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Analysis of Catalysts for Hydropuring Pyrolysis Distillates and Studying the Possibilities of Their Extraction

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Abstract: In this article The patterns of occurrence and determination of the main kinetic parameters of hydrocatalytic reactions and hydrotreating processes of various hydrocarbon feedstocks in the presence of synthesized catalysts were studied. The composition and structure of the active component and active centers of transition metal sulfides, as well as methods for the synthesis of catalysts, are described. Special attention is paid to the features of hydrotreating olefin-containing raw materials.

Keywords: Hydrotreating, process, oil refining, catalyst, concentration, sulfide catalysts.

Hydrotreating is the largest-scale process in modern oil refineries. A wide variety of straight-run petroleum fractions and gas oils of secondary origin (gasoline, kerosene and diesel fractions, vacuum gas oil, various types of oil feedstock) are subjected to hydrotreating, and the process has different technological directions: obtaining ultra-clean diesel fuels, deep purification of gasoline fractions from sulfur, nitrogen and other poisons for their further isomerization or reforming; preparation of vacuum gas oil for further catalytic cracking or hydrocracking, selective removal of sulfur while preserving the olefins of catalytic cracking gasoline, etc.

Environmental requirements played a major role in the development of this process, primarily the fact that when fuel is burned, a very large amount of harmful substances are released into the atmosphere. When processing sulfur and high-sulfur oils, the hydrotreating process is simply indispensable for obtaining products that meet modern quality requirements.

Currently, deep hydrotreating of petroleum fractions to obtain ultra-clean fuels is possible only in the presence of highly efficient catalysts.

To obtain fuels that meet current and future environmental requirements, deep hydrotreating of hydrocarbon raw materials is necessary, which is difficult to carry out without understanding the individual composition of heteroatomic compounds.

Despite the fact that Ni (Co)-Mo(S)/γ-Al2O3 catalysts have been well known since the mid-30s of the last century, when they were used in Germany in the Bergius process for liquefying coal, studies to determine the structure of the active phases and understanding of the workings of its active centers are still ongoing.

The 70s and 80s of the last century were especially fruitful in this regard, when, with the development of new physical methods, many models of the active phase of these catalysts were put forward and studies of catalysts in situ.

Since the late 90s of the twentieth century, publications devoted to the study of the surface morphology of hydrodesulfurization catalysts have resumed in the scientific and technical literature. Currently, new catalysts, and with them new technologies for hydrotreating processes, are associated with research into catalysts at the atomic level.

Modern hydrotreating catalysts, capable of producing motor fuels of the required quality, contain phase II Co (Ni) MoS crystallites on the surface.

The concentration and morphology of this active component, other things being equal, determines the catalytic properties. Therefore, new methods for synthesizing catalysts should ensure the maximum content of type II Co (Ni) MoS phase. The main stages of the synthesis of hydrotreating catalysts are the following: preparation of the carrier and impregnation solution, impregnation of the carrier, drying, possible calcination and sulfidation.

The improvement of supported sulfide catalysts is associated with each stage of preparation; however, the most effective ways to increase catalytic activity should be highlighted.

The main “levers” for increasing the activity and stability of sulfide catalysts are the improvement of catalyst supports and active phase precursors.

The main studied modifiers of the active phase of hydrotreating catalysts are P, F and B, i.e. non-metals, they are introduced into the catalyst either from their corresponding acids and anions, or heteropolycompounds. The promoting effect of modifiers is explained by: - the formation of polymer oxometalates Mo (polyoxometalates (POMs) or heteropoly compounds), which sulfidize more easily than monomeric molybdenum oxide particles; - suppression of the reactivity of the carrier and, as a result, weakening of the negative interaction “active phase - carrier”; - formation of a more active multilayer Co (Ni) Mo (W)S phase II; - suppression of promoter loss due to migration into the carrier through the formation of POM or phosphate anion salts.

With an increase in the content of the above modifiers, the activity of the catalysts passes through a maximum, i.e. The optimal content of the additive is always observed. This may be due to the fact that modifiers such as P, F, B provide, first of all, the acidity of the impregnation solution, including the liquid film formed after impregnation of the carrier and subsequent drying.

The nature of the support has a significant impact on the dispersion of the oxide and sulfide phases of catalysts, sulfidation of the supported precursor, the composition of particles on the surface of the support, particle size distribution of the active component, mass transfer , catalytic properties, process selectivity, deactivation, etc. Therefore, modern developments of highly active catalysts are associated with improving the properties of the support.

Hydrotreating is the final technological process of thermocatalytic purification of dewaxed oil raffinates _

The purpose of hydrotreatment of oil fractions is to increase thermal stability, reduce coking and acidity, and improve the color of base oils.

Hydrotreating of oil fractions is a catalytic hydrogenation process carried out under relatively mild conditions compared to fuel hydrotreating. During hydrotreatment , chemically unstable components are subjected to hydrogenolysis. These are mainly oxidation products and resinous compounds containing sulfur, nitrogen, and oxygen-containing functional groups and unsaturated bonds in the molecule.

The raw materials are distillate and residual oil fractions after dewaxing.

The stability of base and commercial oils (in all cases the same portion of additives was introduced) obtained using the hydrotreating process is higher than that of oils after contact post-treatment. It has also been established that the oil “reacts” to the addition of an antioxidant, the more deeply it is purified and the less aromatic hydrocarbons it contains.

Increasing the quality of oil during hydrotreatment allows for less deep selective purification with a greater selection of raffinate without deteriorating the quality of the final product.

In addition to the listed advantages, the hydrotreatment process is characterized by higher economic indicators: an increase in the yield of the target product by 4-5%, an increase in labor productivity, a reduction in the area of installations, and a reduction in operating costs. The economic disadvantage of the process is higher capital investments, but this factor is compensated by the improvement of other indicators.

The main result of the reaction of aromatic hydrocarbons is the formation of naphthenic hydrocarbons with the same number of rings, as well as naphthenic and aromatic hydrocarbons with a smaller number of rings in the molecule than the original ones.

Naphthenic hydrocarbons of heavy petroleum feedstock are predominantly represented by condensed ring structures. Under mild conditions of the hydrogenation process, these hydrocarbons are quite stable and undergo almost no changes. Under more stringent conditions in the presence of special catalysts, the hydrodecyclization reaction is most typical for them.

In this case, the resulting naphthenic hydrocarbons with a smaller number of rings in the molecule undergo further decyclization with the addition of hydrogen atoms at the sites of rupture of carbon-carbon bonds. As a result, the content of condensed naphthenic hydrocarbons in the product is significantly reduced and the accumulation of monocyclic and non-condensed naphthenic hydrocarbons occurs.

The most progressive significance in the production of high-index base oils is acquired by technological processes of targeted formation in their composition of the maximum content of isoparaffin hydrocarbons with low sulfur content.

An analysis of global trends in progressive innovations from the 60s of the last century to the present day shows that on the path to the best world achievements in the production of base oils, it is fashionable to distinguish three main stages:

1. Application in the production of oils from selected oil oils of catalytic processes of hydrorefining of distillates and raffinates in combination with selective purification and dewaxing processes using new, more efficient solvents;
2. Application for the production of base oils of hydrocracking processes of heavy vacuum gas oil and deasphalted oil , further modified into isocracking , as well as hydrodewaxing processes , then modified into isodewaxing of various raw materials: hydrocracking oils, raffinates , slacks solvent dewaxing. Creation of a fully catalytic flow scheme for the production of VI oils from any oils based on the processes of isocracking and isodewaxing with hydrotreating;
3. Application of technologies for the synthesis of paraffinic (isoparaffin) oils based on α-olefins (hydrogenated poly-α- olefin oils) and on the basis of synthetic oil obtained from natural gas via the Fischer- Tropsch reaction (on cobalt or iron-containing catalysts with subsequent isodewaxing).

The catalytic dewaxing process is a highly flexible and low-cost process for eliminating bottlenecks and expanding traditional solvent production.

Dramatic improvement in the structure of the isomerization catalyst dewaxing MSDW provides high yields and viscosity index, as well as flexibility in raw material selection.

Commercial oils obtained on a high-index base have a high and super-high level of viscosity-temperature properties (IV 130-150-170), low and super-low pour point, and high stability under various operating conditions of equipment.

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