FORMATION OF HIGLY-DISPERSED CARBON IN THE PROCESS OF HYDROCRACKING OF HEAVY PETROLEUM FRACTIONS

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Introduction

In recent times among main methods of synthesis of carboniferous nanocompositions more and more attention is paid to obtaining them by pyrolytic decomposition of various hydrocarbons [1-3]. At the same time it is well known that practically all oil-refining processes are accompanied by deposition of various forms of carboniferous deposits on catalysts and in reaction zone. In the processes of pyrolysis, cracking, hydrocracking these deposits cause deactivation and early failure of expensive catalysts. So, petrochemists search for methods of more efficient fighting this so-called coke deposition phenomenon. However, in the light of new views it is rather interesting to study forms of nanocarboniferous compositions generated in the mentioned processes.

Results and their discussion

We have minutely studied carbon fotmation in the process of mazut hydrocracking carried out both in the absence and presence of various catalysts as well as upon introduction of different amounts of various polymeric additives into the system. Hidrocracking of mazut has been studied in an autoclave at pressure 4-8MPa in the temperature range 400-440^{o}C. Analysis of carbon-containing products of the reaction has been conducted at X-ray diffractometer DRON-3M. Subjected to analysis were coked catalyst particles obtained during filtration of hydrogenation product with their subsequent careful washing with benzene to remove the adsorbed organic compounds and further drying. Dispersity of the obtained particles has been determined by atomic power spectroscopy and X-ray diffractometry and microphotographs of various carbonaceous deposits have been taken. It has been noticed that, when carrying out the process without catalyst in the regime of mazut thermal cracking, formation of highly-dispersed graphitized soot takes plase. Upon introducing only 1%wt. nickel-molybdenic oxide catalyst into the reaction system the indicated carbon form becomes markedly decreased in amount whereas formation of new carbon-containing phase is observed, the amount of which rises with an increase of the quantity of the catalyst introduced into the system. Mean while, with an increase of catalyst addition formation of graphitized soot stops, in fact, completely. New carbon-containing phase of d=3.42Å is a highly-dispersed substance of particles dimensions of the order 4-5 nm. This form of carbon may be ascribed to carboniferous nanosubstances (CNS) and it has been described well in [4, 5]. An enhanced formation of CNS is also observed when conducting the process of mazut hydrocracking without catalyst but with introducing small amounts of polyethylene terephthalate (PTPh) into the reaction system. With an increase of amount of PTPh entered into the system the quantity of the formed CNS also increases, dimensions of nanoparticles of this carbon form remaining practically constant. Upon adding to the reaction system, along with PTPh, various catalysts (nickel-molybdenic oxide, nickel on kieselgur, Engelhardt's catalyst) an abrubt decrease of CNS formation occurs and by increasing catalyst addition it becomes possible to prevent carbon formation practically completely.

Interesting results have been obtained when carrying out the process of mazut hydrocracking on nickel-molybdenic catalyst with addition of small amounts of polyethylene (approximately 0.3%wt.) to the system. In this case formation of significant amounts of highly-carbonized coke-like substance is observed which is exhibited in the diffractograms in the form of wide halo of d=4.67Å. Dimensions of particles of this very highly-dispersed substance vary in the limits 0.8-1.2nm.

Conclusions

As a result of the carried out investigations, there have been revealed various forms of highly-dispersed carbon generated in the process of mazut hydrocracking. Taking into account high productivity of industrial plants for the mentioned process, at necessity, along with petroleum products it is possible to produce various forms of highly-dispersed carbon simultaneously.

References

1. Trefilov V.I., Shur D.V., Tarasov B.P. et al. Fullerenes as a base of future materials. Kiev: ADEF, 2001 (in Russian).

2. Volodin A.A., Fursikov P.V., Tarasov B.P. Synthesis of carbon nanofibres by ethylene pyrolysis on Mg_2Ni. Materials ICHMS 2007. p. 6-7 (in Russian).

3. Pan C., Bao Q. Well-aligned carbon nanotubes from ethanol flame. J. Mater.Sc.Lett. 2002, 21, p. 1927-1929.

4. Peshnev B.V., Nikolayev A.I., Kuzmicheva G.M., Asilova N. Yu., Podlesnaya M.V. Formation of carbon nanofibres by CO dispropertionation. Chemistry of solid fuel. 2007, № 4, p. 66-70 (in Russian).

5. Peshnev B.V., Nikolayev A.I., Estrin R.I. Oxidation of carbon nanofibres and materials produced on their basis. Chemistry of solid fuel. 2008, № 2, p. 48-52 (in Russian).