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COMPOSITE CATALYSTS BASED ON FLY ASH OF THERMAL POWER PLANTS AND NATURAL ZEOLITE FOR PURIFICATION OF GAS EMISSIONS AND CATALYTIC CRACKING OF FUEL OIL

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ABSTRACT

In this research, the hollow microspheres based on fly ash from the Ekibastuz coal deposit (Kazakhstan), produced as a result of the operation of TPP-2 (Almaty, Kazakhstan) were used for investigation of two processes. The composite on the base of cenisheres was applied in the technology of SO_2 oxidation with oxygen in aqueous solution at T=40-60°C. Conditions of selective oxidation of SO_2 (100%) to obtain sulfuric acid as a product were optimized. Specific surface of the catalyst calculated according to full isotherms of low-temperature adsorption of nitrogen by BET method makes 12.6 m^2/g. Integral volume of pores makes 0.57 ml/g. The results showed that the degree of SO_2 removal was up to 94.9%. The catalysts based on fly ash cenospheres with addition of natural zeolite from Tayzhuzgen field (Kazakhstan) were also tested in the process of catalytic cracking of fuel oil (with preliminary electromagnetic excitation of hydrocarbon molecules) to obtain light carbon fractions. On the optimal catalyst in the products of oxidative cracking of fuel oil, the fraction of light gas oil is the main part. Determination of the individual composition of the hydrocarbons included in this fraction showed that the formation of C_7-C_{12} hydrocarbons happened exclusively due to the symmetric decomposition of C_{14}-C_{24} paraffins, since the products of this reaction are the corresponding α-olefins and n-alkanes.

Keywords: fly ash, Almaty TPP-2, Ekibastuz coal, catalytic cracking, natural zeolite, water and gas purification, highly toxic organic compounds.

INTRODUCTION

More than 100 million tons of ash waste is accumulated in landfills as a result of the combustion of solid fuel at a CHP (or TPP) annually [1-6]. Obviously the problem of the utilization of ash and slag of the CHP working on solid fuel is actual. TPP fly ash contains a number of components with valuable and unique technological properties: aluminosilicate hollow microspheres (AHM, which are really the most original and perhaps the most valuable components of ash), magnetite microbeads, the unburnt carbonic particles, ferrosilicon and carbonate microspheres [7-11]. They are hollow, almost perfectly shaped silicate balls with a smooth surface and a diameter from 10 to several hundred micrometers, an average of about 100 microns. The value of AHM is determined by the fact that they can be ideal fillers. The main components of ash and slag are silicon oxide, SiO_2 (45-60%) and alumina, Al_2O_3 (15-25%). The content of iron oxides Fe_2O_3 is from 5% to 15%, of calcium oxide CaO (1.5 - 4.5%) and of potassium oxide K_2O (2.0-4.5 %) and some other oxides, the content of which usually does not exceed 1%. Its most part contains in a form of iron-organic compounds. At coal burning the thermochemical transformation of all these compounds into the mineral magnetite (Fe_3O_4) happens. It is important to note that unlike other components the hollow microspheres are relatively easy to separate from ash. Due to the low density they can float to the water surface of hydraulic structures (ponds, sedimentation tanks, recycled water channels) and can be collected by any means including the simplest. AHM are in great demand in many countries. Ash dumps are, in fact, a technogenic deposits of valuable products [5, 6, 12, 13].

In this research the hollow microspheres based on fly ash from the Ekibastuz coal deposit (Kazakhstan), produced as a result of the operation of TPP-2 in Almaty (Kazakhstan) were selected and used for preparation of composites and testing in two processes: for purification of gas emissions and catalytic cracking of fuel oil. Ekibastuz coal basin (Kazakhstan) is one of the most significant by reserves and ranks first in the world in terms of coal density: on the area of 62 km^2 the coal reserves are estimated at 13 billion tons or 200 tons per m^2 [14-16] and is one of the most promising areas in the world by open-pit coal mining. The main consumers of coal from this basin are in the Urals (Russia) and in the Republic of Kazakhstan.

Features of the chemical and mineral-phase composition of cenospheres make it possible to synthesize microspheric fuel cracking catalysts based on them. Heavy oils and natural bitumens have a high content of aromatic hydrocarbons, resinous-asphaltene substances, a high concentration of metals and sulfur compounds, high density and viscosity, increased coking, which gives an increased production cost of such raw materials and problems during transportation and oil refining.