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Efficient Combustion of Methane in a Fluidized Bed of Catalyst

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Abstract

The process of methane combustion in a fluidized bed of spherical oxide catalyst containing mixed copper and magnesium chromite on toughened alumina (IK-12-73) depending on the temperature and the concentration of methane in the mixture with air was studied. It has been demonstrated that the conversion level of methane oxidation into CO_2 in the case of the methane content equal to 2 % increases from 72 % at 500 °C to 99 % at 700 °C. Increasing the concentration of methane to 8 % does not cause reducing the conversion level of methane oxidation within the temperature range 600–750 °C. It has been demonstrated that the concentration of nitrogen oxides in the course of methane combustion at the temperature values ranging within 500–750 °C does not exceed 3.5 ppm. The presence of H_2 and CO in the reaction mixture does not cause increasing the conversion level of methane oxidation when the volume ratio $\text{CH}_4/(\text{CO} + \text{H}_2) = 4 : 19$.

Key words: combustion, fluidized bed catalysis

INTRODUCTION

The deficiency of fuel resources causes the proposal of using methane (which is emitted in large-scale amounts with the vent gases of coal mines) in the heat power engineering to be attractive. The use of traditional flame combustion is complicated because of low and variable concentrations of methane in ventilation gases [1]. Catalysts allow one to initiate the process of combustion lean mixtures of methane and air at a relatively low inlet temperature, whereas adding them to the methane-air mixture with CO and H_2 results in reducing the ignition temperature to stabilize the catalytic combustion of methane [2].

One of the ways to stabilize the process of methane combustion could consist in the combustion thereof in a fluidized bed of a particulate catalyst [3]. A high heat capacity and isothermal character of fluidized bed allows maintain at any point thereof a constant tempera-

ture required for stable methane combustion. However, in this case there are increased requirements for thermal and mechanical strength of the catalysts used.

The Institute of Catalysis of the SB RAS has developed a spherical oxide catalyst containing mixed copper and magnesium chromite on hardened aluminum oxide (IK-12-73) [4]. The catalyst exhibits a high thermal and mechanical resistance with respect to the combustion of various types of solid and liquid fuels in the fluidized bed. The temperature stabilization is provided by an excess heat abstraction at the expense of heat exchangers immersed in the bed. The experience of continuous commercial operation with the IK-12-73 catalyst in the course of diesel fuel combustion within catalytic heating units demonstrated that the lifetime thereof is more than 8 months while retaining a high catalytic activity [5].

In the present work, we investigated the efficiency of methane combustion in a fluid-

ized bed of the IK-12-73 catalyst and the effect of CO and H₂ presence in the original methane-air mixture in the course of methane combustion process.

EXPERIMENTAL

The experiments concerning the combustion of methane and CH₄, CO и H₂ mixture were performed in a laboratory apparatus consisting of a reactor with the fluidized bed of catalyst, an air heater, combustible gas feeding system, air supply system, a smoke fume purification system, heat removal system for heat released in the course of fuel oxidation.

The reactor represents a stainless steel cylinder with an internal diameter of 40 mm and a height of 1000 mm. At the bottom part the reactor is provided with a gas distribution grid, in the upper part the reactor is equipped with a heat exchanger to remove excess heat from the fluidized bed and to cool the smoke fumes. In order to eliminate a plug mode of fluidized bed operation, within the layer of the particles inside the reactor there are arranged nozzles in the form of gratings with 14 × 14 mm cells, the distance between the gratings being equal to 14 mm. The system for smoke fume purification from dust consists of a cyclone with a hopper. The input of combustible gases to the reactor is performed at a height of 50 mm from the gas distribution grid. As combustible gases we used natural gas containing 94.34 % of CH₄, as well as a mixture of CO and H₂ in nitrogen with the concentration of 3.44 and 6.75 %, respectively.

For the gas sampling from the reactor for analysis, there are fittings provided at a height of 200, 400 and 600 mm. Sampling the smoke fumes for analysis was performed at the output of gases from the cyclone. The heater was used to preliminary heat the air and thus the catalyst bed in a fluidization mode. The maximum power of the heater was equal to 1 kW, the heater power being adjusted using a P133 unit. An electric heater is provided outside the reactor to additionally control the temperature in the fluidized bed. The height of the electric heater was equal to 600 mm, maximum power thereof amounting to 1.5 kW. Supplying the combustible gases was carried out from cylin-

ders. Each line was equipped with a gas pressure regulator, control units and a gas flow rotameter. Supplying the combustible gases and mixtures thereof into the reactor was carried out through the same input. In addition, the unit was provided with facilities for purging the gas lines with nitrogen. The temperature in the reactor was monitored using a chromel-alumel thermocouple and a KSP-4 potentiometric self-recording unit. The IK-12-73 (aluminum-copper-chromium) catalyst loading with a particle size of 1.5–2.0 mm amounted to 600 cm³ (at a bulk density of about 1 g/cm³).

Gas sampling for the analysis was carried out using an air ejector and a system of two six-way valves with sampling loops in order to supply gas samples for chromatography. To analyze the gases we used a LHM-80 chromatograph with a thermal conductivity detectors, equipped with a column packed with NaX for the separation of H₂, O₂, N₂, CO, CH₄ and a column with Porapak Q for determining the CO₂; the columns being 3 m long, helium was used as the carrier gas. The mixture of gases coming into the chromatograph for analysis with Porapak Q, was previously passed through a column packed with silica gel to remove water vapor. The mixture of gases coming into the chromatograph with NaX for analysis was additionally passed through a column packed with ascarite for removing CO₂.

RESULTS AND DISCUSSION

Figure 1 demonstrates the overall conversion level for the oxidation of methane depending on the temperature of the fluidized bed of IK-12-73 catalyst. The methane concentration in the initial mixture is equal to about 2 vol. % not exceeding the ignition limit equal to about 4.4 %. At the temperature of 500 °C, the conversion level of methane oxidation is equal to 92.2 %. At higher temperature values the conversion level of methane oxidation increases to reach 99.7 % at the temperature of 700 °C. The smoke fumes alongside with profound oxidation products such as CO₂ and H₂O contain CH₄ and CO. No hydrogen was detected in the oxidation products. The concentration of nitrogen oxides in the smoke fumes within

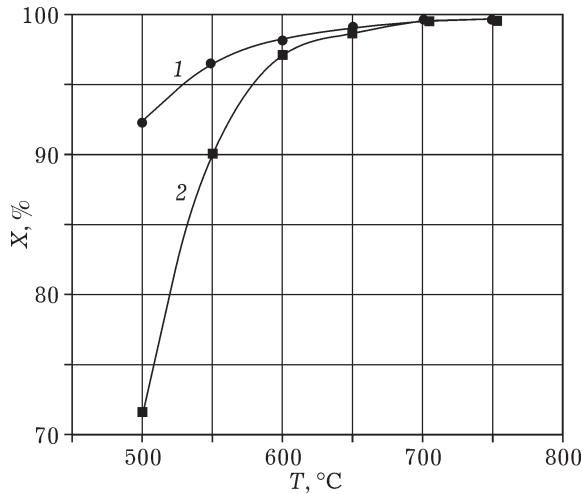


Fig. 1. Methane conversion level (X) with respect to CH_4 (1), CO_2 (2) depending on temperature.

the temperature range of 500–750 °C does not exceed 5 ppm. The level of methane conversion into profound oxidation products, depending on the temperature, is substantially lower than the total conversion level of methane oxidation (see Fig. 1).

Figure 2 demonstrates the methane oxidation rate constant in the fluidized bed of aluminum-copper-chromium catalyst depending on temperature. The reaction rate was calculated for a reactor of perfect mixing according to a first order equation with respect to the conversion level of methane oxidation. The activation energy of methane oxidation at 500–750 °C is

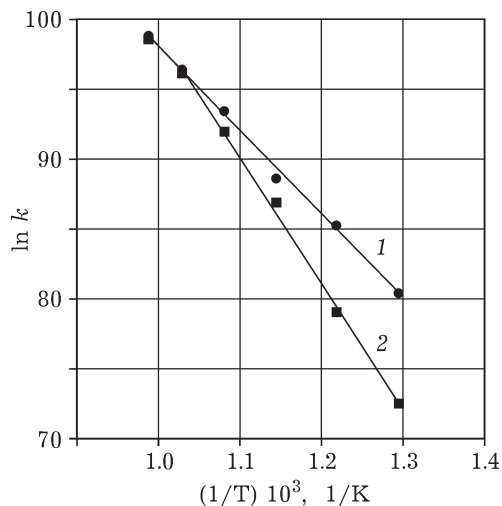


Fig. 2. Rate constant logarithm for methane oxidation ($\ln k$), depending on reciprocal temperature ($1/T$): 1 - with respect to CH_4 , $E = 23.5 \text{ kcal/mol}$, $k_0 = 108.0 \cdot 10^6$; 2 - with respect to CO_2 , $E = 35.5 \text{ kcal/mol}$, $k_0 = 54.8 \cdot 10^9$.

equal to 23.5 kcal/mol being close to the activation energy value for the fixed bed CuCr_2O_4 catalyst at 300 °C within the kinetic region of the process occurring (23 kcal/mol) [6].

The activation energy for the methane oxidation in the fluidized bed to yield profound oxidation products at 500–700 °C is equal to 33.5 kcal/mol (see Fig. 2). However, within the temperature range 600–750 °C this value exhibits a decrease down to 23.5 kcal/mol.

In the fluidized bed of the catalyst the oxidation rate of methane into profound oxidation products is significantly lower than the rate of oxidation of methane, calculated from methane loss (see Fig. 2). Furthermore, the rate of methane oxidation into CO_2 with increasing the temperature above 600 °C is reduced in accordance with decreasing the activation energy of the process (see Fig. 2). Decreasing the activation energy of methane oxidation into CO_2 in the fluidized bed, could be caused, to all appearance, by the fact that the process occurs *via* a radical mechanism involving CO and H_2 . In this case, the addition of hydrogen and CO to the initial reaction mixture should affect both the composition of the products of CH_4 oxidation, and the profound oxidation rate. In particular, the authors of [2] demonstrated that the presence of readily oxidized CO and H_2 causes increasing the level of CH_4 conversion using a monolithic LaMnO_3 catalyst on $\gamma\text{-Al}_2\text{O}_3$ at the temperature values below 800 °C. The reactivity of the compounds decreases in the order of $\text{CO} > \text{H}_2 > \text{CH}_4$.

In the course of the oxidation of H_2 and CO mixture in the fluidized bed of catalyst at temperature values of 600–700 °C, the level of oxidative conversion thereof is greater than 99.9 %. In the case of reducing the process temperature down to 500 °C the oxidation products contain CO. Changing the conversion level of CO oxidation depending on the concentration thereof at 500 °C is presented in Fig. 3. When the concentration of CO increases, the conversion level of CO oxidation remains almost unchanged. However, hydrogen within the temperature range of 500–700 °C can be almost completely oxidized.

Figure 4 demonstrates the conversion level of methane oxidation depending on CO and H_2 concentration in the reaction mixture. It is seen

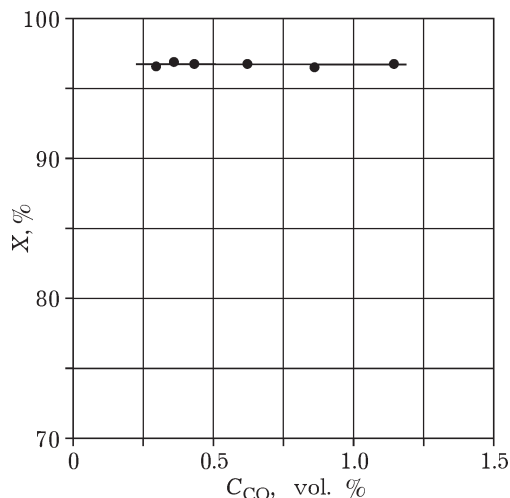


Fig. 3. Changing the level of carbon monoxide conversion (X) depending on the initial concentration (C_{CO}).

that the presence of CO and H_2 in any concentration does not lead to increasing the conversion level of methane oxidation. The maximum concentrations of CO and H_2 in the bottom part of the reactor in the case of mixing with air amounted to about 1.14 and 2.23 %, respectively.

The authors of [7, 8] assumed that at the temperature values lower than 400 °C, the methane oxidation on a uniform surface of copper (I) oxide occurs according to a matched mechanism through the formation of carboxylate compounds on the catalyst surface (probably in the form of formates) and a subsequent destruction thereof on the surface of the cat-

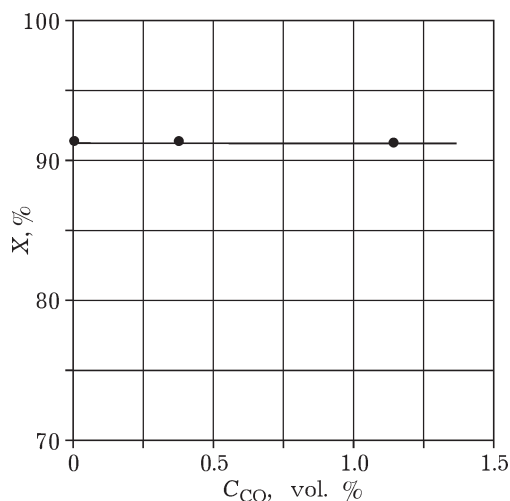


Fig. 4. Changing the methane conversion level (X) at 500 °C, depending on the concentration of CO in the initial CH_4 , CO and H_2 mixture.

alyst in the presence of oxygen in the gas phase. With increasing the temperature, a stepwise oxidation mechanism begins to dominate, whereby the carboxylate complexes are relatively quickly destructed with no oxygen in the gas phase, whereas the oxidation rate is determined by the stage of a reaction between the substance under oxidation and the surface oxygen of the catalyst. In this case, the rate values for methane oxidation calculated from the methane loss and from the CO_2 production are almost identical, both in the matched mechanism region and in the stepwise mechanism region of methane oxidation [9].

The methane oxidation in the fluidized bed of CuO catalyst on $\gamma-Al_2O_3$ within the temperature range 400–700 °C also does not exhibit CO formation in the case of twofold changing the rate of fluidization and changing the concentration of methane from 0.15 to 3.0 vol. % [3]. Among the products of the reaction, there are only CO_2 and CH_4 present.

In the course of the oxidation of hydrocarbons on the surface of heterogeneous copper chromite there are simultaneously present carboxylate and carbonyl compounds, whose decomposition results in the formation of CO and CO_2 [10].

To all appearance, in the fluidized bed of $CuCr_2O_4$ catalyst on $\gamma-Al_2O_3$ there can be also present carboxylate and carbonyl compounds adsorbed on the surface, in the form of formates and formaldehydes. In the course of the decomposition of formaldehyde at a relatively low temperature (400–600 °C), there occurs CO formation as an intermediate in the oxidation of methane (see Fig. 2).

The efficiency of the methane combustion process is determined by the efficiency of the methane conversion into profound oxidation products such as CO_2 and H_2O , and by the amount of nitrogen oxides emitted with smoke fumes. In the course of methane combustion, the oxides of nitrogen are formed via the reaction between atmospheric oxygen and nitrogen, and their amount depends only on the temperature of the combustion process. In the case of the catalytic combustion temperature (500–700 °C), the calculated concentration of thermal nitrogen oxides (NO_x) is not lower than 10 mg/m³, which corresponds to sanitary standards according the NO_x content in the flue

gas [11]. Thus, the efficiency of the catalytic combustion of methane is determined by a completeness of methane oxidation into CO_2 and H_2O . From the data in Fig. 1 one can see that only when the temperature reaches 700°C the level of the catalytic oxidation of methane in the fluidized bed of IK-12-73 catalyst satisfies the health standards for the content of CO in the flue gas (not higher than 0.05 vol. %). The concentration of nitrogen oxides at the same time is equal to 3–8 ppm, or 4–10 mg/m^3 , which also meets the requirements of sanitary standards. At these temperature values, increasing the concentration of methane in the initial mixture from 2 to 8 vol. % does not cause decreasing the efficiency of methane combustion.

Thus, using a fluidized bed of IK-12-73 catalyst one could perform the process of an environmentally safe combustion of methane-air mixtures at the temperature values equal to about 700°C .

The adiabatic temperature for the combustion of methane-air mixture can be approximately determined as

$$T^a = T^{\text{air}} + Q_p C_0 / (\rho c_p)$$

where T^{air} is the initial air temperature; Q_p is the heat of combustion of methane at a constant pressure; C_0 is the concentration of methane in the gas mixture; ρ is the density of the mixture; c_p is the specific heat capacity of the mixture [12]. Typically, the concentration of methane in the mine ventilation gases $C_0 \approx 1\%$. Adiabatic heating such methane-air mixture amounts to $\Delta T \approx 275^\circ\text{C}$, whereas the environmentally safe combustion of methane in a fluidized IK-12-73 catalyst bed, as demonstrated above, requires for maintaining the reactor temperature at about 700°C . To achieve adiabatic heating $\Delta T \approx 700^\circ\text{C}$ the concentration of methane in the ventilation gases should be increased up to 2.5–3.0 %.

Thus, in the case of low-concentration methane mixtures (~1 % methane) the direct combustion in a fluidized bed of catalyst cannot be performed for environmental purposes without adding extra fuel.

The advantages of fuel combustion in a fluidized bed for power and heating purposes are determined, first of all, by high heat transfer coefficients from the bed to heat exchange surfaces immersed in the bed [13]. In the case of a

relatively low temperature gradient between the bed and the heat transfer medium and a high heat transfer coefficient ($350 \text{ W}/(\text{m}^2 \cdot \text{K})$) the heat transfer surface in the bed takes about 70–80 % of the heat from the combustion of stoichiometric fuel-air mixtures (the theoretical adiabatic combustion temperature is higher than 2000°C). This enables performing the combustion process at substantially lower temperature values as to compare with the adiabatic combustion temperature with removing equal or even greater amount of heat comparing to a high-temperature heat exchange in the smoke fumes-coolant system with the heat transfer coefficient amounting to about $35 \text{ W}/(\text{m}^2 \cdot \text{K})$.

In the case of combusting lean fuel-air mixtures, these advantages of the fluidized bed can almost come to naught. All the heat produced is consumed for heating the mixture up to 700°C and removed from the layer with the smoke fumes. Cooling the smoke fumes is carried out in a heat exchanger with a low heat transfer coefficient, *i. e.* $35 \text{ W}/(\text{m}^2 \cdot \text{K})$ located outside the bed.

In the case of mine methane neutralization in the fluidized bed of the catalyst is advisable to use assist coal as the supplementary fuel. As we demonstrated earlier [4, 13], in a fluidized catalyst bed one could combust fossil coal with a high efficiency. The efficiency of the catalytic combustion of coal depends little on the quality thereof. Moreover, the greater the amount of volatile substances in the coal, the higher is the level of its combustion in the catalyst bed. Therefore, it is possible to combine the process of the neutralization of coal mine methane with the coal combustion for heating and energy purposes. In the case of installing an additional heat exchanger, the problem of heating the air supplied to a pit-shaft could be solved.

CONCLUSION

1. The process of methane combustion in a fluidized bed of IK-12-73 catalyst was studied depending on the temperature and the concentration of methane mixed with air. It has been demonstrated that the conversion level of methane oxidation into CO_2 at the content thereof equal to about 2 % increases from 72 % at

500 °C and 99 % at 700 °C. Increasing the concentration of methane up to 8 % does not cause decreasing the conversion level of methane oxidation within the temperature range of 600–750 °C. It has been demonstrated that the concentration of nitrogen oxides in the course of methane combustion within the temperature range of 500–750 °C does not exceed 3.5 ppm.

2. The process of combusting a mixture of H₂ and CO in a fluidized bed of IK-12-73 catalyst was studied depending on the temperature. It has been demonstrated that at the temperature values ranging within 600–700 °C, the conversion level of CO and H₂ oxidation exceeds 99 %. At the temperature of 500 °C the level of CO oxidation is reduced to 96 % being to a considerable extent independent of changing the initial concentration of CO and H₂ in the mixture with air.

3. The process of methane combustion in the mixture with H₂ and CO in a fluidized bed of IK-12-73 catalyst was studied. It has been found that the presence of CO and H₂ in the reaction mixture does not lead to a substantial increase in the conversion level of methane oxidation at a volume ratio $\text{CH}_4/(\text{CO} + \text{H}_2) = 4-19$.

4. The use of the combustion of methane-air mixtures in a fluidized bed catalyst for methane utilization for heating and energy purposes is

possible at the methane content in the mixture ranging within 2–2.5 vol. %, *i. e.* under adiabatic warming the methane-air mixtures (500–700 °C). At lower values of methane concentration, an introduction of additional fuel is required.

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