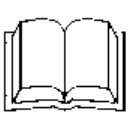
Research Group



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The Russian market of catalysts of platinum group: current status and long-term outlook

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INTRODUCTION

Catalysts are substances that change speed of chemical reactions through repeated intermediate chemical interaction with participants of reactions and do not form part of the end-products.

The overwhelming majority of chemical processes proceeds in the presence of catalysts - more than 70 % of all chemical transformations are carried out with their use whereas as far as new manufactures are concerned their similar parameter exceeds 90%. And a special, individual catalyst corresponds to each chemical reaction frequently picked up by the empirical treatment and differing by chemical composition, porous structure, the size and the form of granules. This circumstance causes presence in the market of the huge amount of catalysts known exceeding one thousand of names today.

From the point of view of their chemical composition catalysts differ by heterogeneity caused by the deposition of an active part on a so-called basis, various natural and synthetic compounds are used that are stable in the process conditions (activated carbon, aluminum oxide, silica gel etc.).

Various methods are used for catalysts manufacture - solutions sedimentation, impregnation, mixture and alloying with the subsequent leaching of an inactive part and also a number of other ways. Thus many catalysts are exposed to special processing - ***activation*** prior to application in the process an active substance is formed as well as porous structure.

Despite of absence of the uniform theory of catalysts selection, conceptions development about the catalysis mechanism allows to formulate some principles of the choice of certain connections suitable for individual types of reaction. Assuming as a basis one or another theory of performance researchers try to find any independent, well known characteristic of a catalyst which could be attributed to catalytic activity. As for today correlation of this parameter is established with a number of *d-electrons* on cation orbital for simple oxides), parameter of a crystal lattice, electric conductivity, an ion charge and radius, energy of chemical bond, etc. The As a rule a basis of this correlation is position of the catalyst elements in periodic system.

Specificity of reaction becomes apparent not only in the strict conformity of a certain catalyst to any chemical transformation, but also in determination of reaction proceeding: various products are formed of the same initial substances depending on catalyst type. Thus a mix carbon oxide and hydrogen in the presence of various catalysts will produce methane, a mix of liquid hydrocarbons, methanol or other kinds of production. A measure of a catalyst specificity is considered to be ***selectivity*** of its effect which is defined as the ratio of speed of a particular reaction to general transformation speed of initial substances in the presence of a given catalyst.

Other major parameter of catalytic properties of substances is ***catalytic activity*** evaluated as a difference of speeds of the same reaction, measured in the presence and

at the absence of a catalyst. The similar parameter is considered to be a specific one because it is usually attributed to a mass unit, volume, concentration or a surface of a catalyst.

Alongside with activity and selectivity of action catalysts are characterized ***by the stability*** determined by expediency of their industrial use in one or another process and securing their service life. The most stable catalysts work for over 10 years (vanadic compounds used for CO2 oxidation are included into this group). On the average 15-20 % of all exploitable catalysts are replaced with new ones every year. Thus it is necessary to emphasize that in some cases there is an opportunity of catalysts special processing named ***regeneration*** that results in the situation when compounds reduce lost properties and are recycled .

It is difficult to overestimate the role of catalysts in the national economy of a country. Deliveries of the given category of products allow to practically completely supervise manufacture of motor and jet fuels, explosives and mineral fertilizers. Alongside with application in the areas providing economic safety of Russia catalytic technologies can resolve important problems of social sphere which are equally important and this includes social objects permanent supply with heat (schools and hospitals) as well as emergency heat supply that is essential to the northern territories of the Russian Federation. In case independent catalytic heating systems are used the economy of fuel heat expenses can reach 30 % in comparison with the traditional centralized systems of heat supply due to exclusion of transportation heat loss. Catalytic methods also provide inhabitancy quality improvement due to neutralization of industrial production waste products. Catalysts application allows to develop household products improving personal comport while being in extreme conditions (for example, the shoe insoles evolving warmth).

I. Use of catalysts containing metal of platinum group in petrochemical and oil-refining industry

I.1 Types and structure of catalysts used in Russia

Up to the present moment uniform classification of catalysts produced by the industry has not been developed. In this connection the division of compounds is carried out on the basis of the following parameters:

a) ***Catalytic reactions type:*** acid-based and oxidation-reduction catalysts are singled out according to it;

b) ***Nature of active substance:*** metal, sulfide, metal-organic, complex, etc. substances are differentiated on this basis;

c) ***Catalytic processes group*** or distinctive features of their technological design (for example, mineral oil cracking, ammonia synthesis etc.).

The last variant of classification is considered to be the most complex one because it provides orientation to the branch structure of the national economy of the country. As a whole it is necessary to emphasize that catalysis and catalytic technologies are of importance in formation of a modern state of a fuel and energy, oil refining and chemical complex of Russia.

According to the chosen approach catalytic processes can be attributed to two major spheres of their application: the oil refining and chemical and petrochemical industry.

In the first case catalysts are involved in such processes of oil refining as *cracking* which basic target is production of motor fuel as well as chemical raw materials as the result of heavy hydrocarbons decomposition; *reforming* which is generally understood as petrol and ligroin oil fractions processing with getting high-octane gasolines and aromatic hydrocarbons and also *hydro refining* - process of selective hydrogenation of organic sulfide, nitrogenous and oxygen compounds that are contained in organic sulfide mineral oil, which, adjoining hydrogen, form accordingly hydrogen sulfide, ammonia and water. This way they are extracted from the product being refined.

Alongside with processes of oil refining, catalysts are widely used in the process holding a special position: *hydrogenation* (reactions of hydrogen addition to simple substances and chemical compounds) as well as the chemical and petrochemical industry - in manufacture of products of organic synthesis, acids and polymers (See Tabl.1).

The analysis of the submitted table allows to single out the processes run in the presence of catalysts, containing metals of platinum group and their compounds. First of all reforming is one of these processes as well as hydrogenation of some chemical products. Besides manufacture of nitric acid through ammonia oxidation ranks among them as well as production of practically all monomers for synthetic rubber

production.

Table 1: Basic fields of catalytic processes use in the Russian Federation industry

Catalytic process	*Catalyst type*
I. Oil refining	
Cracking	Synthetic amorphous and crystal aluminous silicates with rare-earth elements oxides additives
Reforming	Platinum (0,2-0,6 %) on aluminum oxide with chlorine, fluorine and rare metals additives
Hydro refining	Aluminous cobalt molybdenum compounds and aluminous nickel molybdenum compounds with zeolites and aluminous silicates additives
II. Hydrogenation	
Hydrogenation	Metals of platinum group (platinum, palladium) as well as nickel and tungsten on aluminum oxide; silver on aluminous silicate
III. Chemistry and petrochemistry	
Ethylene oxidation to form ethylene oxide	Silver, porous metal, or on inert carriers
Oxidation of naphthalene in phthalic anhydride	Vanadium pentoxide, fused or on carriers
Methanol synthesis from carbon oxide	Zinc - chromic oxide catalysts and copper-containing catalysts
Ammonia synthesis	Metal iron promoted with aluminum, calcium, калия etc. oxides
Oxidation of ammonia in manufacture of nitric acid	Metal platinum (grid), alloys of platinum with some metals, less often catalysts on the basis of oxides (cobalt, bismuth, iron)
Oxidation of dioxide of sulfur in manufacture of a sulfuric acid	Vanadic catalysts on carriers (usually silicate), the active substance has structure V2O5ЧmMe3OЧnSO3 (where Me - alkaline metal);
Manufacture of monomers for synthetic rubber	The basic alumo-chromium and ferro-chromium, calcium - nickel-phosphate catalysts frequently used in fluidized layer; Platinum and platinum-rhenium catalysts on aluminum oxide basis
Vinyl chloride synthesis from acetylene	Mercury chloride (corrosive sublimate) on the activated coal

Source: "InfoMine" Review

By 1990 the assortment of catalysts that were produced in the Soviet Union had reached the level of about 230 grades, and the most numerous class of the compounds was assigned for the use in oil refining (and first of all in catalytic cracking process).The share of these catalysts was about 70 % of the total figure for the country (over 150 names of production), while for the catalysts used in nitric acid manufacture (and finally - in mineral fertilizers) the similar parameter was estimated to be approximately 15 %.

Domestic experts assert that by the moment of disintegration of the USSR (i.e. to the beginning 90es of the XX century) the country had been completely provided with domestic catalysts, and import of the majority of strategically significant types of production was constantly reduced. However in the subsequent years Russia transition to market economy had led to the situation when the state lost control of the economic safety and independence in the field of catalysts manufacture. This negative situation was characterized by regular expansion of foreign manufacturers to the Russian chemical production market. First of all after disintegration of the USSR western companies had started to supersede large-capacity domestic production (and consequently influence the general state of the national economy): processes of ammonia, methanol and a sulfuric acid manufacture. Thus unfair competition as well as open price dumping took place. However the underlying reason behind these events was the suspension of development of new domestic catalysts grades. And meanwhile the specificity of these compounds applications requires not only their regular refeeding but also total updating of the assortment every 5-6 years.

The Russian research organizations as well as industrial sites had returned to development of new catalyst grades in the middle of the 90es and in a rather short period of time a few new compound grades were offered at the home market. By the beginning of 2005 industrial production of over 40 catalysts containing metals of platinum group (the basic ones are submitted in tab. 2) was conducted in the Russian Federation.

Speaking about platinoid inclusion into the structure of various catalysts it is necessary to emphasize original gradation according to which platinum catalysts find an application in reforming processes as well as in nitric acid and synthetic rubbers production whereas palladium compounds are used in hydrogenation. The most numerous reforming catalysts that are characterized by poly functionality usually contain 0,3-0,75 % Pt (by mass). In most cases aluminum oxide is used as a carrier for this type of products. Isomerization catalysts (in particular dearomatization) are represented by compounds where metals (Ni, Pt, Pd, Rh, Ru) are deposited on aluminum oxide or zeolite in quantity of 0,1-1,0 % (by weight).

In the latest years the leading part in the development of new catalysts grades more and more passes directly into manufacturers' hands. In this connection the description of new names of production is submitted in those chapters which cover the present state of the Russian enterprises (See Chapter I.2).

Table 2: Characteristic of catalysts containing metals of platinum group produced in Russia

Name	*Technical Specification (TU) Creator*	*Application*	*Characteristic*	*Comment*
Reforming Catalysts				
AP-56	TU 2177-011-04749189-95 NPO "VNIINeftekhim"	Reforming of non hydro purified petrol fractions with extraction of aromatic fractions	Platinum-containing, on aluminum oxide, promoted with a small amount of fluorine. Extrudates with 2,6-3 mm diameter, length - 5 mm	The catalyst of high processing stability on the raw material containing up to 10 of sulfur compounds
AP-64	TU 2177-011-04749189-95	Reforming of non hydro purified petrol fractions with extraction of petrol components and aromatic hydrocarbons	Platinum-containing on aluminum oxide extrudates in diameter 2,6-3 mm, length - 5 mm	The catalyst is steady against poisonings with the sulphurous and nitrogenous compounds contained in raw material
KR-108	TU 2177-019-04610600-99	Reforming of hydro purified petrol fractions with extraction of petrol components and aromatic hydrocarbons	Platinum-containing on aluminum oxide. Promoted with 2 and 7 group metals. Extrudates diameter 2,6-3 mm, length - 5 mm	The catalyst works steadily at pressure below 1,5 МПа. Catalyzate reforming octane number 95 min.
KR-108U	TU 2177-019-04610600-99 NPF "Olkat", St-Petersburg	Catalytic reforming to extract petrol components aromatic hydrocarbons.	Platinum-containing on aluminum oxide. Promoted with 2 and 7 group metals. Extrudates with diameter of 1,6-2 mm, length - 5 mm	The catalyst is less sensitive to sulfur impurity in raw material and performs steadily with 1 ppm of sulfur and working pressure 1,0-3,0 МПа. Catalyzate reforming octane number 93-98
Name	*Technical*	*Application*	*Characteristic*	*Comment*

	Specification (TU) Creator			
KR-110	TU 2177-014-04749189-96	Reforming of hydro purified petrol fractions with extraction of petrol components and aromatic hydrocarbons	Platinum-containing on aluminum oxide. Promoted with 2 and 7 group metals. Extrudates diameter 2,6-3 mm, length - 5 mm	The catalyst works steadily at average pressure
RB-1	TU 21-145-04749189-96	Reforming of hydro purified petrol fractions with extraction of petrol components and aromatic hydrocarbons	Poly metallic, platinum-containing on aluminum oxide. Contains 2 and 7 group metals. Extrudates diameter 2,6-3 mm, length - 5 mm	-
RB-11	TU 301-03-003-90	Reforming of hydro purified petrol fractions with reception of petrol components and aromatic hydrocarbons	Contains platinum and 2 and 7 group metals. Carrier - aluminum oxide. Экструдаты in diameter 2,6-3 mm, length - 5 mm	The catalyst is used in a combination with other reforming catalysts and this provides increase of target fractions selection
RB-33U	TU 2177-012-23092878-99 NPF "Olkat", St-Petersburg	Catalytic reforming with extraction of petrol components and aromatic hydrocarbons C6-C8	Platinum-containing catalyst based on especially pure carrier characterized by the improved structure, providing high thermal stability of highly dispersed platinum	Allows to produce reformat with 95-100 while processing wide petrol fractions at pressure of 1,0-1,3 MPa

Name	*Technical Specification (TU) Creator*	*Application*	*Characteristic*	*Comment*
RB-22U	TU 21-142-04749-189-95 NPF "Olkat", St-Petersburg	Catalytic reforming of hydro purified petrol fractions with extraction of petrol components and aromatic hydrocarbons	Composition of active platinum and rhenium components and also promoters, dispersed on an internal surface of the carrier (modified active aluminum oxide) at regular intervals. Экструдаты in diameter 1,6 - 2,0 mm, characterized by increased durability (> 1,3), catalytic activity and selectivity. High rhenium, alum platinum	catalyst. It is characterized by the highest performance stability and it is assigned for operation in severe vode of operation. An optimum range 12-15 MPa. Reforming catalyzer octane number - 95-100
REF-21	TU 2177-005-04706192-97 NII "Neftekhim"	Reforming of hydro purified petrol fractions with extraction of aromatic hydrocarbons and petrol components with октановым number 85-87.	Chlorinated, platinum-containing, on rhenium modified aluminum oxide. Экструдаты in diameter 2,6-3 mm, length - 5 mm	Steady performance on raw material containing up to 5 ppm of sulfur