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Catalysts of hydrogenation processes (hydrocracking, hydrotreating and hydrodesulfurization): Production, Market and Forecast in CIS

Sample PDF

Moscow
September, 2012

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ANNOTATION

The report is devoted to investigation of the current standing of the market of catalysts of hydrogenation processes (hydrocracking, hydrotreating and hydrodesulfurization) in Russia and the CIS and forecast of its development. The report consists of 5 chapters, contains 118 pages, including 15 figures, 56 tables, 4 Appendices and address directories.

Methodologically, the work was carried out as a "desk" research. The following information sources were analyzed: first of all, data of state bodies - Federal Service of State Statistics of Russia (Rosstat), Federal Customs Service of Russia (FCS), railage statistics of Russia. In addition, data of the sectoral and regional press, annual and quarterly reports of companies, web-sites of companies, as well as scientific and technical literature, were used.

The introduction briefly summarizes the hydrogenation processes of oil refineries.

The first chapter is devoted to the production of hydrotreating catalysts in Russia. This section provides the nomenclature and characterization of catalysts produced. The statistical and estimated data on volumes of production of these catalysts in Russia are presented. Also, this chapter describes the major scientific organizations dealing with the catalyst technology, as well as enterprises producing catalysts (in Russia and Ukraine).

The second chapter of the report presents data on foreign trade in hydrotreating and hydrocracking catalysts in Russia in 2007-2012, and supplies of hydrotreating catalysts to Ukraine in 2007-2012. In addition, a description of the main foreign suppliers of catalysts of hydrogenation processes to Russia is given.

The third chapter of the report presents data on export and import prices for hydrotreating and hydrocracking catalysts (in 2007-2012) and their comparison with domestic prices in Russia.

The fourth chapter of the report describes the consumption of catalysts in Russia. This section provides a balance of production - consumption in the Russian Federation. The characteristic of the oil industry of Russia and the CIS countries is presented.

The fifth chapter presents a forecast of development of the Russian market of hydrotreating and hydrocracking catalysts for the period up to 2020.

Appendicies 1-4 show the current and projected hydrotreating and hydrocracking units in Russia and the CIS countries.

The addresses and contact information of enterprises producing and consuming catalysts are also given.

INTRODUCTION

Hydrogenation processes are the thermocatalytic conversion of crude oil by the action of hydrogen. Depending on the depth and purpose of the hydrogen action the following types of hydrogenation processes are distinguished: hydrotreating, hydrocracking, and hydrodesulfurization.

It is not always possible to separate the process of hydrotreating and hydrodesulfurization. On hydroforming units, currently acting at Russian crude oil refineries, the processes of desulfurization, denitrogenation, and hydrogenation of unsaturated and polynuclear aromatic hydrocarbons, etc., take place.

To ***hydrodesulfurization*** are subjected, mostly, sour heavy oil fractions (the boiling range of 540-580°C) and the residue of the oil distillation (heavy oil, tar, deasphaltizates). The purpose of hydrodesulfurizationis is the preparation of raw materials for catalytic cracking and hydrocracking, and raw materials for the production of low-sulfur electrode coke and fuel oil.

The main reactions occurring during hydrodesulfurization are the following: the partial hydrogenolysis of bonds carbon - heteroatom in sulfur-, nitrogen- and oxygen-containing compounds with the simultaneous formation of easily removable H_2S, NH_3 and water vapor; the hydrogenation of polycyclic aromatic and unsaturated hydrocarbons. During the hydrodesulfurization also resin-asphaltene and organometallic compounds break down, which leads to the deactivation of the catalyst due to deposition on it of coke and metals.

If the content of resin-asphaltene substances in the raw material is up to 5% (by weight) and the content of metals (as organo-metallic compounds) is up to 200 g/ton, the process is carried out in a fixed bed catalyst. If the raw material contains more than 5% of resin-asphaltene substances and 200-300 g/ton of metals, the process is conducted in a moving or fluidized-bed catalyst.

The process flow diagram of hydrodesulfurization is as follows: a heating of raw materials and a hydrogen-containing gas mixture in tube furnaces; their mixing and the processing in the demetallization reactor; the actual hydrodesulfurization in the main reactor (there may be several reactors); cooling the resulting hydrogenation product; its separation from hydrogen and hydrocarbon gases, in the separators of high and low pressures, respectively, followed by distillation to the desired products with the subsequent cleaning of gases from H_2S, NH_3 and H_2O.

Hydrodesulfurization is carried out at 360-430°C, 10-20 MPa, the volumetric feed rates of 0.3-1.5 h^{-1}, the ratio of hydrogen-containing gas : raw material= (600-1000):1. The hydrogen content in the gas is at least 80% by volume. Demetallization catalysts are usually aluminum-cobalt-molybdenum or aluminum-nickel-molybdenum, containing 2-15% of oxides or sulphides of Mo, Ni, Co; carriers are wide-porous, on the basis of bauxite or $A1_2O_3$. For the hydrodesulfurization the same catalysts are applied, promoted with 10-20% of these oxides or sulphides, carriers are narrow-porous, based on $A1_2O_3$. The yield of liquid products usually reaches 92-94%, the rest are petroleum gas, gasoline, hydrogen sulfide, ammonia, water vapor.

As a result of hydrodesulfurization the content of the following admixes can be reduced in products: of sulfur from 2.5-3.0% to 0.1-0.2% (by mass), of nitrogen -

from 0.4-0.6% to 0.05-0.1%, of resin-asphaltene substances from 5-10% to 1-2%, of metals (V + Ni) from 200-300 to 5-15 g/ton.

To ***hydrotreating*** are subjected not only target fractions (diesel, gasoline, kerosene), but also raw material components for other units, in which the presence of sulfur-, nitrogen-, oxygen-containing compounds and heavy metals (vacuum gas oil, oil fractions) is unacceptable or undesirable.

At hydrotreating the aluminum-cobalt-molybdenum (9-15% of MoO_3, 2-4% of CoO) or aluminum-nickel-molybdenum (up to 12% of NiO, 4% of CoO) catalysts are commonly used, the carrier is Al_2O_3, sometimes with the addition of zeolites, aluminosilicates and others.

Hydrotreating catalysts occupy about 40% of the world market for the oil refining catalysts. In the coming years a progressive deterioration of the quality of oil is expected, so more of heavy and sour crude oil will come for processing. Because of this, and also because of increasing demand for high quality fuel due to more stringent environmental requirements, the role of catalytic hydrotreating processes will increase. And, therefore, the demand for hydrotreating catalysts will also increase.

Hydrocracking is a major deepening processes used in the industrial practice to produce motor fuel from vacuum gas oil (VGO) and heavy gas oils of secondary processes. The hardware design and operating practices of hydrocracking vary depending on the challenges posed by the technological scheme of the particular refinery, and the raw materials used.

Hydrocracking combines the catalytic cracking and the catalytic hydrogenation. Hydrocracking catalysts must combine the hydrogenation and acid functions. In the industry there are hydrocracking catalysts of two types: amorphous and zeolite-containing. They contain as hydrogenating metals nickel, cobalt and molybdenum. To enhance the cleaving activity of the catalyst, amorphous aluminosilicate or a zeolite-containg component is added to it. Splitting and hydrogenation properties of catalysts are controlled by varying the amount and nature of relevant components.

In order to obtain low-sulfur vacuum gas oil (which, as a rule, is the raw material for the process of catalytic cracking) and the relatively small amount of light fractions, the process is conducted at a pressure of up to 80 atm and a temperature of about 350°C ("mild" hydrocracking). In the process of "deep hydrocracking", with more than 50% conversion of raw materials, the process is carried out at pressures above 100 atm and a temperature from 380 to 440°C. In the units of hydrocracking of vacuum gas oil the feedstock conversion per pass can reach 90%, and the variant with the recycle mode provides the conversion of more than 95%.

One of the advantages of the "deep" hydrocracking is the high quality of the products: kerosene and diesel (low sulfur, with a small amount of polycyclic aromatic compounds). In addition, changes in the process conditions can regulate the output of fuels based on seasonal demand and market conditions. There are currently no Russian technology of the production of the catalyst of "deep" vacuum gas oil hydrocracking. Domestic catalysts, employed in the "mild" hydrocracking, can not be used in installations of a "deep" hydrocracking.

In Russia, until recently, a hydrocracking process was virtually not used. The hydrocracking of distillates was represented by the imported installation of the capacity of 1 million tons per year, acting on "Ufaneftekhim". Since 1987, this unit was modified to work on the two-stage technology developed at VNII NP, using domestic catalysts. In the 2000s, the capacities were introduced at plants in Angarsk, Perm (2004), Yaroslavl (2005), in a number of plants the hydrotreating units are reconstructed for the process of a mild hydrocracking (see Appendix 1). The construction of the installation at JSC "Kirishinefteorgsintez" is close to completion. The construction of a hydrocracking unit at JSC "Taif-NK" has already begun. There are plans to build similar units in plants of JSC "Rosneft" ("Komsomolsk Refinery", ANKhK, "Tuapse Refinery"). In all in the coming years 12 units will be erected.

Table 1 shows the main directions of catalytic processes in the petroleum industry of the Russian Federation.

Table 1: The main directions of the use of catalytic processes in the petroleum industry of the Russian Federation

Catalytic processes		**Type of caralysts**
Oil processing		
Hydrogenation processes	Hydrotreating	Aluminum-cobalt-molybdenum and aluminum-nickel-molybdenum compounds with additives of zeolites and aluminosilicates
	Hydro-desulfurization	
	Hydrocracking	The modified zeolite with a hydrogenation metal [Pt-group metals or oxides of nickel (cobalt), tungsten (molybdenum)] and a binder (Al_2O_3)
Reforming		Platinum (0.2-0.6%) on alumina with additives of chlorine, fluorine and rare metals
Cracking		Microspheric and ball zeolite-containing aluminosilicates, including ones with the addition of rare earth oxides

Source: "InfoMine"

An analysis of the current state of the development and production of domestic oil refining catalysts shows a massive decline in their areas of development, updating and upgrading the range of production, compared to the years prior to the collapse of the Soviet Union. As a result, the oil sector has developed a catalyst dependence on imports, the share of which has reached 60-80% of the total consumption. This situation does not correspond to the national interests and the economic security of Russia.

In addition, a catalyst production itself depends on imports: many kinds of raw materials are supplied by imports, even such a common raw material as alumina. According to experts, there are some difficulties in the selection of alumina raw materials with a low content of impurities of iron, sodium, calcium and magnesium. In this regard, during the production of catalyst carriers not only domestic, but also

supplied from overseas high-purity powders of aluminum hydroxide and active alumina are used.

Meanwhile, the production of alumina with a polydisperse pore size distribution is mastered in a number of Russian catalyst plants. However, for the intensification of the oil refining a new modification of the oxide material is requires - a wide-porous alumina with a monodisperse pore size distribution (Sspecific = 340-360 m^2/g; Vpores = 0.8-1.0 cm^3/g, the average pore diameter - 10-11 nm). The presence of such pores simultaneously provides the greatest dispersion of the active component of the catalyst and minimizes a steric hindrance for the occurrence of the desired reaction, particularly during hydrotreating of a wide range of petroleum fractions.

The development and industrial production of such carriers is capable of ensuring the competitiveness of Russian hydrotreating catalysts of diesel and vacuum gas oil for the next 10 years.

I. Production of catalysts for hydrogenation processes in CIS

I.1. The main scientific organizations in Russia involved in the development of catalysts for hydrogenation processes

In the field of catalysis 20-25 science and technology institutions are currently successfully working: state research centers of the chemical profile, RAS institutes and reincorporated trade institutes. Among them, there are about 10 organizations concerned with development of catalysts, including catalysts for hydroforming of crude oil (Table 2).

Table 2: The main domestic developers of catalysts for oil refining

Organization	Activities in the development of catalysts
"Boreskov Institute of Catalysis of the Sibirian Branch of the Russian Academy of Sciences"	Basic research in the field of catalysis, new catalysts and catalytic technologies for various industries
LLC "Company Katakhim", Moscow	Catalytic systems and technologies for hydrotreating motor fuels
LLC NPF "Olkat", St. Petersburg	Catalysts and adsorbents for oil refining
JSC "VNII NP", Moscow	Catalysts, adsorbents and zeolites for petrochemistry and oil refining
JSC NPP "Neftekhim", Krasnodar	Catalysts and adsorbents for petrochemistry and oil refining
"Institute of Hydrocarbons Processing SB RAS", Omsk	Catalysts for cracking, reforming, hydrotreating, sorbents and desiccants, carbon nanomaterials
The Gubkin State Academy of Oil and Gas, Moscow	Catalysts for hydrocarbon processing

*Source: "*Boreskov Institute of Catalysis of the Sibirian Branch of the Russian Academy of Sciences*"*

The most powerful specialized structure that develops catalysts and catalytic technologies is the **Joint Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences** (1958), which was in the Soviet time the parent organization of MNTK "Catalyst".

Currently the Boreskov Institute of Catalysis of the Sibirian Branch of the Russian Academy of Sciences is one of the largest structures in Russia, which is working in the field of both fundamental and practical catalysis.

Applied research in the Institute of Catalysis is conducted in the framework of the federal programs of national importance and focused on the specific practical problems. The Institute is a permanent member of major international and Russian projects, has partnered with many companies and factories in Russia and abroad. The institute created and developed for various industries more than 50 catalysts and catalytic technologies. Developments of the Institute are frequently distinuguished by high awards and diplomas at prestigious forums and exhibitions.

The promotion of the development from original ideas and basic research to implementation is a complex, multistage process that sometimes takes several years. However, in recent years, new high-performance catalysts for industry and technology are created and implemented. These developments include those

perfomed with the participation of the Institute of Catalysis SB RAS. Such technologies are modern and are in demand not only in the Russian market. It can be stated that currently the domestic market of the development of catalysts and catalytic processes of a high scientific and technological level is being formed. Examples are the developed in the Institute of Catalysis SB RAS refining catalysts: microspherical catalysts for dehydrogenation and cracking, bimetallic reforming catalysts, catalysts of improvements and ***deep desulfurization of petroleum distillates***; oxide block catalysts for production of nitric acid; low-temperature catalysts for the ammonia synthesis; the technology of production of new synthetic carbon materials and composites based on them, and many other examples.

In order to meet the requirements of technical regulations on the quality of motor fuels at the Institute of Catalysis SB RAS is developed and commercially produced by CJSC "Industrial catalysts" (Ryazan) the catalyst of *deep hydrodesulfurization of diesel fractions IK-GO-1*, that can provide residual sulfur content in diesel fuel no more than 10 ppm at temperatures of a hydrotreating process no higher than 340-350^{o}C. For its activity in the hydrodesulfurization of diesel fractions, this catalyst corresponds to the best foreign analogues, it is adapted to the domestic raw material base and can be used in domestic units of hydrotreatment L-24-5 (6,7).

Beginning in the late 2007, the catalyst IK-GO-1 is used at the hydrotreatment unit L-24-6 at JSC "Saratov Refinery", which fully confirms the basic guaranteed performance indicators.

One of the main deepening process for the production of motor fuel from vacuum gas oil (VGO) is a catalytic cracking process. A preliminary hydrotreatment of VGO, ensuring the removal of sulfur- and nitrogen-containing compounds, not only can significantly improve the quality of the gasoline and diesel fuel, but also leads to a better performance of catalytic cracking and to the increase of the yield of the desired products.

VGO usually contains up to 3% of sulfur and the reduction of its content in VGO to 450 and 190 ppm allows to produce gasoline containing less than 25 ppm and 10 ppm of sulfur, respectively.

At the Institute of Catalysis SB RAS *the hydrotreating catalyst for vacuum gas oil* is designed and prepared for the industrial production, which provides at the temperature of 380°C, a pressure of 50 atm and flow rate 1.0 h^{-1} the reduction of the sulfur content from 2-3% by weight to the level of 190-200 ppm.

A further development of hydrotreating processes of crude oil is hydrotreating of heavy petroleum fractions (vacuum gas oil and fuel oil), which is required for a subsequent destructive processing. In order to solve these problems, the Institute of Hydrocarbons Processing SB RAS has developed a massive trimetallic hydrotreating catalyst, not inferior in its properties to known catalysts such as Nebula. A distinctive feature of this system is the method of its production, which is based on the principles of mechanochemistry and eliminates the use of any solvents in the technology of preparation of the catalyst.

At present, there are works at the Institute of Catalysis SB RAS for the preparation for commercial development of a promising Russian *catalyst of*

hydrocracking of vacuum gas oil - $Ni/W/Al_2O_3$. The catalyst has already passed the pilot tests in the Institute of Catalysis SB RAS. At a pressure of 100 atm this catalyst provides a depth of the VGO conversion up to 80% with a yield of the gasoline fraction of 25-35 wt %, and the diesel fraction up to 50-55 wt %.

LLC "Company KATAKHIM" is working on the Russian market since 1992. Main tasks of the company are: the development of catalysts, the development of their industrial production, the supply of catalysts to refineries and the engineering service at loading, commissioning, regeneration, activation and the operation of catalysts.

LLC "Company KATAKHIM" incorporates a research laboratory, a department of the synthesis of catalysts, pilot plants to determine the activity and stability of catalysts for hydrogenation processes and devices to determine the activity of catalytic cracking catalysts.

The main directions of the company's activity are ***the catalysts of hydrogenation processes (hydrotreating, hydrocracking)*** and ball catalysts for catalytic cracking units "Termofor" of the type 43-102.

During the time of its work, LLC "Company KATAKHIM" received 47 patents of Russia, published about 40 publications based on research and on the materials of the work of catalytic units at Russian refineries.

"Company KATAKHIM" cooperates with the catalyst plants in Russia: CJSC "Industrial Catalysts", CJSC "Nizhny Novgorod sorbents", LLC "Sterlitamak plant of catalysts", for the activation of the catalysts with JSC "Ufaneftekhim" on the basis of license agreements. Through licensing agreements those companies manufacture catalysts of hydroforming crude oil (hydrotreating, hydrodesulfurization, hydrocracking), which at various times have been uploaded to the units of 21 refineries in Russia.

Catalysts of hydroforming crude oil

Stricter requirements for petroleum products are accompanied by more stringent requirements for products of catalytic processes. Simultaneously the resource base is expanding through the inclusion in hydrogenation processes of secondary distillates.

These trends are expressed in a common task of developing catalysts and processes for specific products. In particular, the release of diesel fractions with the sulfur content of 0.001-0.005% (Euro-IV, V) is based on hydroprocessing with specific parameters for a volume velocity and a flow rate of hydrogen.

LLC "Company KATAKHIM" has a range of catalysts tested repeatedly in industrial settings in various hydroprocesses (RK-222, RK-442Co, RK-442Ni, PK-438W, RK-438Mo, RK-231Co, RK-231Ni), as well as new developments of catalysts and catalytic systems to effectively process a wide range of straight-run and secondary raw materials.

The technologies of the manufacture of these catalysts can be implement at the production line of CJSC "Industrial Catalysts", and at the new production line of LLC "Sterlitamak plant of catalysts".

In 2008, the catalyst RK-442Ni, developed by LLC "Company KATAKHIM", was manufactured on the equipment of LLC "Sterlitamak plant of catalysts". This catalyst is based on the aluminum oxide powder for hydroforming vacuum gas oil, which is a feedstock for catalytic cracking. The catalyst was loaded at the unit L-16-2 of JSC "Salavatnefteorgsintez", where at the hydrotreatment of vacuum gas oil at a flow rate of 1.2 h^{-1} the residual sulfur content is 0.2-0.3 wt%, and with a decrease in a flow rate to 0.6 h^{-1} the residual sulfur content drops to 0.05% by weight. In 2009, for the first time in Russia, at the equipment of LLC "Ishimbai specialized chemical plant of catalysts" a powdered active alumina was produced by a zero-discharge method. The technology was developed by LLC "Company KATAKHIM", which also provided the information support.

On the basis of powdered products of the oxide, hydroxide and amorphized nature, a hydrotreament catalyst of the diesel fraction was manufactured on the equipment of LLC "Sterlitamak plant of catalysts" in a volume of 20 tons to download to units of JSC "Salavatnefteorgsintez". The testing during the hydrotreatment of the diesel fraction showed that the use of this catalyst allows to obtain a product with a sulfur content of 0.001% by weight at temperatures that 15-25^{o}C lower than on the catalyst, based on active alumina, produced by the method of a reprecipitation of alumina trihydrate.

Below in Tables 3-8, the technical specifications of catalysts for hydroforming of crude oil, produced by LLC "Sterlitamak plant of catalysts" (KNT Group) by licenses of LLC "Company KATAKHIM", are presented.

The RK 231M catalyst (Table 3) - Patent of the Russian Federation number 2103065 – is recommended as a catalytic system consisting of catalysts of series RK-231Ni, RK-231Co.

RK-231Ni is applied for hydrodesulfurization, denitrogenation, hydrogenation of unsaturated and polynuclear aromatic hydrocarbons of gasoline and middle-distillate fractions.