: Oxidation of CH₄ and propane-butane mixture by air at GHSV = 10×10³ h⁻¹ on MnREEAEE/2 % Ce/θ-Al₂O₃ catalyst supported on block from α-Al₂O₃

Oxide content in catalyst (%)	Concentration (%)		Temperature (K)
	CH ₄	C ₃ H ₈ + C ₄ H ₁₀	
7.5	-	0.5	773 - 873
15.0	-	0.5 – 3.0	773
20.0	-	0.5 – 1.0	773

Research has shown that the temperature - 623 K, space velocity – 10,000 h⁻¹ and concentration of propane-butane mixture in air – 2 % are optimal operating conditions of the Mn-containing oxide catalyst on metal carrier. Under these conditions, the catalyst passes to the auto-thermal operation and temperature of the air-gas mixture leaving the reactor reaches 873-923 K. The process can be carried out automatically at a space velocity of 5,000 h⁻¹ by increasing hydrocarbon concentrations up to 3 %.

It should be noted that biogas consisting of a CH₄ and CO₂ was also tested in catalytic heat generator on MnREEAEE/2 % Ce/θ-Al₂O₃ supported on the block from α-Al₂O₃ with W = 10×10³ h⁻¹. It has been shown that degree of methane oxidation was lower by 10-12% compared with the initial mixture without CO₂. However, the biogas can also be successfully used for this purpose, especially in farms where there is its production.

The above optimal operating conditions of the catalytic heat generator were recommended for flameless combustion of propane-butane mixture used for heating of greenhouse with an area of 100-120 m².

3.4 Test of heat generator efficiency

Experienced heat generator was designed to test the block (or granular) catalysts having a diameter of 68 mm and a length of 150 mm in the catalytic combustion of methane of natural gas, or propane-butane mixture. It represents the cylindrical stainless steel tube with an inner diameter of 70 mm. Fittings for supply of air, natural gas and mixtures as well as the mixer were installed in the front. Combustion chamber with catalyst has been installed downstream of the gas stream. The combustion chamber is equipped with connections for gas sampling for analysis and measuring the temperature at the inlet and outlet of catalyst. The combustion chamber was provided with an external electric heater in the form of winding of nichrome wire with refractory electrically insulating plaster, which is covered with the insulating layer from asbestos for heating the catalyst up to ignition temperature.

Rated power of the reactor - 25 kW. Gas consumption - up to 2.4 nm³/h. Air flow - up to 25 nm³/h.

The test of heat generator for the implementation of additional fertilizing of plants with carbon dioxide was performed in the experimental compartment of greenhouse using of plants the following crops: cucumbers, tomatoes, beans, radish, carrots, lettuce, dill, and barley. Plants that were grown in isolated compartment of greenhouse, heated by electric heaters and served as controls. Plants were grown in pots in the four or five-fold replicates. All plants were grown under the same conditions outside of greenhouse before the heating season. In late of September, the containers with plants were placed in a greenhouse, when the temperature in the greenhouse during the day under the influence of solar radiation does not exceed the permissible levels for plant growth. The results of dynamics of the content of CO₂ in the experimental and control compartments of greenhouse are shown in Figure 3.

Increased content of carbon dioxide in atmosphere of greenhouse had a beneficial effect on plants grown. Significant differences with the control were obtained for plants, which intensively accumulated its mass, despite the relatively short test period (61 days). Wet weight of the aboveground parts of plants obtained in the experimental compartment, exceeded the control by 5.7 - 24.5 %, and the dry weight - by 7.1 - 35.8 %. Tested culture reacted differently to carbon dioxide fertilizing. The greatest increase in dry weight was obtained for cucumbers and radishes (by 30.8 - 35.8 %), while the lowest - for barley.

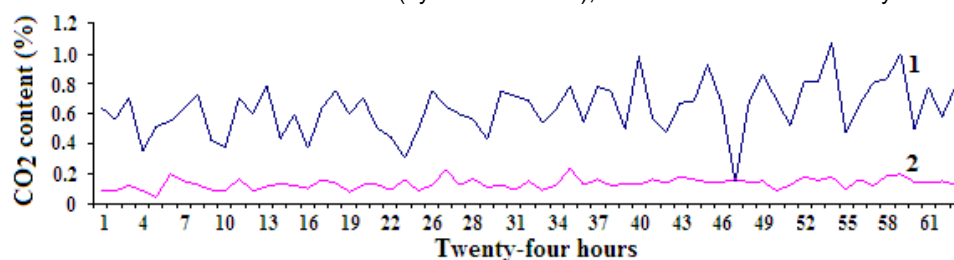


Figure 3: Dynamics of the content of CO₂ in the greenhouse atmosphere (1 – test, 2 - control)

Roots were also more weighty in the experimental compartment of greenhouse. In this case the plants, forming roots (carrots and radishes), were the most receptive to the carbon dioxide fertilizing. Exceeding the weight of roots reached 30.7 - 35.6 %. Tomatoes and cucumbers that are most reacted to carbon dioxide fertilization form a dry mass to a greater extent than, for example, barley. Barley yield increase was absent.

Thus, the catalytic heat generator can be used in greenhouses for providing heat and carbon dioxide simultaneously. Using of heat generator to feed plants with carbon dioxide in greenhouses promotes increase their productivity, increasing the yield of different crops to 5 – 7 %.

4. Conclusion

It was established that MnREEAEE catalyst supported on 2 % Ce/ θ -Al₂O₃ has a higher thermal stability (up to 1,473 K) and specific activity in the reaction of deep oxidation of methane, compared to known catalysts (IC-40 and Ni-Cu-Cr/2 % Ce/ θ -Al₂O₃) which are used for purification of gases from organic substances and combustion of CH₄.

The results indicate the real possibility of practical use of thermally stable up to 1,473 K MnREEAEE/2 % Ce/ θ -Al₂O₃ catalyst for utilization of lean mixtures of CH₄ in catalytic heat generators. The developed catalyst does not concede to known analogues both in activity and thermal stability, where perovskites and manganese hexaaluminates were used.

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