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Activation and Restoration of Hydration Catalysts

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ABSTRACT

The most promising method for synthesizing aluminum-nickel-molybdenum catalysts is dry absorption of carriers with solutions of salts of active components. Among the factors that determine important technological parameters, such as the activity, selectivity and stability of contacts of the catalytic process, the main focus is on the regulation of mechanical compatibility, comparative surface, porosity and conditions for the formation of active phases. The study of beggar and sulphidized forms is limited to several works.

I.INTRODUCTION

In recent years, an increase in interest in the development of hydrotosing processes of diesel distillates has been associated with an increase in the volume of processing of sulfur and high-sulfur oils, as well as extensive dieselization of vehicles.

It is known that low-sulfur diesel fuels with improved performance are capable of directly operating fractions [1; 312-315 p.].and secondary raw materials [2; 53-60 p.] is obtained by hydrotreating.

Proper driving diesel fractions are hydrotosed in the presence of catalysts, their group and fractional composition are constant, at a temperature of 350-400^{0}C, a pressure of 3-6 MPa, a speed of 2-5 c^{-1} the circulation of gas containing raw materials and hydrogen is 200-600 m^3 / m^3. The hydrosulfurization rate in this case is 85-95%.

Mercaptans (~86%), sulfides (~86%) and disulfides (~88%) are most completely removed. At the same time, the service life of catalysts is 4-6 years [3; 53-60 p.]. Depending on the type of raw materials, the activity of the catalyst used and the conditions of the process, hydrogen consumption in the process of hydrotreating diesel fractions is from 0.16 to 0.45%, of which only ~ 50% is spent on hydrogenation of sulfur compounds [3; 36-48 B., 5; 422-428 p.].

The depth and speed of the hydrogenation reaction of sulfur compounds of diesel distillate fractions is significantly influenced by the ratio of pressure, temperature and hydrogen: raw materials.

When the partial pressure of hydrogen in the system is lowered to 3.0 MPA, the depth of hydrogenation of sulfur compounds and alkenes decreases, and the service life of the catalyst is reduced due to an increase in the rate of Coke deposition. As the temperature of the process rises, the rate of hydrodesulfurization increases, but selectivity decreases, gas and gasoline emissions increase, hydrogen consumption increases, and the overall service life of the catalyst decreases.

Hydrogen ratio: affects the duration of the reaction of raw materials with a catalyst and the evaporation of raw materials [3; 36-48 p., 5; 422-428 p.].

Hydration catalysts are supplied as commodity products of the catalyst industry in the form of stable oxide. Therefore, before launching, their activation is carried out. Sulfidation or recovery with a gas containing hydrogen or hydrogen. The procedure for performing this operation is strictly regulated, it has its own characteristics for each specific connection, since the activity and stability of the catalyst largely depends on this stage. [1; 456-461 p.) It has repeatedly stated that activation at the launch of an industrial device at work is the most responsible operation. During the activation process, the catalyst is transferred from the oxide form to the state that provides the hydrodesulfurization process.

II. SIGNIFICANCE OF THE SYSTEM

Despite a number of studies, the structure of sulphided hydrodesulfurization catalysts is not clearly defined, but the layered model of “compensation cations” most appropriately reflects the properties of industrial contacts. [2; 923-927 p.] The work notes that the Ni - Mo-S active surface phase is characteristic in the localization of Ni^{2+} promotor cations at the edge edges of suitable crystals bound to the carrier. The hydrodesulfurization activity of aluminium-nickel-molybdenum catalysts has been found to be related to the amount of sulfur bound to the promoter in MoS_2. Oxide-shaped catalysts have a low initial activity, which increases over time as a result of gradual sulfurization with raw materials. Pre-re-catalysts are much more active and reach the stationary mode faster. At the same time, the technological parameters of the hydrotreating process strongly depend on the conditions of recovery (temperature, pressure and concentration of the darkening agent), the lower the recovery temperature, the higher the level of stable activity. The recovery capacity of catalysts is determined by a number of factors: recovery conditions (temperature rise rate, pressure), the composition of the recovery environment, carrier binding strength of the active components, degree of dispersion and uniformity of the pre-active phase distribution. The highest activity in the sulfur mitigation reaction is predicted to be achieved when a theoretical single-layer coating is achieved based on the molybdenum atom's area of 1 nm^2 of the molybdenum 4 atom, i.e. 0.17 nm^2.

III. METHODOLOGY

Given the nature of the catalyst and the quality of the purified fuel fraction, the catalysts of hydrogenation processes are activated in one of the following methods [1; 456-461 B.]

- Heating at a temperature of 450-500^{o}C;
- Recovery by pre-Thermal oxidation treatment with hydrogen or hydrogen-containing gas;
- By sulfurization or sulfidation.

As a rule, aluminum-nickel-molybdenum catalysts are used in the process of hydrotreating in sulfidated form.

IV. THE EXPERIMENTAL RESULTS

Although the uniform distribution of hydrogenating metals cannot be achieved under real conditions, the nickel promoter in the catalyst is highly dependent on the preparation method, nevertheless, the authors [3; 81-86 p.] based on the assumption of an ideal multilayer distribution of nickel and molybdenum in the carrier, the following model has been proposed. According to the idea of the nature of the action of nickel cations on the edges and complexion cations on MoS_2 crystals, the following reactions occur during activation of catalysts:

$Ni^{2+} + H_2S \rightarrow 2H^{+} + Ni$

$Ni + 2\ Mo^{4+} \rightarrow Ni^{2+} + 2\ Mo^{3+}$,

$2Mo^{3+} + RS + H_2 \rightarrow 2Mo^{4+} + RH_2 + S^{2-}$,

$2H^{+} + S^{2-} \rightarrow H_2S$

Apparently, these reactions are associated with the transfer of electrons and proceed with the direct participation of hydrogen. Therefore, it is important to study the restored forms of catalysts. For example, the work [4; 17-20 p.] shows the emergence of recovery centers during hydrogen activation of molybdenum oxide catalysts with the formation of structures with Mo^{5+}, Mo^{4+} and Mo^{3+} ions containing hydroxyl groups in their coordination area.

V.CONCLUSION AND FUTURE WORK

The service life of hydrodesulfurization catalysts is determined by the rate of decontamination, depending on the composition of the catalyst, the distribution of metals in the carrier, the presence of various modifying additives, mixtures, the composition of raw materials, process parameters, etc. The main causes of decontamination are the accumulation of Coke layers on the surface and the sulfation of catalysts, therefore, thermal oxidative regeneration to restore initial activity [5; 15-22 p.] is occasionally performed at temperatures of 450-550°C. [6; 49-56 p.] The work found that the maximum regeneration temperature for aluminum-nickel-molybdenum catalysts is 460°C above which begins the intensive transition of nickel ions to the spindle structure. Most of the current inventions are devoted to the study of modified aluminium-nickel-molybdenum hydrotreating catalysts. As promising additives, it is possible to distinguish between crystalline and amorphous aluminosilicates, boron, silicon and phosphorus compounds, which are structural promoters of the formation of nickel-molybdenum associations in the high dispersion state, regulators of the strength and concentration of acid-base centers. There are positive examples of the use of natural polymineral sorbents as part of Hydro desulfurization catalyst carriers, but there is little data on the interaction of components in such complex systems. There is almost no information about the effect of dilute phosphorus and boron acid on the interaction in the alumokaolin system and the formation of previous structures of the catalytic active phases. A number of authors claim that the surface properties of carriers are related to the activity of catalysts and their resistance to Coke, while no systematic studies have been conducted involving the type and concentration of acid-base centers of multicomponent systems, especially transition metal ions and natural minerals. Despite the large volume of sulfur oil recovery at the enterprises of the Republic of Uzbekistan, due in part to the shortage of aluminum hydroxide, there is practically no production of domestic catalysts for the oil refining industry. In this regard, it is necessary to develop carriers and Catalysts using domestic raw materials and assess the possibility of using them instead of imported ones.

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