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Types of Catalysts in Oil Refining

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Annotation. This article is devoted to summarizing information about the current state and development trends of the catalytic cracking process. The main directions of using the process in the world are studied: obtaining high-octane gasoline, hydrocarbon gases, diesel fuel. In the course of the generalization, the possibilities of involving polymeric waste and biofuel production waste in raw materials were considered, helping to solve the problem of their disposal. The state of the process catalysts and their development trends were studied: a decrease in the content of rare earth metals and an increase in the content of iron. Mention is made of methods of preparation of raw materials that improve the performance of the process.

Keywords. Catalysts, inhibitor, refinery industry, catalytic process, liquid and solid acid.

A catalyst is a substance that speeds up a chemical reaction but is not part of the reaction products. With the help of a catalyst, fast reactions can be carried out at low temperatures. The process by which chemical reactions are accelerated by catalysts is called catalysis. This term was introduced by the Swedish chemist Jöns Jakob Berzelius in 1835. The process in which one of the reaction products or its starting materials acts as a catalyst is called autocatalysis.

Catalysts can be divided into two types: heterogeneous and homogeneous. Homogeneous catalysts are in the same phase with the reactants. Acids and bases are used as homogeneous catalysts. Heterogeneous catalysts form an independent phase, which is separated by an interface from the phase in which the reactants are located. Metals, as well as their oxides and sulfides, can be classified as heterogeneous catalysts.

In all living beings, metabolism depends on biological catalysts called enzymes. These are RNA molecules or protein molecules, as well as their complexes, which accelerate the metabolic process, which is vital for living organisms.

Many industrial processes are also based on the action of catalysts. So, in the production of ammonia, iron acts as a catalyst. Catalysts are also widely used in oil refining and the creation of new materials such as plastics [16].

Also called a catalyst is a part of the exhaust system in cars, which reduces the content of harmful substances in exhaust gases. Thanks to such a catalyst, a chemical reaction takes place, in which harmful substances such as carbon monoxide (CO), hydrocarbons and nitrogen oxides participate. The reaction produces carbon monoxide (CO_2) and nitrogen (N_2), which are less harmful.

A substance that slows down a reaction is called an inhibitor [1].

The refining industry uses the process of isobutane alkylation to produce a high octane gasoline component . Sulfuric and hydrofluoric acids are used as catalysts in industry . Apparently, the use of solid acid catalysts is promising. In the practice of the oil refining industry , zeolites in their pure form are not used as cracking catalysts. They are used in the form of zeolite-containing catalysts , which are conventional amorphous aluminosilicate catalysts , in which up to 25% (mainly 10-20% powder) of type X or Y zeolites is introduced.

Alumina-platinum catalysts in the oil refining industry are mainly used for flavoring and increasing the octane number of gasoline fractions .

In the oil refining industry, several types of catalysts are used for hydrotreating and hydrogenation. The following are methods for detecting activity aluminumcobaltmolybdenum catalyst hydrodesulfurization of petroleum products and hydrogenating nickel -kieselguhr catalyst. Synthetic aluminosilicate catalysts are most widely used in the oil refining industry , especially granular and powdered ones [2].

Currently , macroscopic (ball, tablet), finely dispersed (powder) and microspherical catalysts are used in catalytic cracking processes.

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Due to their high activity and selectivity, zeolite aluminosilicate catalysts are increasingly used in the oil refining industry . Catalyst particles are given a certain shape , most often the shape of a ball with a diameter of 3-6 mm (ball-shaped) or 20-150 microns (microspherical). A pulverized catalyst with a particle size of 1-150 microns is also used; it is obtained by grinding a spherical catalyst or chips. The particles of such a catalyst do not have a definite shape and have an increased attrition. In a number of industries, continuous catalytic processes are used with a moving catalyst, which is also a coolant. Such processes are implemented in the oil refining industry, where they are used under the name thermophore and fluid processes. In the first case, the catalyst-coolant in the form of granules moves from top to bottom . In the second case , the catalyst particles are very small (less than 0.4 mm in diameter) and are suspended in the jet of reacting gases or vapors.

A standard hydrogenation catalyst consists of a mixture of nickel, nickel oxides and diatomaceous earth, formed into pellets and containing 50-55% nickel. Before a liquid- phase hydrogenation catalyst of the type described above can be used , it must be reduced in a stream of hydrogen at 430°. The reduced catalyst is cooled in a stream of hydrogen ; it can be stored under alcohol or saturated with carbon dioxide and stored in a hermetically sealed flask. For use in the present synthesis pelleted catalyst must first be ground into powder. Described catalyst widely used in the oil refining industry. The most common systems among adsorbents (carriers) and catalysts are two-component systems based on silicic acid and hydroxide of any metal.

The porous structure of such mixtures is influenced by both factors affecting individual oxides and a number of additional factors, namely the composition of the mixture , the interaction of hydroxides in the processes of maturation and dehydration. Co-deposition leads to a change in the size of the globules, and, consequently, to a change in the nature of porosity and the value of the specific surface area mixed system . During the precipitation of binary systems , one of the components of which is 5102, and the other is metal hydroxide , which crystallizes over time, silica has a protective effect , which prevents crystallization. Binary oxide systems , such as aluminosilicate gels , are used as catalysts for processes in the chemical and oil refining industries.

Modern oil refinery the industry is characterized by a significant development of catalytic processes . Catalytic processes are also used to purify petroleum products, to give them the required qualities.

Depending on the purpose of the process various catalysts are used. Low-temperature hydrogenation is not used in the oil refining industry , since it does not produce gasoline, which is the main product of cracking and hydrogenation [3]. In addition, catalysts such as platinum or nickel, which are very active at low temperatures , are extremely sensitive to the poisoning action of sulfur compounds contained in petroleum products , and quickly lose their activity as a result of poisoning. Recently, a new technological method for applying coatings on the surface of products has been developed , which consists in immersing the products in a bath in which the polymer powder is in a fluidized state. In the oil refining industry for the production of hydrogen GIAP-3 type catalysts are used.

This catalyst is relatively quickly destroyed (crushed), which increases the hydraulic resistance in tube furnaces . In this regard, it is necessary to unload the furnace by screening the catalyst, which is associated with high costs. Over the past fifteen years, catalytic cracking , carried out in the presence of a spherical aluminosilicate catalyst , has become one of the leading processes in the oil refining industry . Over the same years, the production and direct distillation of sour oils have increased significantly throughout the world , as a result of which oil refineries are forced to use oil products with a significant content of organosulfur compounds . As a result, there is a need for an in -depth study aluminosilicate catalysis of organosulfur compounds. In the oil refining industry as heat transfer fluids widely used high-heated distillates and distillation residues, as well as oil vapours. In some cases, high-temperature bulk solids , including solid catalysts and coke, as well as special liquid heat carriers diphenyl, diphenyl oxide , silicones and highly superheated (at a pressure of 220 atm) water. All these coolants allow heating only up to 250 ° C [4]. Above this temperature, heat transfer is carried out using fire heaters - tube furnaces.In connection with the widespread introduction of gasoline catalytic reformers operating on a platinum catalyst into the oil refining industry, hydrotreatment began to be used as a process for preparing raw materials. The catalytic cracking process is one of the main processes in the oil refining and petrochemical industries . It

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has been used in industry for almost forty years with its steady development. Before the cracking process, the raw material is purified from sulfur, nitrogen and metals that reduce the activity of the catalyst .

In the oil refining industry where reactor devices must be very high productivity, the use of the reactors described above could not solve the problems of catalytic oil refining. Therefore, new, more advanced installations with a moving bed (flow) of a granular catalyst and a fluidized pulverized catalyst were created . Currently , these units are increasingly used in the technology of petrochemical synthesis. The choice of pressure for the process mainly depends on the quality of the initial benzene used for hydrogenation. As you know, at present there are two sources for obtaining benzene - the coke and oil refining industries. A feature of coke -chemical benzene is the content in it in significant quantities impurities of sulfur compounds, only in the most recent years, in connection with the introduction of the hydrotreatment process, the coke industry began to produce benzene with a sulfur content of about 0.0002%. For the processing of sulfur benzene hydrogenation method requires special catalysts containing oxides and nickel , molybdenum, cobalt and sometimes tungsten sulfides.

These catalysts are used in the temperature range of the order of 300-350°C [5]. Alkylation isoparaffins to olefins is the reaction on which processes carried out on a large scale in the oil refining industry are based . Any isoparaffins and almost any olefins can be used for this purpose , and a broad fraction of branched chain products is formed . Catalytic product alkylation usually contains carbon atoms in an amount equal to the sum of the carbon atoms in the paraffin and olefin. The first report on the alkylation of a paraffin with an olefin was published in 1935 by W. V. Ipatiev and A. V. Grosse, who alkylated isobutane with ethylene and isobutylene, and isopentane and 2,2,4-trimethylpentane with ethylene, using boron fluoride as a catalyst. In the chemical and oil refining industries, a large number of various contact apparatuses are used , where processes proceed in the presence of a catalyst. Probably the largest consumer of ion exchangers as catalysts is the oil refining industry, where these materials are used mainly in the processes of cracking and oil refining.

The question is which components of these catalysts timed to their chemical activity has not yet found a full resolution. Thomas studied the structural features of aluminosilicate zeolites and suggested that the active element of the catalyst is hydrogen acid . gel groups (HA15U4). The maximum catalytic activity and maximum acidity corresponds to the ratio of aluminum to silicon equal to one. The areas of application of sorbents are currently very numerous. Sorbents are used not only for the absorption, purification and separation of substances , but also in a number of other specific cases. Mineral sorbents of various structures are widely used as carriers of catalytically active substances and as catalysts.

Catalytic cracking with a powdered catalyst is used in the oil refining industry in the production of high-octane aviation and motor gasolines. On an industrial scale carried out two other processes moving bed reformers both processes use peplatinum catalysts [6]. Using the system thermofor ball catalyst circulation between the reactor and the regenerator led to the development of the catalytic reforming thermofor . The ball catalyst for this process contains about 32% chromium oxide and 68% alumina. In recent years Of great importance is the synthesis of spherical and mythospheric alumina , which are used as catalyst carriers in the oil refining, petrochemical, and chemical industries. The polymerization process is used in the oil refining industry mainly for processing propylene into polymer gasoline , which is a mixture of mainly di- , tri- and tetramers of propylene with an octane number of about 80 according to the motor method . It is also possible to obtain di - and trimers of butenes and the polymerization of mixed raw materials containing propylene and butenes.

The dodecenes obtained in this process are used for the production of detergents. Process catalysts are prepared on the basis of phosphoric acid.

Alkylation of phenols with olefins was first carried out by Koenigs in 1890 using the example of the interaction of phenol with isoamylene in the presence of H_2SO_4. Now, many catalysts are used for this reaction . Until about 1935, the reaction of alkylation of phenols with olefins was mainly of scientific interest. Over the past 20-25 years, in connection with the intensive development of the oil refining industry, especially the processes of cracking and pyrolysis, which supplies truly unlimited quantities of olefins, it has acquired great practical importance and is being widely introduced into the industrial industry. The reaction takes place under mild temperature conditions (80 + 100 ° C) in a tubular reactor with a stationary catalyst bed , which is used as ion exchange resin . Isobutylene for synthesis can be used in a

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mixture with n -butylene , butane and butadiene at its concentration of 35 + 50% (gas fraction of catalytic cracking and pyrolysis). Liquid coming out from the bottom of the reactor the product contains 98+99% ma . MTBE, the rest are impurities of methanol, n - butylene , di- and triisobutylene , and dare/n-butanol [7-9].

The process of obtaining MTBE is much simpler in terms of instrumentation and cheaper in terms of operating costs compared to traditional adkylation of isobutane with olefins and isomerization and should be widely used in the domestic oil refining industry. Catalysis by liquid and solid acids widely used in the oil refining industry. The catalytic action of acids is due to the formation of cations during their interaction with hydrocarbons, called carbonium-ibnes or carbkgGthions. Typically, carbocations are formed by the transfer of a proton from a catalyst (HX acid) to an unsaturated hydrocarbon molecule. REEs are widely used in metallurgy as deoxidizers , degasifiers, and desulfurizers . Introduction of percentages Mischmetal (52% Ce, 24% La, 5% Rg, 18% Nd, etc.) in steel of various grades helps to purify them from impurities, increases heat resistance and corrosion resistance. S alloys, which are light and have a high melting point, serve as structural materials in rocket and aircraft construction. Alloys of Ce with iron, magnesium and aluminum differ low coefficient of expansion and are used in mechanical engineering in the production of parts piston engines . REE addition to cast iron improves their mechanical properties REE addition to chromium, nickel and iron alloys is practiced in the production of heating elements of industrial electric furnaces. REE are also used in the manufacture of control rods that absorb excess thermal neutrons in nuclear reactors . Gd, Sm, Eu have anomalously high neutron capture cross sections. S compounds are used in the manufacture of phosphors , as catalysts in the chemical industry , in the chemical technology of nuclear fuel, in the oil refining industry to obtain catalysts oil cracking , for the production of synthetic fibers, plastics, for the synthesis of liquid hydrocarbons , in non-ferrous metallurgy . REE are used for glass polishing (in the form of polyrite, consisting of Ce, La , Nd and Pr oxides), in the silicate industry for coloring and discoloration of glasses, for the production of chemically and heat-resistant, optical, X-ray resistant , highly electrically conductive and high-strength glasses, for painting porcelain and ceramics . R SE They are also used in lighting engineering, electronics, radio engineering, in the textile and leather industries , in the production of computers, in medicine, and in X-ray technology [10-12]. Natural sorbents are used in various industries for clarification of wines, oils, etc. In the oil refining industry, they are used for both contact and non- collation purification of petroleum products , as well as for additional purification of lubricating oils after their main treatment with selective solvents. In recent years , research has been expanding on the production of active carbons, silica gels, aluminosilicate catalysts and adsorbents, including synthetic zeolites - molecular improvement of properties natural sorbents by their activation and modification. Over the past decade in the global oil refining industry to obtain special aromatic hydrocarbons , high-octane motor fuels and hydrogen steel widely apply the processes of reforming various hydrocarbon feedstocks over platinum catalysts . In many countries there are a large number of platforming installations in operation , and a significant number of installations are under design and construction.

The platforming process is becoming the main catalytic process in the oil refining industry , second in power only to catalytic cracking. Currently _ platforming , together with other processes based on the use of platinum catalysts , accounts for 85% of the production capacity of all reforming]. In addition to platforming , platinum catalysts are used in hydrodesulfurization processes. Flame retardants are negative catalysts that inhibit the reaction at a constant combustion temperature due to a purely chemical effect on it. The mechanism of their influence on the combustion process is to break the reaction chains during the oxidation of the fuel . The inhibitor easily reacts with active .m and reaction centers, turning them into stable products . Various halogen derivatives are mainly used as flame retardants , and the inhibitory activity bromo derivatives are significantly higher than chlorine derivatives. The action of halogen derivatives more effective than inert components, for example, tetrafluorodibromoethane is more than 10 times more effective than carbon dioxide and 20 times more effective than water vapor . Looking for others effective flame retardants. In the oil refining industry Flame retardants are used to extinguish fires [13-15].

An analysis of the prospects for the development of the petrochemical industry in the field of zeolite catalysis shows that the primary task here is the development and implementation of domestic technology for the synthesis of nanosized high-silicon zeolites of the MFI, BEA, MWW and MOR structural types, which are necessary to provide existing petrochemical industries.

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In addition, the creation of new zeolite catalysts and technologies to ensure the integration of refineries and petrochemical companies seems to be an urgent task; creation of direct processes for the conversion of oil into valuable petrochemical products; implementation of “closed cycle” processes – conversion of CO2, waste and plastics into monomers and fuels; the conversion of biomass into fuels and valuable chemicals, as well as the conversion of methane into hydrogen and olefins or aromatic hydrocarbons. The implementation of these tasks will make it possible to make the transition to a new energy policy.

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