High-efficient solid-fuel combustion catalysts

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Abstract. The process of catalytic combustion of solid fuels in the presence of manganese dicyclopentadienyl tricarbonyl was studied. The results of industrial tests have showed an improvement in the basic technical and economic indicators of the coal burning process (AH grade) and an increase in the boiler unit efficiency.

Keywords: coal combustion, catalyst, manganese carbonyl

1. Introduction
In the modern world, the state of the environment and the need to protect it, as well as the growth of energy consumption in all sectors of human society, together with the reduction of the reserves of energy raw materials, dictate the need to design novel technologies to ensure a high level of the use of natural raw materials and to reduce the anthropogenic load upon the environment.

The environmental safety of energy facilities is one of the criteria for the energy industry development in the 21st century, which leads to the priority choice of the fuel to be used.

In this regard, it is particularly topical to design fundamentally new universal technologies applicable to energy processes involving solid, liquid and gaseous fuels.

The catalytic process of burning fuel in the presence of some substances which allow to increase the heat transfer of the fuel and to reduce the toxicity of the flue gases from heat and power plants is the most promising one.

Transition metals exhibit high activity in homogeneous and heterogeneous catalysis, which is due to their electronic state and ability to form intermediate compounds with fuel components and intermediate products of their oxidation [1].

The activity of compounds of platinum, palladium, nickel, cobalt, copper and other metals in redox reactions is known [2].

Taking into account the high-temperature process of burning fuels, it is advisable to use heat-resistant catalysts and their carriers.

Deep catalytic oxidation of hydrocarbons to carbon dioxide is mainly used for purification of exhaust gases from industry or transport and for the production of catalytic heat sources (catalytic flameless combustion). Platinum group metals in highly dispersed form deposited onto heat-resistant carriers are universal combustion catalysts. Due to the high cost of platinum metals and the tendency to their “poisoning” with impurities, mono- and multicomponent oxides of transition metals are often used as catalysts. Highly porous permeable cellular metal and ceramic materials were shown to be promising supports for methane deep-oxidation catalysts [3].

In addition, it is proposed to use an activated additive consisting of a carbon fulleroid nanocluster to intensify solid fuel combustion.

The patent [4] discloses metal-containing combustion catalyst, including tricarbonyl manganese compounds.
The purpose of this work was to design a catalyst for burning solid fuel that meets such requirements to combustion processes as energy efficiency and environmental safety.

2. Experimental technique
Catalytic fuel combustion was studied under industrial conditions in an operating heat generator-boiler when burning pulverized coal (AH grade) at temperatures within 1,500–1,700°C. The temperature of the combustion products was measured with a thermocouple, and the gas composition was analyzed with an AGM-510M gas analyzer.

3. Results and discussion
A catalytic system for solid fuel combustion, comprising 5–20 wt. % manganese dicyclopentadienyl tricarbonyl and methylbenzene as an organic solvent, was designed. The catalytic composition was uniformly sprayed into the fuel combustion chamber through an aeration system in the amount of 70–100 ml per 1,000 kg of solid fuel [5].

Manganese dicyclopentadienyl tricarbonyl is a “sandwich” with a transition metal (manganese) atom located between two cyclopentadienyl rings, it decomposes to produce manganese oxide in the presence of oxygen under fuel burning conditions.

Manganese dicyclopentadienyl tricarbonyl was obtained by a method based on the interaction of divalent manganese compounds with cyclopentadienyl salts of potassium, sodium, lithium and aluminum (or with magnesium cyclopentadienyl bromide or the cyclopentadienyl compounds of other elements) and carbon monoxide. When alkali metal (sodium, potassium, lithium) cyclopentadienyls were used, the best yields were achieved.

A significant reduction in the content of combustible in fly ash was achieved as a result of our tests. Poor coal burnout, and as a result, a high content of combustible substances in fly ash lead to large losses with mechanical underburning. The use of our manganese-containing catalyst during pulverized coal combustion makes it possible to reduce the content of combustible substances in the fly ash from 24.7 down to 18.5%.

Reducing the combustible content in the ash by 1% leads to 1.4 g/kWh equivalent fuel savings.

The reduction of gas costs for boosting when burning solid fuel is no less significant result. The use of a manganese dicyclopentadienyl tricarbonyl solution makes it possible to reduce several times the amount of natural gas used as a booster, with a stable combustion mode of the boiler.

In addition, our catalyst simultaneously allows efficient flue gas cleaning from nitrogen oxides and carbon (II) oxide. Analysis of the composition of the flue gases of coal combustion has showed that the content of hydrocarbons, nitrogen and carbon oxides meets the requirements of maximum allowable concentrations (see Table).

| Fuel | NOx, mg/m³ | C₉H₈, mg/m³ | CO, mg/m³ | CO₂, vol.% | O₂, vol.% |
|------|------------|-------------|----------|------------|----------|
| Coal | 87         | 52          | 17       | 7.4        | 12.2     |

Thus, our comparative analysis of the coal combustion mode with the recommended boosting and with no catalyst and the mode with the supply of manganese dicyclopentadienyl tricarbonyl in an organic solvent confirms the improvement of the basic technical and economic indicators of the boiler and the increase in its efficiency.
References

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