Catalytic combustion of light alkanes on Mn multicomponent catalysts

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Abstract: The development of energy-saving and environmentally friendly catalytic combustion technologies of light hydrocarbons for heating of greenhouses and use of formed CO_2 for carbon dioxide additional fertilizing of plants is the aim of the present work. Polyoxide heat resistant (up to 1473 K) highly efficient Mn-containing catalysts for deep oxidation of methane and propane-butane in vapor-air mixture have been developed. Prototype of catalytic heat generator was created for ecologically clean methane and propane-butane burning.

Keywords: Flameless combustion, Manganese, Heat generation.

1. Introduction

Flameless catalytic combustion of natural and oil gases without the formation of nitrogen oxides is a promising way to utilization of natural methane and other alkanes to produce heat, carbon dioxide and products for organic synthesis (CO, H_2). Calculating the cost of heat produced during deep methane combustion in a pilot plant showed that it is lower than cost of coal-fired boiler heat at the concentration of CH_4 0.6-0.85%. Catalytic oxidation of CH_4 to CO_2 in order to generate heat is a promising way to dispose of mine, ventilation and burnt in flares methane. Catalytic combustion is fundamentally different from thermal combustion, as occurs on the surface of solid catalysts without the flame selectively to CO_2 at much lower temperatures, which prevents the formation of nitrogen oxides and other pollutants. In this regard, the purpose of work is the creation of energy-efficient and environmentally friendly catalytic technology for combustion of gaseous hydrocarbon fuel to heat the greenhouses and the use of produced CO_2 for carbon dioxide plant nutrition.

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. Granulated θ-Al_2O_3 (S = 100 m^2/g), modified by 2% Ce, forming surface $CeAlO_3$ perovskite resistant to 1373 K was used as a carrier. Oxide catalysts were promoted with platinum and palladium (0.05%) to increase the activity and thermal stability.

The catalysts were prepared by capillary impregnation of alumina by mixed aqueous solutions of metal nitrates on water capacity with subsequent drying at 453-473 K (4-5 h) and calcination at 873 K (1-1.5 h) in air. The catalyst activity was determined in oxidation of CH_4 in flow apparatus at 673-973 K. The study of deep oxidation of CH_4 (0.5-4%) was carried out by varying the space velocity from 10 to 20×10^3 h^{-1} and O_2 concentrations from 2 to 20%.

3. Results and discussion

Table 1 shows the data obtained at the oxidation of 0.5% CH_4 in air at GHSV = 10×10^3 h^{-1} on the synthesized catalysts after heating at 873 K and 1473 K. It is seen that after heating the catalyst at 873 K for 1 h at 973 K provided 85-99% conversion of methane. Catalysts (heating at 873 K, 1 h) at 973 K can be arranged in a series of degree of oxidation: AP-56 (100%), NiCuCr+Pd (99%), NiCuCr+Pt (96%), MnREEAEE/2% Ce/θ-Al_2O_3 (92%), NiCuCr/2% Ce/θ-Al_2O_3 (91%), MnREEAEE+Pd (90%), MnREEAEE+Pt (85%). The contact based on Ni-Cu-Cr/2% Ce/θ-Al_2O_3, close by effectiveness to known commercial Pt contact AP-56 (0.56% Pt) is the most effective catalyst for the oxidation of methane at 973 K.

Due to the fact that the catalysts in combustion process of CH_4 can undergo significant over heating (1473 K), they lose their activity. Therefore synthesized contacts were heated in air first at 873 K 1 h, then sequentially 5 h at 1073, 1273, 1373, and 1473 K.

Heating at high temperatures are affected differently on the degree of oxidation of CH_4 on different catalysts. Table 1 shows that the heating of catalysts at 1473 K resulted in significant reduction of the surface of all catalysts. Warming has no negative effect on the degree of oxidation of CH_4 on MnREEAEE catalysts up to 1373 K. Only upon heating at 1473 K there was a slight decrease in α_{CH4} (maximum 10%) in contrast to the Pt/Al_2O_3 (AP-56) contact, the effectiveness of which decreased sharply especially after 1373 K. As a result of this α_{CH4} reached 60% at 973 K, and only 10% at 773 K. Activity of MnREEAEE contact decreases slightly for the initial and heated contacts at 973 K (by 2-7%). Sharp decrease in the degree of conversion of CH_4 occurred after warming since 1373 and especially at 1473 K for Ni-Cu-Cr catalyst which reached 63% at 973 K, and at 773 K dropped up to 0.

Table 1. Oxidation of 0.5% CH_4 at GHSV = 10×10^3 h^{-1} in air at 773 and 973 K after heating at 873 K and 1473 K

Catalyst	weight % of the active phase	α_{CH4} after heating at 873 K/1473 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)	0.56	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

4. Conclusions

A comparative study of oxide catalysts of methane combustion to CO_2 has been shown that the MnREEAEE/2% Ce/θ-Al_2O_3 is the most thermally stable up to 1473 K catalyst (not promoted by Pd and Pt) which provides 92-88% oxidation of CH_4 at 973 K and flow rate 10×10^3 h^{-1}. Study of changes in the phase and surface composition of MnREEAEE/2% Ce/θ-Al_2O_3 in the heating process, as well as adsorption properties with respect to oxygen using XRD, TEM, BET, ESDO, TPD, TPR, TPO were conducted to determine the causes of its thermal stability.