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Heat Generation in the Catalytic Combustion of Light Hydrocarbons

Svetlana A. Tungatarova*, Zauresh T. Zheksenbaeva, Tolkyn S. Baizhumanova, Valentina P. Grigoriyeva, Rabiga O. Sarsenova

D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry, 142 Kunaev str., 050010, Almaty, Kazakhstan
tungatarova58@mail.ru

Data on the study of thermally stable (up to 1,473 K) manganese oxide catalysts for deep oxidation of lean CH_4 and propane-butane mixtures are presented. New approaches to the synthesis of polyoxide catalysts based on Mn, modified with rare earth elements (La, Ce) and alkaline earth elements (Ba, Sr) when its supporting onto the alumina granules stabilized with 2 % Ce were used. It was shown by BET, XRD and TEM methods that the Mn catalyst contains crystalline CeO_2 and nanoparticles of Mn_2O_3 (d = 30 - 40 Ǻ), the amount of which decreases by heating to 1,173 K through a partial interaction with rare earth elements with the formation of $La(Ce)MnO_3$, $CeAlO_3$, then $LaMnAl_{11}O_{19}$ hexaaluminate at 1,273 – 1,473 K. The aim of the work is the development of active polyoxide Mn catalysts for deep oxidation of poor methane and propane-butane mixtures to CO_2 for use in catalytic heat generators, solving environmental problems and studying the thermal stability of the developed catalysts.

1. Introduction

Gaseous hydrocarbons (methane, ethane, and propane) have particular importance among the organic fuels. They are mainly used in the form of household and motor fuel or burned in the composition of waste gas in the "torch". Each year, approximately 403 million m^3 of dilute gases (0.5 - 1.0 % CH_4) of coal mines in Kazakhstan is released into the atmosphere without processing. In this case, a potential source of energy is lost and ozone layer of the Earth is destroyed (Popova et al., 2006). The problem of their efficient processing and optimal use for various technological purposes (production of heat and electricity, as well as organic synthesis) is relevant (Bayle et al., 2016).

The catalytic oxidation of CH_4 to CO_2 for the production of heat is a promising method for utilization of mine, ventilating and flared methane. Calculate the cost of heat produced during deep combustion of methane in pilot plant have shown that it is below the cost of coal-fired boiler heat. Catalytic combustion is fundamentally different from thermal combustion, as it occurs on the surface of solid catalysts without flame formation selectively to CO_2 at much lower temperatures, which eliminates the formation of nitrogen oxides and other harmful substances. Most known oxide and mixed catalysts, except for hexaaluminate, do not withstand high temperatures (up to 1,473 K) when methane is burned in heat generators and gas turbines due to their interaction with carriers (Dossumov and Popova, 2009).

The development of catalysts for the complete combustion of CH_4, aimed on increasing the thermal stability of oxide contacts due to the modification of carriers (Baizhumanova et al., 2016) by the synthesis of perovskites and hexaaluminates becomes particularly urgent (Landi et al., 2010). The purpose of this paper is to develop active polyoxide Mn catalysts for deep oxidation of poor methane and propane-butane mixtures to CO_2 for use in catalytic heat generators and to study their thermal stability.

2. Experimental

2.1 Catalysts preparation

New approaches to the synthesis of thermally stable multicomponent oxide catalysts were used for the development of catalysts for combustion of CH_4 and C_3H_8-C_4H_{10} in heat generators. The rare earth elements

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(REE - La, Ce) and alkaline earth elements (AEE - Ba, Sr) were added 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 total amount of oxides – 7.5, 15, 20 %). The granulated θ-Al_2O_3 (S = 100 m^2/g, particle size between 40 and 50 μm) modified by Ce, which forms resistant surface $CeAlO_3$ perovskite up to 1,373 K was used as a carrier. Catalysts were prepared by capillary impregnation of Al_2O_3 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. The prepared oxide catalysts have been promoted with Pt and Pd (0.05 %) to improve the activity and thermal stability.

Microspherical MnREEAEE/Ce/θ-Al_2O_3 catalysts were supported on ceramic block carriers of the honeycomb structure (d = 15 mm; h = 20 mm, 30 holes per 1 cm^2, wall thickness 0.5 mm). The essence of the process was layering of prepared catalyst by using of aluminum oxynitrate as the binder (15 – 20 % by weight with respect to the supported catalyst) in several stages.

2.2 Experimental

Experiments were carried out on flow type installation at atmospheric pressure in tubular quartz reactor with fixed catalyst bed. Catalyst was placed in the central part of reactor and quartz wool placed above and below the catalyst bed. Temperature was measured by a thermocouple inserted in a jacket of the reactor. Activity of catalysts was determined at oxidation of CH_4 by air at 673 - 973 K. Investigation of deep oxidation of CH_4 (0.5 - 4 %) on catalysts was carried out by varying the space velocity from 10×10^3 h^{-1} to 20×10^3 h^{-1} and the O_2 concentration from 2 % to 20 %.

Deep oxidation was carried out on the PKU-2VD catalytic installation. Analysis of the initial mixture and reaction products were carried out using CHROMOS GC-1000 chromatograph with CHROMOS software. The temperature of thermal conductivity detector – 473 K, evaporator temperature – 553 K, column temperature - 313 K. The rate of carrier gas Ar - 10 mL/min.

3. Results and discussion

3.1 Oxidation of 0.5 % CH_4 in air on MnREEAEE catalysts by 2 % Ce/θ-Al_2O_3

Table 1 presents the data obtained during the oxidation of 0.5 % CH_4 in air at GHSV = 10×10^3 h^{-1} at the studied contacts before and after heating at 1,473 K. The initial contacts ($T_{heating}$ = 873 K) at 973 K provide the conversion of CH_4 up to 85 – 100 %. The initial catalysts ($T_{heating}$ = 873 K) can be arranged in a series according to the oxidation degree at 973 K: AP-56 (100 %), MnREEAEE (92 %), MnREEAEE + Pd (90 %), MnREEAEE + Pt (85 %), where AEE - alkaline-earth elements, REE - rare-earth elements.

Table 1: Oxidation of 0.5 % CH_4 on MnREEAEE and NiCuCr supported on 2 % Ce/θ-Al_2O_3 catalysts at GHSV = 10×10^3 h^{-1} in air at 973 and 773 K before and after heating at 1,473 K

Catalyst	Active phase, %	α_{CH4} before and after heating at 1,473 K 973 K	773 K	S, m^2/g before and after heating
MnREEAEE	7.90	92/88	39/14	62.9/3.1
MnREEAEE +Pd	7.50	90/81	31/16	56.4/3.6
MnREEAEE +Pt	7.60	85/86	40/17	51.1/2.8
AP-56 (0.56 % Pt)	0.56	100/60	54/14	119.6/2.9

Heating at high temperatures (up to 1,473 K) affects differently the degree of oxidation of CH_4 on different catalysts. It can be seen from Table 1 that the heating of catalysts at 1,473 K led to significant decrease in the surface area of all catalysts. Heating did not affect the degree of oxidation of CH_4 on MnREEAEE catalysts up to 1,373 K. Only at $T_{heating}$ = 1,473 K there was insignificant decrease in α_{CH4} (maximum by 10 %) in contrast to Pt/Al_2O_3 (AP-56) contact, the efficiency of which decreased sharply, especially above 1,373 K, as a result of which α_{CH4} reached 60 % at 973 K and only 14 % at 773 K. Additions of Pt and Pd to the MnREEAEE catalyst slightly change the properties of the MnREEAEE. In a comparative study of oxide catalysts for combustion of CH_4 to CO_2 has been shown that the Mn catalyst (with Ba, Sr, La, Ce additives) supported on granulated θ-Al_2O_3 stabilized by Ce is the most thermally stable up to 1,473 K. It provides 92 % oxidation of CH_4 at 973 K and space velocity of 10×10^3 h^{-1}.

3.2 Oxidation of methane on the granulated MnREEAEE/2 % Ce/θ-Al_2O_3 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 CH_4 to CO_2 for industrial purposes (receiving of heat, cleaning of ventilation gases of coal mines from CH_4, creating an atmosphere for storage of agricultural products, using of CO_2 for fertilizing of plants). Effect of the CH_4 and O_2 concentrations to completeness conversion of CH_4 to CO_2 on the

7.5 % MnREEAEE/2 % Ce/θ-Al_2O_3 catalyst at GHSV = 10×10^3 h^{-1} is shown in Figure 1. 90 - 92 % conversion of CH_4 is provided at 973 K at CH_4 concentrations from 0.5 % to 4 %, and O_2 concentrations from 2 % to 20 % (Tungatarova et al., 2014). Change in the concentration of CH_4 in initial mixture in the range of 0.5 - 4 % have a little effect to completeness of CH_4 oxidation into CO_2 at 873 - 973 K (α_{CH4} is changed to 4 - 7 %, and at 823 K - to 5 - 12 %).

Thus, the study of influence of process parameters on degree of CH_4 conversion on the most thermally stable 7.5 % MnREEAEE catalyst supported on 2 % Ce/θ-Al_2O_3 has shown that contact provides 90 - 92 % oxidation by varying the O_2 concentration from 2.0 % to 20.0 %, CH_4 - from 0.5 % to 4.0 % at space velocity 10×10^3 h^{-1} at temperature of 973 K.

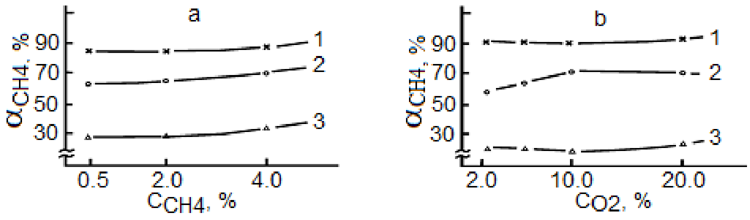

Figure 1: Influence of the concentration of CH_4 (a) and O_2 (b) on degree of CH_4 conversion to CO_2 on the MnREEAEE/2 % Ce/θ-Al_2O_3 at GHSV = 10×10^3 h^{-1} (1 – 973 K, 2 – 923 K, 3 - 873 K

3.3 Oxidation 0.5 % propane-butane in air at GHSV = 10×10^3 h^{-1} on the MnREEAEE and MnREEAEE (0.1 % Pt) catalysts

Investigation of the oxidation of 0.5 % C_3H_8 - C_4H_{10} mixture (C_3H_8 – 87 %, C_4H_{10} – 13 %) was carried out by varying the temperature and concentration of hydrocarbons and O_2 at 10×10^3 h^{-1} on MnREEAEE/2 % Ce/θ-Al_2O_3 at promotion of catalyst by Pt before and after heating for 25 h in air at 1,373 K. The mixture of C_3H_8 - C_4H_{10} begins to oxidize at 573 K (25 – 30 %) and completely (98 – 100 %) at 773 – 873 K. The addition of Pt to the Mn catalyst and its heating at 1,373 K did not have a significant effect on their activity (Table 2).

Table 2: Oxidation of a mixture of 0.5 % propane-butane in air at GHSV = 10×10^3 h^{-1} on MnREEAEE and MnREEAEE (0.1 % Pt) catalysts

Catalyst	$T_{heating}$, K	α_{C3-C4},%			
		573 K	673 K	773 K	873 K
MnREEAEE/2 % Ce/θ-Al_2O_3	873 K (initial)	49	92	98	~100
MnREEAEE/2 % Ce/θ-Al_2O_3	1,373 K (25 h)	41	88	98	100
MnREEAEE/2 % Ce/θ-Al_2O_3 with the addition of 0.1 % Pt	873 K (initial)	23	88	96	99
MnREEAEE/2 % Ce/θ-Al_2O_3 with the addition of 0.1 % Pt	1,073 K (5 h)	36	87	100	100
MnREEAEE/2 % Ce/θ-Al_2O_3	1,373 K (25 h)	29	89	100	100

Obtained results indicate the high activity of the initial MnREEAEE catalyst without and with the addition of Pt and its greater thermal stability (up to 1,473 K) during the combustion of CH_4 and C_3H_8 - C_4H_{10} mixture. Effect of the concentration of C_3H_8 + C_4H_{10} hydrocarbons in mixture with O_2 on oxidation process is shown in Figure 2. Figure 2a shows that increase in the concentration of C_3H_8 + C_4H_{10} mixture from 0.5 to 2.0 % almost does not cause decrease in the degree of conversion (by 5 %), which is 85 – 100 % at 673 – 873 K. Change in O_2 content in the mixture has a more significant effect on the oxidation process of 0.5 % (C_3H_8 + C_4H_{10}) (Figure 2b). The degree of hydrocarbon oxidation is low (17 – 45 %) at 2 – 5 % O_2 and sharply increases to 70 – 95 – 100 % with a content of 10 – 12 % O_2, when a large excess of O_2 is present in the gas phase. Comparison of data on the activity of granulated Mn catalyst on θ-Al_2O_3 in oxidation of CH_4 (Table 2) and hydrocarbon mixtures (Table 3) indicates on a lighter oxidation of C_3H_8 - C_4H_{10} in comparison with CH_4: reduction of temperatures of the beginning of oxidation and α = 90 % on 160 and (180) - 270 (300) K are observed.

The study of influence of technological parameters of the CH_4 and C_3H_8 - C_4H_{10} combustion on 7.5 % MnREEAEE catalyst supported on 2 % Ce/θ-Al_2O_3 showed that the catalyst provides 98 – 100 % oxidation at 973 K and O_2 concentration variation from 2 to 20 %, CH_4 - from 0.2 to 4.0 % at GHSV = 10×10^3 h^{-1}. Complete oxidation of the C_3H_8 - C_4H_{10} mixture proceeds at temperatures lower (by 300 K) than CH_4 (Table 3). MnREEAEE catalyst was thermally stable up to 1,373 – 1,473 K for the oxidation of both hydrocarbons.

Promotion of the catalyst with Pd and Pt traces does not significantly affect the efficiency of catalyst both in the oxidation of CH_4 and C_3H_8 - C_4H_{10}.

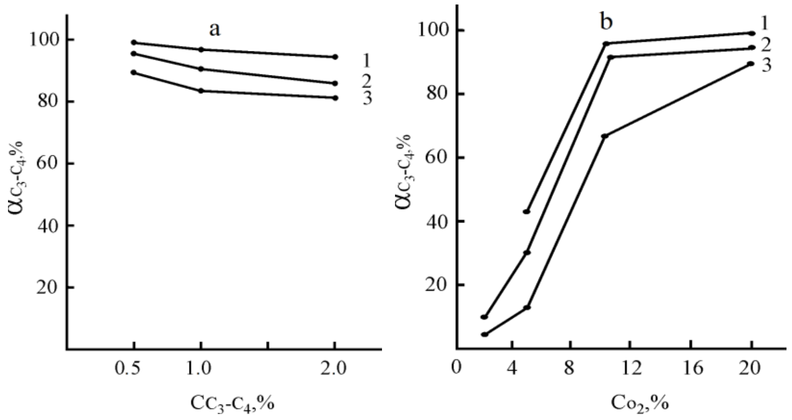

Figure 2: Influence of the C_3H_8 + C_4H_{10} (a) and O_2 (b) concentrations on oxidation over 7.5 % MnREEAEE/2 % Ce/θ-Al_2O_3. Reaction temperature, K (a, b): 1 – 873, 2 – 773, 3 - 673. GHSV (a, b) = 10×10^3 h^{-1}, (b): 0.5 % (C_3H_8 + C_4H_{10})

Table 3: Oxidation of CH_4 and C_3H_8 + C_4H_{10} on catalysts at GHSV = 10×10^3 h^{-1} in air

Catalyst	T, K			
	Propane-butane		Methane	
	α = 20 – 30 %	α = 90 %	α = 20 – 30 %	α = 90 %
MnREEAEE/2 % Ce/θ-Al_2O_3	<573	673	733	943
MnREEAEE/2 % Ce/θ-Al_2O_3 + Pt (0.1 %)	573	673	753	973

3.4 Investigation of multicomponent oxide catalysts based on Mn supported on 2 % Ce/θ-Al_2O_3 by the XRD method

The phase composition of catalysts based on Mn/2 % Ce/θ-Al_2O_3 was determined on DRON-4-7 X-ray diffractometer, Co-anode: 25 kV, 25 mA, 2θ – 5 - 80°.

The presence of θ-Al_2O_3 (35-121 JCPDS) (2.44, 2.73, 1.39, 2.84 Å lines) and a certain amount of α-Al_2O_3 (10-173 JCPDS) (2.09, 2.55, 1.60, 1.74 Å lines) as well as crystalline CeO_2 (34-394 JCPDS) (3.12, 2.16, 2.54, 2.49 Å lines) was recorded in the initial 7.5 % MnREEAEE/2 % Ce/θ-Al_2O_3 after its heating in air at 873 K by the X-ray diffraction method (Table 4).

The obtained X-ray diffraction patterns of mixed Mn catalysts show that reflections from CeO_2, θ- and α-Al_2O_3, reflexes of 2.80, 2.90; 2.12, 1.99, 1.49 Å, corresponding to hexaaluminate, as well as reflections from β-MnO_2, α-Mn_2O_3 are present in the X-ray diffraction pattern when Ba, Sr, Mn, La, Ce are supported on 2 % Ce/θ-Al_2O_3. The number and intensity of the lines corresponding to the hexaaluminate $LaMnAl_{11}O_{19}$ (2.80, 2.52, 2.64, 3.30, 1.98, 2.45, 2.00 Å), on the X-ray diffraction pattern of the microspherical catalyst MnREEAEE/Ce/θ-Al_2O_3, prepared by precipitation of elements with ammonia, is increased. The resulting picture practically repeats the one that corresponds to $La_{0.8}Ba_{0.2}MnAl_{11}O_{19}$.

The lines corresponding to crystals of Ba, Sr, La, Mn oxides were not detected on the X-ray diffraction patterns of catalysts heated at 1,273 – 1,473 K. This indicates their high dispersity and resistance to sintering. Reflexes 2.64, 2.50 and 2.80 Å, referred to manganese hexaaluminates, appear at temperatures of heating 1,273 K and above. $LaMnAl_{11}O_{19}$, as well as low-intensity reflections from $CeAl_2O_3$, $BaAl_2O_4$, MnO, SrO, Ce_6O_{11}, $BaAl_{9.2}O_{14.8}$ were detected in MnREEAEE catalyst promoted by Pt after heating at 873 – 1,473 K. This indicates the partial interaction of both Mn and other elements (Ba, Sr) with Al_2O_3 to form more complex aluminates than with Ni, Cu. Promoting the catalyst with Pt, Pd causes partial formation of complex hexamaluminate $LaMnAl_{11}O_{19}$, spinels $CeAlO_3$, $BaAl_{9.2}O_{14.8}$, the amount of which increases at 1,473 K, especially when using cordierite as a carrier.

Long heating with a gradual increase in temperature affects the overall surface and phase composition of the 7.5 % MnREEAEE catalyst. The content of α-Al_2O_3 and CeO_2 was estimated quantitatively by intensity of the 1.74 and 1.91 Å reflections in the X-ray spectrum. Figure 3 shows that as the catalyst was heated, the concentration of crystalline CeO_2 increased, and the formation of α-Al_2O_3 sharply increased above 1,273 K.

This was accompanied by a slight decrease in specific surface at temperatures up to 1,273 K and its sharp decrease up to 2 - 5 m^2/g at 1,473 K.

From the data of phase composition studies of the initial and heated MnREEAEE catalysts is evident that the formation of α-Al_2O_3 increases only at 1,473 K. $LaMnAl_{11}O_{19}$ was detected in the MnREEAEE catalyst promoted by Pt after heating at 873 – 1,473 K. A comparison of the obtained data indicates that the weaker drop in surface of the MnREEAEE catalyst during heating does not occur due to the formation of α-Al_2O_3, but mainly due to the crystallization of CeO_2 and the appearance of new phase of Mn hexaaluminates. This is evidenced by the appearance of corresponding reflexes at 2.80, 2.64, 2.52 Å, especially when heating the promoted by Pt contact.

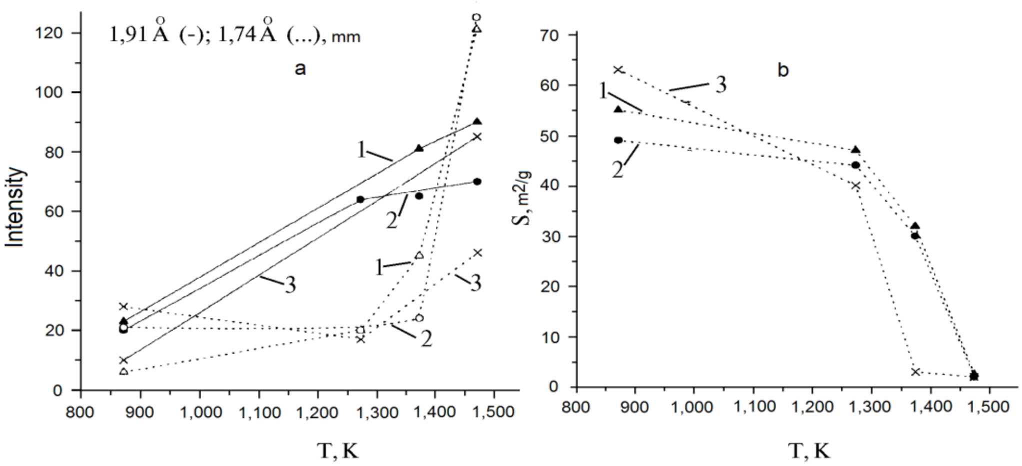

Figure 3: Influence of the heating temperature in air of the 7.5 % MnREEAEE/2 % Ce/θ-Al_2O_3 catalyst (1) and the same catalyst with the addition of Pt (2) and Pd (3) on: a - the intensity of CeO_2 reflexes (1.91 Å, solid line) and α-Al_2O_3 (1.74 Å, dotted line), b - total specific surface area

Table 4: X-ray phase analysis of polyoxide catalysts supported on 2 % Ce/θ-Al_2O_3

Catalyst	Promoter, %	$T_{heating}$, K	CeO_2, 1.91 Å	α-Al_2O_3, 1.74 Å	θ-Al_2O_3, 2.31 Å	$Al_{11}O_{19}$, 2.80 Å	Less intensive phases, GA-hexaaluminate (Å)
7.5 % MnBaSrCeLa		873	22 (27)	5	9		BaO (3.34), Al_2O_3 (2.12)
		1,273	60	18	11	10	
		1,473	93	121	10	22	GA (2.64, 2.50), MnO
		1,273 (50 h)	75	37	10	14	
7.5 % MnBaSrCeLa	Pd, 0.05	873	11	27	18	13	Pd (2.25)
		1,273	59	15	8	6	Pd, Al_2O_3 (2.12)
		1,473	87	46	17	23	Pd
7.5 % MnBaSrCeLa	Pt, 0.3	873	20	20	18	15	Pt (2.27)
		1,273	66	19	20	7	Pt
		1,373	65	25	15		Pt, $CeAlO_3$ (2.66)
		1,473	71	123	10	10	Pt (3.15)
	Pt, 0.1	873	12	8	6	6	MnO, BaO, $BaAl_2O_4$, Al_2O_3 (2.12)
-//-	Pt, 0.1	1,073	35	16	8		
$La_{0,8}Ba_{0,2}Mn_1Al_{11}O_{19}$ (without carrier)		1,373	20	13	7	15	GA (2.80, 2.52, 2.64, 3.30, 1.98, 2.45, 2.00), β-MnO_2 (3.22)
7.5 % $Ce_{0,7}Sr_{0,1}Ba_{0,1}La_{0,1}$ $Mn_1Al_{11}O_{19}$		1,373	40	32	15	15	GA (2.80, 2.9, 2.12, 1.99, 1.49), β-MnO_2 (3.11), α-Mn_2O_3 (2.72, 1.66)

$NiAl_2O_4$, $CuAl_2O_4$ (1.43 Å) were not detected

Obtained data on the formation of Mn hexaaluminates also correspond to the results of investigation of catalysts by electron microscopy with microdiffraction of electrons. The high efficiency and thermal stability of Mn catalysts was due to the presence of dispersed Mn oxides in their composition, which form perovskites on heating on the one hand, and on the other hand - Mn hexaaluminates that are active in the oxidation of CH_4. The obtained results of studies of catalysts by the X-ray diffraction method are confirmed by electron microscopy data.

According to XRD data, it is shown that the initial Mn catalyst contains crystalline CeO_2, Mn_2O_3 nanoparticles (d = 30 – 100 Å), the amount of which decreases with heating to 1,173 K due to interaction with REE with the formation of $La(Ce)MnO_3$, $CeAlO_3$, and then $LaMnAl_{11}O_{19}$ hexaaluminate at 1,273 – 1,473 К, as well as Ba-, Mn-oxides, which are active in the oxidation of CH_4 to CO_2 (Grigor'eva et al., 2002). The developed MnREEAEE/2 % Ce/θ-Al_2O_3 catalyst provides 90 – 98 % conversion of CH_4 to CO_2 at 973 K and GHSV = 10×10^3 h^{-1} and has a higher thermal stability than the known oxide catalysts for deep oxidation of hydrocarbons (Tungatarova et al., 2016).

A similar catalyst supported on blocks from α-Al_2O_3 was used for oxidation of CH_4 and C_3H_8 + C_4H_{10} mixture in catalytic heat generator that was designed to heat greenhouses. Analysis of the composition of gases formed during the oxidation of hydrocarbons showed that they contain CO_2 and traces of hydrocarbons, but there are no nitrogen oxides completely.

4. Conclusions

Thus, the oxide MnREEAEE/2 % Ce/θ-Al_2O_3 catalyst showed high thermal stability (up to 1,473 K) and specific activity in the deep CH_4 oxidation reaction compared to the known IC-40 and NiCuCr/2 % Ce/θ-Al_2O_3 catalysts, which are used to purify of waste gases from organic substances and combustion of CH_4. The obtained results indicate a possibility of practical use of a thermally stable up to 1,473 K MnEEAEE/2 % Ce/θ-Al_2O_3 catalyst for utilization of poor CH_4 mixtures in catalytic heat generators. The catalyst is not inferior to the known analogs on activity and thermal stability, in which perovskites and Mn were used.

Acknowledgments

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