Industrial Catalysts Production, Market and Forecast in Russia

3rd Edition, revised and supplemented

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ANNOTATION

The report is devoted to the investigation of the current standing of the market of industrial catalysts in Russia and the forecast of its development. The report consists of 7 chapters, contains 296 pages, including 35 figures, 106 tables and the Appendix.

Methodologically, the work was done in two stages. In the first phase the so-called "desk" research was carried out. Multiple sources of information were analyzed, particularly data of state bodies - Federal Service of State Statistics (Rosstat), Federal Customs Service (FCS), the statistics of railway transportation of the Russian Federation. In addition, we used data of the sectoral and regional press, the annual and quarterly reports of companies, websites of enterprises, as well as the scientific and technical literature.

In the second stage of research the interviews with manufacturers of catalysts were conducted in order to confirm the information received during the first phase.

The introduction summarizes the characteristics of the catalysts.

The first chapter is devoted to the classification of catalysts by application (oil refining, chemicals, petrochemicals, gas cleaning, car converters) and by the chemical composition (metallic, oxide, sulfide, organometallic, complex, etc.).

The second chapter of the report presents data on resources required for the production of catalysts and their characteristics. In addition, data on the main suppliers of raw materials are given.

The third chapter characterizes the production of catalysts in Russia. This section describes the produced catalysts. The statistics is given on volumes of manufactured catalysts in Russia by main producers, as well as estimates for companies that do not provide data to the Federal Service of State Statistics. Also this chapter gives a detailed description of the 25 Russian manufacturers of catalysts, foreign companies established in Russia their subsidiaries for the production of catalysts, and the main scientific organizations dealing with the technology and the nomenclature of catalysts.

The fourth chapter of the report presents data on foreign trade with the catalysts in Russia in 2001-2009, including exports and imports of catalysts containing precious metals. In addition, a description of the main foreign suppliers of catalysts to Russia is given.

The fifth chapter presents data on export-import prices of various types of catalysts in 2001-2009.

The sixth chapter of the report describes the consumption of catalysts in Russia by end-uses. This section provides a balance of the production - consumption of the product, the sectoral structure of consumption, describes the main consumers, as well as the current state and prospects of the largest consuming businesses.

The seventh chapter presents the forecast of development of the Russian market of catalysts for the period up to 2015.

The Appendix presents addresses and the contact information of enterprises producing and consuming catalysts.
INTRODUCTION

Generally, catalysts are substances, which, entering into an intermediate chemical interaction with the reagents, cause an increase in the rate of chemical reactions, but restore their chemical composition at the end of the catalytic act and are not included in the final products.

The vast majority of chemical processes occur with the application of catalysts - more than 90% of all chemical reactions are carried out using them. At the same time every chemical reaction requires a special, separate catalyst, often chosen empirically and having a different chemical composition, the porous structure, the size and the shape of the granules. This fact stipulates a very large number of the presently known catalysts, over a thousand items.

In terms of the chemical composition the catalysts are characterized by heterogeneity caused by the application of the active part to the so-called carrier, which can represent a variety of natural and synthetic compounds, that are stable in the conditions of the process (activated carbon, alumina, silica, etc.).

For the production of catalysts a variety of methods are used – the precipitation from solutions, soaking, blending and fusion followed by leaching of the inactive part, as well as a number of other ways. However, many catalysts before use are subjected to a special treatment - activation, during which the formation of the active substance and the formation of porous structure are carried out.

The choice of a catalyst for a given process is determined mainly by the technological and economic considerations. For the evaluation of the effectiveness of the catalyst it is necessary to know the performance (activity), the selectivity, the service life, the cost, etc.

The specificity of action is manifested not only by a strict correspondence of a specific catalyst for each type of chemical reactions, but also by determining the direction of reactions: from the same starting materials, depending on the type of catalysts, the formation of various products occurs. Thus, a mixture of carbon monoxide and hydrogen in the presence of various catalysts can produce methane, a liquid mixture of hydrocarbons, methyl alcohol (methanol) or other products. The measure of specificity is the selectivity of the action of catalysts, which is defined as the ratio of the rate of the target reaction to the overall rate of the conversion of precursors in the presence of the catalyst.

Another important indicator of the catalytic properties of substances is the catalytic activity, expressed as the difference between the rates of the same reaction as measured in the presence and the absence of a catalyst, other things being equal. Such a measure is specific, since it usually refers to a unit of mass, volume, concentration or the surface of a catalyst.

Along with the activity and selectivity of action, the catalysts are characterized by the stability, which is defined by the suitability for their industrial use in a particular process and determines the service life. The most stable catalysts work more than 10 years (to them belong the vanadium compounds used for the oxidation of CO₂). On average, 15-20% of all used catalysts are replaced annually. It should be emphasized that, in some cases, there is the possibility of a special treatment of the
catalyst, which is called the **regeneration**, after which the catalysts restore the lost properties and can be used again.

The catalysts belong to the low-tonnage functional materials and are high-tech products with wide cross-sectoral applications, including refineries, chemical and petrochemical, pharmaceutical and food industries, the environment and energy. In Russia, according to "TsNIITENeftehim", up to 15% of the material component of GDP is manufactured with the use of catalysts. In the U.S. this proportion is much higher and reaches 30%. The development of new catalysts, the update of their product range, the increased use in various sectors of the economy determine the structure, technical level and the progress of the chemical and allied industries.

The analysis of the current state of the development and the production of domestic industrial catalysts shows a large-scale decline in the areas of their development, renovation and modernization of production as compared to years prior to the collapse of the Soviet Union. As a result, the oil and gas sector has developed the catalyst dependence on imports, which share reached 60% of the total consumption. This situation does not correspond to the national interests and the economic security of Russia.
I. Classification of catalysts

I.1. Classification of catalysts by application

So far no unified systematization of the commercially available catalysts is developed. In this regard, the classification of compounds is carried out based on the following parameters:

a) the type of the catalyzed reaction, according to which the acid-base and redox catalysts are distinguished;
b) the nature of the active substance, by which the different metallic, sulfidic, organometallic, and other complex catalysts are distinguished;
c) groups of catalytic processes or features of their technological design (for example, petroleum cracking, ammonia synthesis, etc.).

The last variant of the classification appears the most comprehensive, since it implies the orientation on the sectoral structure of the national economy.

In accordance with the chosen approach, catalytic processes can be assigned to one of the two most important areas of their applications: petroleum refining or chemistry and petrochemistry.

In the first case, the catalysts are used in refining processes such as
- cracking, the main purpose of which is to obtain motor fuels and chemical raw materials by the decomposition of heavy hydrocarbons;
- reforming, under which, in general, the processing of gasoline and naphtha fractions of petroleum to produce high octane gasoline and aromatic hydrocarbons is understood;
- hydrotreatment - the process of selective hydrogenation of petroleum products containing the organic sulfur, nitrogen and oxygen compounds, which, by adding hydrogen, form, respectively, hydrogen sulfide, ammonia and water, and in this form are removed from the purified product.

Along with the processes of oil refining, catalysts are widely used in the process of hydrogenation (the reaction of the hydrogen addition to simple substances and chemical compounds), as well as in chemistry and petrochemistry for the manufacture of organic synthesis products, acids, and polymers (Table 1).
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*Source: “InfoMine”*
I.1.1. Petroleum refining

Catalysts of the oil refining processes speed up the catalytic cracking, hydrodesulfurization, hydrocracking, hydrodearomatization, reforming, etc.

The process of catalytic cracking of petroleum fractions is one of the large-tonnage refinery processes. The essence of a catalytic cracking process is based on the splitting of higher hydrocarbons into smaller molecules with a redistribution of hydrogen, released due to a break-up of the "carbon-carbon" bond in the presence of the microspherical zeolite-containing catalyst.

This process is also relevant because, being a secondary, it significantly affects the depth of oil processing and provides a total yield of light oil of up to 85-87% due to the formation of high-octane components of gasoline, diesel fuels, butane-butylene and propane-propylene fractions, as well as dry gas (fractions C₁-C₂), used as a fuel for a refinery.

Over a long period of its development the catalytic cracking is much improved with respect to the contact of raw materials and catalysts (a fixed bed, a moving bed of a spherical catalyst, a "fluidized" bed of a microspherical catalyst), and with respect to applied catalysts (tabletted catalyst based on natural clays, spherical synthetic alumosilicates, microspherical alumosilicates, including zeolite-containing ones).

The progress to date allowed the processing of the increasingly heavier materials. In recent years, there is an increase in a number of installations that use as raw materials the petroleum residues: fuel oil, deasphalted oil and its mixtures with the vacuum distillates (the most popular option at present is vacuum gas oils).

To maximize the yield of desired products and minimize a number of side ones, as well as to achieve high technical and economic parameters of the cracking process, a catalyst should have the following properties:

- the high activity, which determines a greater conversion of the feedstock at other conditions being equal;
- the high selectivity, which is evaluated as the ability of the catalyst to accelerate the reaction in the desired direction, and to reduce the rate of side reactions;
- the stability. The stability of the activity, selectivity, and mechanical properties of the catalyst during operation is particularly important in systems with a fluidized bed of a catalyst. The catalyst must be resistant to abrasion, cracking and pressure of the overlying layers, and shall not wear the equipment;
- the high degree of regeneration, characterized by the ability to quickly and repeatedly restore their activity and selectivity in the oxidative regeneration without affecting the porous structure and without the particle destruction.

Currently the following types of catalysts are widely used:

- the spherical zeolite catalyst with rare earth elements and platinum (producer - "Salavatnefteorgsintez");
- the microspherical aluminosilicate zeolite catalyst with rare earth elements (Omsk NPZ).
The process of catalytic reforming is widely used to improve the antiknock properties of gasoline and for the production of aromatic hydrocarbons (benzene, toluene, xylene). The major product of the catalytic reforming process is also hydrogen, which can be used in refineries in the process of hydrotreating and other processes of hydrogenation.

At the core of the catalytic reforming is the transformation of the petroleum fractions with boiling points in the intervals of 85-180°C into a high-octane component of motor fuel. In the early 50s, it was found that platinum deposited on alumina is an excellent catalyst for reforming. The first installations of the upgraded process, called platforming (due to the use of platinum catalysts), had the working pressure of 2-3 MPa. Then a process of continuous improvement of catalysts and reforming technologies of straight-run gasoline began.

The development of the refining process proceeded in the following areas: improving the stability of the catalyst, increasing the degree of conversion of raw materials, increasing the selectivity of the process, primarily by increasing the formation of aromatic hydrocarbons, improving and optimizing the process parameters, especially in reducing the pressure of the process. As a result, polymetallic catalysts were developed. They contain, in addition to platinum, rhenium, cadmium, and gallium.

Currently as catalysts of this process platinum and ruthenium metals are mainly used, being deposited on the pre-chlorinated carrier - aluminum oxide. According to existing ideas about the course of this process, the dispersed on the support’s surface metal (platinum) is a catalyst for the hydrogenation-dehydrogenation, while the carrier (halogenated alumina) is a catalyst of the acid-base type (isomerization, cracking, cyclization). The forms of platinum in the catalyst are different, and the selectivity of the process depends on their percentage.

The undisputed leader in the development of modern catalysts for the catalytic reforming process (PR-50 and PR-51) is the Boreskov Institute of Catalysis of the Siberian Branch of the Russian Academy of Sciences. The technology of the production of the catalysts, developed in this institute, was implemented on an industrial scale in CJSC "Industrial catalysts" (Ryazan) and JSC "Angarsk plant of catalysts and organic synthesis". These catalysts (PR-50 and PR-51) are now successfully operated at platforming facilities of JSC "Ryazan NPK" and LLC "Kirishinefteorgsintez".

Domestic catalytic reforming catalysts are not inferior to foreign analogues (Table 2), and in a number of technological parameters even surpass them. An important advantage of the PR series of catalysts is the reduced content of benzene in gasoline, with a simultaneous increase in the concentration of aromatic hydrocarbons C8 and C9, which have higher octane number compared to benzene. This is essential in obtaining commercial gasoline, in which the content of benzene should be minimized while the the proportion of other aromatic hydrocarbons should be optimized.
Table 2: Comparison of the PR-51 catalyst with foreign counterparts

<table>
<thead>
<tr>
<th>Indicator</th>
<th>PR-51</th>
<th>Foreign counterpart</th>
</tr>
</thead>
<tbody>
<tr>
<td>Output gasoline / hydrogen, mass%</td>
<td>86-88/2.0-2.2</td>
<td>82-85/1.6-2.0</td>
</tr>
<tr>
<td>The hydrogen concentration in the circulating gas, % vol.</td>
<td>83-86</td>
<td>73-80</td>
</tr>
<tr>
<td>Mean integral temperature, °C</td>
<td>472</td>
<td>480</td>
</tr>
<tr>
<td>The total temperature drop, °C</td>
<td>120-140</td>
<td>80-100</td>
</tr>
<tr>
<td>The yield of aromatic hydrocarbons, % by weight:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>benzene</td>
<td>3.0</td>
<td>5.5</td>
</tr>
<tr>
<td>toluene</td>
<td>15.8</td>
<td>21.3</td>
</tr>
<tr>
<td>hydrocarbons C₈</td>
<td>26.0</td>
<td>23.0</td>
</tr>
<tr>
<td>hydrocarbons C₉</td>
<td>18.2</td>
<td>15.1</td>
</tr>
<tr>
<td>total</td>
<td>63.0</td>
<td>64.9</td>
</tr>
</tbody>
</table>

Source: "Russian Oil, gas, industry" №4, 2004

The main routes of increasing the efficiency of catalytic reforming is to reduce the pressure in the reactor block and to develop new methods for the synthesis of catalysts of this process.

Modern requirements for the process of the synthesis of catalysts:
- the possibility to regulate the composition and the surface structure of the platinum compounds in accordance with existing ideas about the structure of the active sites on the catalyst surface;
- the possibility to regulate the optimal distribution of the active component in the porous structure of the catalyst;
- the possibility to optimize the chemical composition of the carrier and its porous structure.

Several years ago, in the Boreskov Institute of Catalysis SB RAS two new types of reforming catalysts, PR-61 and PR-71, have been developed. The properties of these catalysts in comparison with the base catalyst PR-51 are shown in Table 3.

Table 3: The main characteristics of reforming catalysts
(1.8-2.8 mm diameter grains, the average safety coefficient - 13 N/mm)

<table>
<thead>
<tr>
<th>Type of catalyst</th>
<th>Pt, % by mass</th>
<th>Re, %</th>
<th>Bulk density, kg/m³</th>
<th>The specific surface area, mg/g</th>
<th>Pore volume, cm³/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>PR-51</td>
<td>0.25</td>
<td>0.30</td>
<td>670</td>
<td>230</td>
<td>0.67</td>
</tr>
<tr>
<td>PR-61</td>
<td>0.24</td>
<td>0.30</td>
<td>670</td>
<td>250</td>
<td>0.68</td>
</tr>
<tr>
<td>PR-71</td>
<td>0.23</td>
<td>0.35</td>
<td>680</td>
<td>280</td>
<td>0.63</td>
</tr>
</tbody>
</table>

Source: "Russian Oil, gas, industry" №4, 2004
The comparison of catalysts PR-61 and PR-71 with the base catalyst PR-51 allowed to draw the following conclusions:
- the PR-61 catalyst has almost the same activity as the base catalyst, but it demonstrates a more selective reforming;
- on the catalyst PR-61 the yield of reforming-gasoline is 2-3% (by weight) higher than on PR-51;
- on the catalyst PR-61 a greater selectivity of the aromatization of paraffinic hydrocarbons is achieved (58-60% vs 49-51% for PR-51);
- PR-71 has a greater activity compared with PR-61 and PR-51:
  - using the catalyst PR-71 the reformate octane numbers at the level of 95-96 are achieved at 464°C, and the octane numbers 98-100 - at 474°C, which are 6-7°C lower than for the catalysts of PR-51 and PR-61;
  - the process selectivity in the presence of PR-71 occupies an intermediate position between the PR-51 and PR-61;
- the main advantage of the catalyst PR-71 is its increased activity together with higher selectivity in comparison with PR-61 and PR-51.

In 2005 CJSC "Industrial catalysts" mastered the production of reforming catalyst PR-71 (the catalyst was loaded at facilities of JSC "Saratov NPZ", CJSC "Ryazan NPZ", LLC "Linos", JSC "SPC-Galichina").

**Hydrogenation processes** is a thermocatalytic conversion of crude oil under the action of hydrogen. Depending on the depth and the destination of the hydrogen action there are the following types of hydrogenation processes: hydrotreating, hydrodesulfurization, and hydrocracking.

**Hydrotreating catalysts** (hydrotreating of gasoline, diesel and jet fuels) account for about 40% of the world market for catalysts for oil refining. In the coming years we should expect a progressive deterioration in the quality of oil, so an increasing number of heavy and sour crude oil will be processed. In this regard, and also because of increasing demand for high quality fuels, and due to stringent environmental requirements, the role of catalytic hydrotreating processes will become more important. And, therefore, the demand for hydروprocessing catalysts will rise.

In the diesel and gasoline fractions the presence of compounds containing sulfur, nitrogen and oxygen is strongly discouraged, because it leads to a deterioration of diesel engines and internal combustion engines, causing the formation of a sludge and the so-called lacquer films. The content of these compounds is also undesirable from an environmental point of view. **Hydrotreating** is used not just for commodity target fractions, but also for raw materials for other units, where the presence of sulfur, nitrogen, oxygen-containing compounds and heavy metals is unacceptable or undesirable.

In the hydrotreating the following catalysts are commonly used: Al-Co-Mo AKM (9-15% of MoO₃, 2-4% of CoO) or Al-Ni-Mo ANM (up to 12% of NiO and 4% of CoO), the carrier is Al₂O₃, sometimes with the addition of zeolites, aluminosilicates, etc.

The installations for hydrotreatment of gasoline are mainly working on the catalyst ACM. Catalysis ANM, GO, GKB, and their mixtures are also used. The vast
majority of units for the diesel fuel hydrotreating use mixtures of catalysts AKM (ANMS) with GKD and GS.

Vacuum gas oil as a feedstock for catalytic cracking is subjected to **hydrodesulfurization** with the use of the GO catalyst.

**Hydrocracking** is a process aimed at obtaining high-quality kerosene and diesel distillates and vacuum gas oil by cracking the hydrocarbon feedstock in the presence of hydrogen. Along with the cracking, the products are cleaned of sulfur, olefins and aromatics are saturated, which leads to a high operational and environmental performance of fuels derived.

In Russia, until recently, the hydrocracking process was practically not used. Hydrocracking of distillates was presented by an import unit of the capacity of 1 million tons per year, working on "Ufaneftekhim." Since 1987, this unit is modified to perform a two-stage process developed in VNIINP, using domestic catalysts NMG-90 and GK-8. In the 2000s, the hydrocracking capacities were commissioned on plants in Perm (2004), Ryazan (2005), Yaroslavl (2005), Ufa (2005); and on a number of factories the hydrotreatment units were reconstructed for the process of light hydrocracking. The construction of the unit at JSC "Kirishinefteorgsintez" is carried out. The construction of a hydrocracker at JSC "Saratov NPZ" has already begun. Similar units are planned at JSC "Rosneft" ("Komsomolsk NPZ", ANKhK, "Tuapse NPZ"). In all there are plans to build in the coming years nine units.
1.1.2. Production of sulfuric acid

All industrial methods for the synthesis of sulfuric acid include several stages. The first step is to obtain sulfur dioxide by the oxidation (calcination) of sulfur-containing materials (a need in this stage is not necessary if raw exhaust gases are available, as in this case the firing of sulfides is one of the steps of other processes). The next step is the conversion of sulfur dioxide (IV) \( \text{SO}_2 \) to sulfur oxide (VI) \( \text{SO}_3 \). This oxidation process is characterized by a very high value of the activation energy, which can be decreased with the use of catalysts. The final stage is the absorption (i.e., the interaction of \( \text{SO}_3 \) with water).

The second stage of the production of sulfuric acid - *the oxidation of sulfur dioxide* - is implemented in two ways, which differ by the method of the oxidation of \( \text{SO}_2 \) - the contact method (with the use of solid catalysts) and the nitrous method (with the use of oxides of nitrogen).

*The contact method*, known since 1900, is used for the production of concentrated sulfuric acid. About 80% of \( \text{H}_2\text{SO}_4 \) in the world are produced by this method. The method consist of the one-stage or two-stage catalysis, resulting in a 99.7% conversion of \( \text{SO}_2 \) to \( \text{SO}_3 \).

At present, modern enterprises use *vanadium catalysts*, which replaced platinum and the iron oxides ones. A pure vanadium oxide (\( \text{V}_2\text{O}_5 \)) has a weak catalytic activity, which increases sharply in the presence of alkali metal salts, with the greatest influence of the potassium salts.

During the production of sulfuric acid by the contact method, sulfur dioxide, purified from contact poisons (e.g., arsenic) and the suspended particles by washing in special towers, and then by wet and dry electrofiltration, is enriched with oxygen and passed over the catalyst. During the process the active ingredient in catalysis is in the molten state. The scheme of the oxidation of \( \text{SO}_2 \) to \( \text{SO}_3 \) can be represented as follows:

\[
2\text{V}^{5+} + \text{O}^{2-} + \text{SO}_2 \rightarrow 2\text{V}^{4+} + \text{SO}_3;
\]
\[
2\text{V}^{4+} + \frac{1}{2}\text{O}_2 \rightarrow 2\text{V}^{5+} + \text{O}^{2-}
\]

On the first stage the equilibrium is reached; the second stage is slow and determines the rate of the process.

The \( \text{SO}_3 \) yield as a white mist is 99%. In the absorber tower \( \text{SO}_3 \) reacts with concentrated \( \text{H}_2\text{SO}_4 \) to form pyrosulphuric acid \( \text{H}_2\text{S}_2\text{O}_7 \). From this compound by a controlled dilution with water a pure (colorless 100%) sulfuric acid or concentrated aqueous solutions of \( \text{H}_2\text{SO}_4 \) are obtained.

Vanadium catalysts (VC) are used in the manufacture of sulfuric acid since 1937. Their number at each facility is determined by the productivity, i.e., for 1 ton of the daily output of acid it is necessary to have in a contact device 100 kg of catalyst containing 10% of \( \text{V}_2\text{O}_5 \).

A variety of raw materials and advances in the manufacturing technology for acids and vanadium catalysts led to the use of different types of VC.

*Barium-aluminum-vanadium catalyst* (BAV) corresponds to the formula \( n\text{V}_2\text{O}_5 \cdot 12\text{SiO}_2 \cdot 0.5\text{Al}_2\text{O}_3 \cdot 2\text{K}_2\text{O} \cdot 3\text{BaO} \cdot m\text{KCl} \) and contains: 8% of \( \text{V}_2\text{O}_5 \); 11% of \( \text{K}_2\text{O} \);
35% of SiO₂; 28% of BaO; 4% of Al₂O₃; 5% of KCl и 9% of other compounds (in mass fractions).

_Sulfovanadate-diatomic mass (SVD)_ contains: 6-7% of V₂O₅; 9-10% of K₂O; 56-62% of SiO₂; 2-3% of CaO; no more than 5% of (Al₂O₃ + Fe₂O₃); 18-19% of sulfates (in terms of SO₃).

_Sulfovanadate on silica gel (SVS)_ contains: 8% of V₂O₅; 12% of K₂O; 55-60% of SiO₂; less than 3% of Al₂O₃; 10-15% of sulfates (in terms of SO₃).

_The catalysts IK-1-6_ (developed by the Boreskov Institute of Catalysis) contains: 9% of V₂O₅; 30% of K₂SO₄; 55-60% of SiO₂. Its latest modification - a new generation of high performance catalyst IK-1-6M - is developed in CJSC "Samara Catalyst Plant" in 2003.

_A fluidized-bed catalyst (KS)_ contains: 7% of V₂O₅; 7% of K₂O; 4-6% of Al₂O₃; 55-60% of SiO₂; 16% of sulfates (in terms of SO₃). In the process, it wears out and is carried away in the dust form.

The service life of catalysts is 1-2 years on the upper shelves of the contact apparatus and 4-5 years at the lower layers. The decrease in the catalytic activity occurs due to:

- the transition of a large part of vanadium to the tetravalent state;
- changes in the porous structure of the carrier at violations of the thermal regime of the catalyst;
- as a result of the accumulation of contact poisons - arsenic, iron(II) sulfate, sulfuric acid mist;
- the loss of vanadium in the form of volatile compounds formed with some components of the gas at a low-quality gas treatment.
I.1.3. Production of ammonia, technical hydrogen

The steam conversion of hydrocarbons is the most economical process for producing hydrogen. Currently, Russian plants use the steam conversion of natural gas (methane):

**Hydrogen production** lines, using natural gas, are constructed as follows:
- a purification of natural gas from sulfur compounds, which poison nickel. In the hydrodesulfurization unit thiols are reduced to hydrogen sulfide and olefins on the *Al-Co-Mo catalyst* at 290-370°C. Then, H₂S is removed using zinc oxide.
- a steam conversion of methane (SCM) – primary reforming.

\[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \]

The process is determined by the composition of the catalyst, its activity, the specific surface area, microstructure, porosity, mechanical resistance, thermal and chemical stability, resistance to deposition of coal. Most of the SCM catalysts are based on nickel: cobalt and precious metals are also active, but they are expensive.

Due to the high reaction temperature the carriers with a low specific surface are used (5-10 m²/g): Al₂O₃, MgO, CaO and CaAl₂O₄. Such surfaces are suitable to maintain the stability of the dispersed nickel.

- the medium-temperature and low-temperature conversion of CO to CO₂ and H₂ first occur at 450°C and 3.1 MPa using a *catalyst on the Fe-Cr oxide basis*, then at 200-260°C and 3.0 MPa on *Cu-Zn-Al oxide catalysts*.

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \]

- the cleaning of H₂ from CO₂ by the adsorption of the solution of monoethanolamine (MEA) or a hot solution of K₂CO₃ at 2.8 MPa.

In the process of obtaining **ammonia**, in addition to the above steps (the cleaning, the steam conversion of methane and the conversion of carbon monoxide), the following stages are carried out:
- a steam conversion of residual methane in the mine converter (secondary reforming) at 990-1000°C and 3.3 MPa on a *Ni-Al catalyst*. At this stage the hydrogen is enriched by the air nitrogen to produce a mixture of the composition \( \text{H}_2: \text{N}_2 = 3:1 \), coming to the synthesis of ammonia;
- a purification of a gas by hydrogenation of residual CO and CO₂ in the presence of *Ni-Al catalyst* at 280°C and 2.6 MPa;
- a compression of a purified nitrogen-hydrogen mixture up to 30 MPa;
- a synthesis of ammonia on an *iron promoted catalyst* at 420-500°C.

\[ \text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3 \]

All operating and under construction production units are of the same type. The differences consist mainly in variations of technological parameters, constructive designs and construction materials used. In Russia, under operations are installations designed by: the State Institute of Nitrogen Industry (GIAP), of the French firm Ensa (with the capacity of 600 tons/day), of the American company Kellogg (600-1500
tons/day), of the Japanese company TAK, of the Danish company Haldor Topsoe, etc.
I.1.4. Dehydrogenation of hydrocarbons

Dehydrogenation is the process of removal of the hydrogen atoms, used in particular in the synthetic rubber industry to produce monomers from saturated compounds.

Dehydrogenation catalysts accelerate the cleavage of hydrogen from organic compounds. To dehydrogenation catalysts belong mainly various solid substances, which by the composition can be divided into several groups:
- oxides of alkaline earth, transition and rare-earth elements such as Ca, Zn, Ti, Zr, Cr, Mn, Fe, Mo, Th - catalysts for the dehydrogenation of alcohols, alkanes, alkenes, cycloalkanes, cycloalkenyl, heterocyclic compounds;
- sulfides, tellurides, stibides, arsenides, selenides of Mo, Cd, Zn, Cd, Zr, Ga, Pb, Cr, Ni, Mo, Re, etc. - catalysts for dehydrogenation of alcohols and cycloalkanes;
- borides, nitrides, carbides, silicides, phosphides of V, Zr, Ti, Cr, Mo, W - catalysts of dehydrogenation of cycloalkanes;
- metals Ni, Cu, Rh, Ir, Re, Os, Ru, Pd, Pt - catalysts of dehydrogenation of alcohols, cycloalkanes, naphthene, paraffins, olefins, heterocyclic compounds.

The catalysts of these classes in the form of individual compounds are mainly used in theoretical studies to determine the relationship between their physico-chemical and catalytic properties.

In carrying out industrial processes the multi-component catalyst systems are always used.

The main industrial products derived by dehydrogenation include: isoprene, butadiene, styrene, alpha-methylstyrene. In addition, in the U.S. and Canada 60% of ethylene is obtained by dehydrogenation of ethane on a nickel catalyst, in Russia, this method is used by a single company (JSC "Kazanorgsintez").

Thus, for the dehydrogenation of linear and branched alkanes to olefins Al-Cr, Al-Mo, and Al-Pt catalysts are usually used. By dehydrogenation of isopentane isoprene is produced:

\[
\text{CH}_3\text{CH}(_2\text{CH}_3)\xrightarrow{\text{Cr}_2\text{O}_3, \text{Al}_2\text{O}_3} \text{CH}_2=\text{C}-\text{CH}=\text{CH}_2 + 2\text{H}_2
\]

This is a two-step process. In the first stage in a fluidized bed of Al-Cr catalyst at 530-610°C isoamylene is formed. In the second stage isoamylene, diluted with superheated steam, is dehydrogenated in the fixed bed of Cr-Ca-P or iron oxide catalyst at 550-560°C.

In particular, at JSC "Nizhnekamskneftekhim" in the first stage of dehydrogenation (of isopentane to isoamylene) a microspherical Al-Cr catalyst promoted with potassium oxide is used. The second stage of dehydration (of isoamylene to isoprene) is carried out on the iron oxide catalyst.

In a similar manner on the same catalysts butadiene from butane is obtained.

The Al-Cr catalyst is obtained by impregnating the carrier by solutions of chromium compounds, followed by molding of pellets and calcining. This catalyst works in short cycles of 0.2-0.5 h at 570-590°C; the temperature of the regeneration is 640-650°C, the duration is 0.2-0.5 h.
Cr-Ca-Ni-P catalysts of the stage II are obtained by the co-deposition of phosphates of Ca, Ni, and Cr. The process on this catalyst is carried out in short cycles of 0.25-0.5 h at 600-650°C with the dilution of raw materials by steam.

For the dehydrogenation of butylene the Fe-Cr-Zn catalyst is used, which works in cycles of 4-12 h at 580-630°C with the dilution of raw materials by steam (a regeneration of the catalyst is done in the air-steam mixture). The Fe-Cr-Zn catalyst can be prepared by mixing oxides of Fe and Zn (1.9:1) with the solution of CrO₃, followed by the reduction of Cr⁶⁺ to Cr³⁺ with an organic reducing agent and calcination at 500-550°C.

The Al-Cr and Fe-Cr catalysts are used for dehydrogenation of alkylbenzenes. The main catalyst for the dehydrogenation of ethylbenzene to styrene is Fe-Cr-K oxide with small additions of the compounds of rubidium, zirconium. The process is carried out at temperatures around 600°C with a dilution of raw materials with steam, the styrene yield is about 63% by weight with the selectivity of about 90%. Such a catalyst can be prepared by mixing oxides of Fe and Cr with a K₂CO₃ solution and the promoter, followed by molding pf pellets and calcination at 600-650°C.

For the dehydrogenation of cycloalkanes and cycloalkenes platinum and palladium catalysts on activated carbon, Al₂O₃, CaCO₃ and special ceramic carriers are usually employed. In some cases, the deposited nickel catalysts are also used.

The dehydrogenation of alkanes to form aromatics (dehyrocyclization of paraffins) is carried out at 500-550°C using a catalyst containing oxides of Al, Cr, and V.

The dehydrogenation of naphthenes to cycloolefins is performed on an oxide catalyst at a temperature of 500-600°C. Catalysts for the dehydrogenation of alcohols are various copper compounds such as chromate (III) of copper, in some cases - the deposited nickel catalysts, promoted with tin.

Currently, a process of obtaining formaldehyde by the dehydrogenation of methanol on Zn-Cu catalysts at 600°C is under development. While the method has not received the extensive development, it is very promising because it allows to obtain anhydrous formaldehyde.
I.1.5. The selective oxidation of hydrocarbons

The selective catalytic oxidation, i.e. the oxidation with the preferential formation of a certain product, is one of the main ways of obtaining valuable chemical compounds from hydrocarbons.

The selectivity of the oxidation process is often a necessary condition for its realization in the industry. One of the functions of the catalyst is precisely such an increase in selectivity. In the absence of a catalyst the oxidation of hydrocarbons is characterized by a wide range of products of the oxidation and high temperatures of the reaction.

The catalytic oxidation processes are used to produce oxides of olefins, aldehydes, ketones, quinones, and acids. The main industrial reactions are: the obtaining of formaldehyde, phthalic anhydride, acrylonitrile, and ethylene oxide.

The epoxidation is the process of obtaining olefin oxides by adding an oxygen atom to the double bond of an olefin.

In Russia and abroad, ethylene oxide is produced by the direct gas-phase oxidation of ethylene with air or oxygen in the presence of a catalyst. Virtually the only industrial catalyst is a silver catalyst, used in various modifications. The composition of the catalyst plays an important role, and it is continuously improved through the selection of carriers and promoters. As carriers on a number of Russian enterprises pumice is used, and the Dzerzhinsky "Plant of ethylene oxide and glycol" is applied the catalyst on a corundum porous carrier.

One of the most common technologies of the production of phthalic anhydride is the process of German companies Wacker-Chemie and Lurgi, called the von Hayden process. The initial product is the ortho-xylene, which is oxidized by atmospheric oxygen in a tubular reactor; the reactor tube is filled with a vanadium-titanium oxide catalyst and cooled with a circulating salt melt.

In addition, phthalic anhydride is obtained by the oxidation of naphthalene of the coke production (a catalyst is vanadium salts).

The main way of obtaining formaldehyde is the oxidation of methanol:

$$2\text{CH}_3\text{OH} + \text{O}_2 \rightarrow 2\text{HCHO} + 2\text{H}_2\text{O}$$

In the industry the process is carried out:

I. in the vapor phase at 680-720°C on a silver catalyst, the methanol conversion is 97-98%. This is a highly developed technological process, and 80% of formaldehyde is obtained by this method.

II. in an excess of air using a catalyst from oxides of iron-molybdenum-tungsten at 250-400°C. The conversion of methanol is 98-99%. In this method, formaldehyde is produced by companies Alder-Luciani and Perstorp Formox (in Russia, this technology is implemented only in JSC "Togliattiazot").

There is also an industrial process for the preparation of formaldehyde by the oxidation of methane:

$$\text{CH}_4 + \text{O}_2 \rightarrow \text{HCHO} + \text{H}_2\text{O}$$
The process is carried out at a temperature of 450°C and a pressure of 2.1 MPa, as a catalyst aluminum phosphate AlPO₄ is used.

Table 4 shows the comparative data of the parameters of the traditional technology that uses the silver catalyst, and a more progressive technology with the use of an iron-molybdenum oxide catalyst.

**Table 4: The comparative analysis of parameters of the formaldehyde production by the oxidation of methanol on various catalysts**

<table>
<thead>
<tr>
<th>Production parameters</th>
<th>Silver catalyst</th>
<th>Iron-molybdenum catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting materials</td>
<td>Methanol-water mixture</td>
<td>Methanol</td>
</tr>
<tr>
<td>Service life of a catalyst</td>
<td>Up to 6 months</td>
<td>Up to 3 years</td>
</tr>
<tr>
<td>Temperature of the reaction, °C</td>
<td>650</td>
<td>340</td>
</tr>
<tr>
<td>Yield of formalin from 1 ton of methanol, ton</td>
<td>1.84</td>
<td>2.35</td>
</tr>
<tr>
<td>The maximum concentration of formaldehyde in the end product, %</td>
<td>37.0±0.5</td>
<td>Up to 57</td>
</tr>
<tr>
<td>The content of methanol in a commodity product, %</td>
<td>4-8</td>
<td>No more than 0.3</td>
</tr>
</tbody>
</table>

*Source: “InfoMine” based on data of "Berg-kollegiya" №1(2) 2001*

The one-step synthesis of acrylonitrile is based on the catalytic oxidation of propylene and ammonia. The reaction proceeds as follows:

$$\text{CH}_3\text{CH} = \text{CH}_2 + \text{NH}_3 + 1.5\text{O}_2 \rightarrow \text{CH}_2=\text{CHCN} + 3\text{H}_2\text{O}$$

The synthesis of acrylonitrile is carried out at 450-485°C (the pressure at the reactor outlet is not more than 0.2-0.3 MPa) in the presence of various catalysts. For the reaction of the oxidative ammonolysis of propylene a variety of catalysts are patented. Practically all industrial catalysts fall into two main groups: on the basis of bismuth molybdate and on the basis of antimony oxide. The maximum activity have catalysts with the atomic ratio of Bi:Mo, close to 1 (for example, Bi₂O₃·2MoO₃). The introduction of phosphorus (in the form of salts of polyacids) leads to the stabilization of the activity of Bi-Mo catalysts at their long-term operation.

The process can take place in 2-4 seconds in a stationary (fixed) and in 10-20 seconds in a mobile (fluid) layer of a catalyst.
I.1.6. Hydrogenation of hydrocarbons

The hydrogenation is a process of the transformation of organic compounds under the influence of molecular hydrogen. Hydrogenation reactions are exothermic. To shift the equilibrium to the right it is necessary to use low temperatures, but in this case the rate of a reaction is low. The increased rate is possible with the use of heterogeneous catalysts. The most commonly used hydrogenation catalysts are metals of a variable valence, their oxides and sulfides.

The main technological processes involving hydrogen (without oil refining) are: the production of caprolactam, aniline, alcohols and the hydrogenation of fats.

Caprolactam is produced from benzene, phenol or toluene. The most popular method for the synthesis of caprolactam is from benzene. The technological scheme includes:

- the hydrogenation of benzene to cyclohexane in the presence of Pt/Al₂O₃ or a nickel-chromium catalyst at 250-350°C and 130-220°C, respectively;
- the liquid-phase oxidation of cyclohexane to cyclohexanol at 140-160°C, 0.9-1.1 MPa in the presence of naphthenate or Co stearate;
- cyclohexanol, obtained by the oxidation, is converted to cyclohexanone by dehydrogenation on the zinc-chromium (360-400°C), zinc-iron (400°C) or copper-magnesium (260-300°C) mixed catalysts;
- the transformation to oxime is carried out under the action of an excess of an aqueous solution of hydroxylamine sulfate in the presence of alkali or NH₃ at 0-100°C;
- the final stage of the synthesis of caprolactam is the treatment of cyclohexanone oxime with oleum or concentrated H₂SO₄ at 60-120°C (the Beckmann rearrangement). The yield of caprolactam counting on benzene is 66-68%.

The method for the synthesis of caprolactam from phenol include the phenol hydrogenation to cyclohexanol in the gas phase over the Pd/Al₂O₃ catalyst at 120-140°C, 1-1.5 MPa; the dehydrogenation of the obtained product to cyclohexanone and the further processing as in the method of synthesis from benzene. The yield of caprolactam counting on phenol is 86-88%.

The preparation of caprolactam from toluene comprises the following steps: the oxidation of toluene at 165°C in the presence of Co benzoate; the hydrogenation of the resulting benzoic acid at 170°C, 1.4-1.5 MPa in the presence of 5% Pd on the suspension of finely divided carbon; the nitrosation of cyclohexanecarboxylic acid under the action of nitrosyl hydrogen sulfate at 75-80°C to the crude caprolactam. The yield of caprolactam is 71% based on the starting product.

The main method of the production of aniline is the catalytic reduction of nitrobenzene with hydrogen in a gas (steam) or a liquid phase:

\[ C₆H₅NO₂ + 3H₂ → C₆H₅NH₂ + 2H₂O \]

In the vapor-phase process, aniline is evaporated, mixed with an excess hydrogen and passed through a contact apparatus, filled with a solid catalyst. The
reduction process takes place on the surface of the catalyst until the complete conversion of nitro compounds to aniline.

The advantage of this method is in the fact that the catalyst is not carried away by reaction gases. **Catalysts for this process are active alloys of nickel, aluminum, tungsten, copper, deposited on silicon oxide.** The most suitable catalyst for the reduction of nitrobenzene to aniline is copper, because it acts only to the nitro group without affecting the aromatic ring. In the presence of the copper catalyst the conversion of nitrobenzene to aniline starts at 230°C, and in the temperature range 300-400°C the reaction is fast. With an excess of hydrogen the yield of aniline reaches 98%, and the resulting product contains only traces of azobenzene. Hydrogen can be replaced by a water gas (a mixture of CO and H₂), and carbon monoxide also plays a role of a reducing agent, transforming to dioxide.

Copper, obtained by the reduction of copper hydroxide (II), is more active as a reduction catalyst than that obtained from copper nitrate (II). Copper, deposited on asbestos, is more active than copper deposited on pumice or used without a support. However, copper deposited on asbestos loses its activity quicker.

In the industry, a catalyst is copper carbonate suspended on pumice in a solution of sodium silicate with reduced hydrogen. The catalyst works fine for about a year, but during this period it should twice be regenerated. **The consumption of copper is 1 kg prt 1000 kg of aniline.**

Good results are obtained with a nickel catalyst, combined with vanadium oxide. The reduction on this catalyst is carried out in the temperature range 240-300°C and gives a yield of aniline up to 99%.

The catalytic reduction of the nitro group (NO₂) with hydrogen to the amino group (NH₂) **in the liquid phase** is of no lesser importance than the vapor-phase reduction. Since one of the ingredients of the reaction (hydrogen) is gaseous, then to increase its concentration the process is carried out under the hydrogen pressure in the autoclave. In the periodic liquid-phase process, nitrobenzene, mixed with the solid catalyst is treated with hydrogen under pressure until the absorption of the latter is stopped. After settling of the formed aniline from the catalyst it is siphoned and purified. After a few cycles, the catalyst is filtered off and regenerated. The hydrogenation is carried out with vigorous stirring of the reaction mass to achieve a uniform distribution of the catalyst in the reaction volume.

**Liquid-phase hydrogenation catalysts in the industry are the nickel metal, in the laboratory platinum and palladium as well.** Nickel catalysts are produced by the reduction of nickel oxide with hydrogen formed during the calcination of nitrate, carbonate or oxalate of Ni. The active and stable nickel catalyst can be prepared by heating a mixture of nickel formate, paraffin and paraffin oil to 250°C, followed by rinsing with alcohol and petroleum ether.

A very wide use as the hydrogenation catalyst has the skeletal nickel catalyst, the so-called Raney nickel. It is obtained by treating the nickel-aluminum alloy with caustic when heated until the complete leaching of aluminum. The remaining finely divided nickel has a very large surface area and is very active. The catalyst is stored under water or alcohol as the dry catalyst is pyrophoric. The use of Raney nickel...
catalyst allows producing amines from nitro compounds at atmospheric pressure and room temperature.

By the hydrogenation of aldehydes on the zinc-chromium, nickel-chromium, cobalt catalysts alcohols are obtained.

At the first stage of the alcohols production (in the reaction of the oxo synthesis) aldehydes of the normal and isomeric structures are formed. By this method from propylene butyraldehyde and isobutyric aldehydes are formed, and after the hydrogenation from them n-butyl and isobutyl alcohols are produced. The ratio of products of the normal and isomeric structures varies from 1.5:1 to 3.5:1. This ratio can be improved by changing the reaction conditions and by modifications of catalysts.

The greatest demand in the industry has normal butanol (n-butanol), which is used in the manufacture of plasticizers, in the wood-chemical and paint industries. A more limited use in Russia has isobutanol, the main consumer of which is the paint industry, in addition, it is used as an additive to oils.

In Russia, butanols are produced by 4 companies: "Sibur-Khimprom", "Angarsk Petrochemical Complex", "Salavat" and "Nevinnomyssk Azot".

Technical aspects of the butyl alcohols production at Russian enterprises are different. On "Angarsk Petrochemical Complex" at the first stage of the hydroformylation of propylene, a mixture of normal and isobutyric aldehydes is formed, which in the next stage in the presence of catalysts is reduced with hydrogen to give n-butyl and isobutyl alcohols.

In JSC "Salavatnefteorgsintez" and CJSC "Sibur-Khimprom" the obtained in the first stage mixture of aldehydes is separated, and then the part of the normal butyraldehyde is sent to the production of 2-ethylhexanol.

A growing demand for solid fats is mostly satisfied by the hydrogenation of liquid fats (with obtaining hydrogenated fats).

As catalysts to accelerate the process of saturation in the industry nickel and copper salts are used in the form of fine powders, which increase the contact surface between fats and hydrogen. The process of the fat saturation with hydrogen is carried out at temperatures 190-220°C.

The nature of the reaction of hydrogen in the presence of a catalyst determines its reversibility, i.e., along with the process of the hydrogenation there may be the reverse process - the dehydrogenation.

The reaction of the hydrogen addition proceeds in a heterogeneous environment, where the reactants are in the three states of aggregation (liquid - oil, solid - a catalyst, and gaseous - hydrogen). The saturation is taking place during a simultaneous collision of these three substances. The reaction can go in the opposite direction, if in the points of contact of the catalyst and the fat there will not be hydrogen. Under these conditions the dehydrogenation occurs.
I.1.7. The purification of gas emissions

Gases in industry are usually contaminated with harmful impurities, so cleaning is widely used in factories and enterprises for technological and sanitary (environmental) objectives. Industrial methods of cleaning the exhaust gases from the gases and vapors of toxic impurities can be divided into three main groups:
- the absorption by fluids;
- the adsorption by solid absorbers;
- the catalytic purification.

The catalytic purification of gases is associated with the chemical transformation of toxic components in the non-toxic ones in the presence of catalysts. It is used for the purification from volatile organic compounds, nitrogen oxides, sulfur compounds, carbon, ammonia, ozone.

Known catalysts for the purification can be divided into three main groups:
- catalysts containing precious metals;
- catalysts consisting of transition metal oxides;
- mixed catalysts, including oxides of d-elements and platinum group metals.

Examples of industrial platinum and palladium catalysts on porous substrates (γ-Al₂O₃, silicagel, aluminum silicate, ceramics, aluminum oxide) are catalysts containing 0.5-0.6% (mass.) of Pt and 1.4-2.0% (mass.) of Pd. They are characterized by a high activity. However, high prices and the increasing scarcity of precious metals make their large-scale use in the gas cleaning problematic. Among the oxide catalysts, as cheap ones, oxides of Mn, Co, Cu, Zn are well-proven. The activity of oxide catalysts can be improved by introducing into them small amounts of precious metals.

Nitric oxide is reduced by a reducing gas (CO, CH₄) in the presence of catalysts. As catalysts different metals are used, which are deposited onto carriers (refractory materials). Often a palladium catalyst deposited on alumina is used. The reaction temperature is 400-470°C.

The process of the hydrogenation of carbon monoxide on nickel and iron catalysts is carried out at high pressures and high temperatures.

The removal of sulfur dioxide is based on the principle of oxidation of SO₂ to SO₃ by the contact method in the presence of the V₂O₅ catalyst at 450-480°C.

On most metallurgical enterprises in Russia sulfurous gases are utilized in the form of sulfuric acid, but one of them - the Polar Division JSC "MMC" Norilsk Nickel" (Norilsk) - from the waste gases of the metallurgical production produces elemental sulfur. In addition, the method of cleaning with the obtaining of ammonium sulfate, which can be sold as a fertilizer, is used. SO₂ is oxidized to SO₃. Then, at a temperature of 220-260°C gaseous ammonia is injected. The resulting crystals of ammonium sulphate is separated in cyclones and electric filters.

In the catalytic purification of gases from organic materials Cu, Cr, Co, Mn, Ni, and in some cases - bauxite, zeolites are used as catalysts. The catalysts may be divided into:
- metallic (platinum group metals or base metals deposited on the tape, wire mesh, stainless steel spirals);
Catalysts deposited on metallic carriers have an advantage. They are more thermally stable, durable, and easily regenerated.

As catalysts for the hydrogenation of organosulfur compounds with hydrogen the contact masses based on oxides of Fe, Co, Ni, Cu, Zn are used. For the hydrogenation with steam the catalysts containing as a component the iron oxide are employed.

Table 5 shows the basic types of catalytic systems for the gas purification.

<table>
<thead>
<tr>
<th>Catalyst Type</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-Mn oxide catalyst</td>
<td>A high-temperature catalyst for the purification of industrial gas emissions from organic compounds and carbon monoxide, as well as for the catalytic combustion of methane and other fuels.</td>
</tr>
<tr>
<td>Al-Cu-Cr catalyst</td>
<td>A medium-temperature catalyst for the purification of industrial gas emissions from organic compounds and carbon monoxide.</td>
</tr>
<tr>
<td>Al-Cu oxide catalyst</td>
<td>The low-temperature catalyst for the purification of gases from impurities of formaldehyde, methanol and carbon monoxide.</td>
</tr>
<tr>
<td>Al-Co-Cr catalyst</td>
<td>Purification of industrial gas emissions from organic compounds, hydrogen and carbon monoxide.</td>
</tr>
<tr>
<td>Al-Pd catalyst</td>
<td>Purification of gas emissions from the impurities of organic compounds and carbon monoxide.</td>
</tr>
<tr>
<td>Al-V catalyst</td>
<td>Selective reduction of nitrogen oxides with ammonia in the flue gas of the nitric acid production in UKL units.</td>
</tr>
<tr>
<td>Co oxide catalyst of ozone decomposition</td>
<td>Purification of industrial gas emissions from ozone and ozone-catalytic removal of volatile organic compounds. It is used in the &quot;corona discharge&quot; installations.</td>
</tr>
<tr>
<td>Al-Fe-V catalyst</td>
<td>Catalytic afterburning of tail products of the Claus process.</td>
</tr>
</tbody>
</table>

*Source: data of JSC "Katalizator"*
I.1.8. Neutralization of automobile exhausts

Changing requirements for vehicles, improving the technical regulation of the environmental safety in Russia led to the development of special regulations on automobile emissions. Thus, Russia not only put in place the technical standards for vehicle emissions, but also significantly stimulated the domestic market for the production of means to ensure the implementation of these standards.

An autocatalyst (or a catalyst for post-combustion of solid and liquid fuels), in general, is a cellular (block) structure coated with a layer of platinum or palladium alloy, increasing the contact area of exhaust gases with the working surface. Remains of unburned CO, CH, NO, touching the surface of the catalyst bed, are completely oxidized by oxygen present in exhaust gases. The reactions give off the heat, warming up the catalyst, resulting in the activation of the oxidation reaction.

The process of the production of autocatalysts, also known as neutralizers or converters of exhaust gases, comprises two main phases, the first of which is manufacturing the catalyst directly on the metallic or ceramic carrier; and the second one is its packaging in a metallic case (canning). The key technology operation is the first stage - the production of catalysts, while canning is not a serious technological problem and can be performed on most engineering companies with the stamping and welding equipment.

Speaking about the content of various platinum group metals in autocatalysts of different types, it is important to emphasize that, traditionally, diesel driven cars, which include most of the trucks and buses in the world, are equipped with converters with platinum catalysts. These catalysts have a high efficiency in neutralization reactions of hydrocarbons (including those present as the dispersed particles) and CO, but their disadvantage is the high activity in the oxidation of sulfur to form SO₃.

Palladium autocatalyst are less effective than the platinum analogues in the oxidation reaction of products of an incomplete combustion, but they are characterized by lower activity in the oxidation of sulfur dioxide to sulfur trioxide. In this context, with an appropriate revision palladium or combined platinum-palladium catalysts can replace conventionally used platinum catalysts in diesel converters.

Converters for gasoline engines are based on a system platinum-palladium-rhodium, and the amount of rhodium in the total loading of platinum group metals with the improvement of the engine design is reduced from 17-20% to 9-11%.

The works on a partial or a complete replacement of platinum by palladium are going on quite a long time - more than 30 years. The problems in the technological aspect do not arise, however, when developing the final catalyst it is necessary to carefully consider the requirements for a converter, which depend mainly on the type and the quality of the engine, the exhaust gas composition, current environmental standards, the fuel, resources, etc.

When choosing a catalyst composition, as a rule, there are no universal solutions, and depending on the particular motor vehicle it is necessary to carry out a considerable amount of finishing works in the support of the selected catalyst.
I.2. The classification of catalysts by the chemical composition

By the nature of the active substance catalysts can be divided into: metallic, oxide, sulfide, organometallic, complex, etc.

**Oxide catalysts**

An important role in the catalysis have transition metal oxides (Cr$_2$O$_3$, Al$_2$O$_3$, Cr$_2$O$_3$/Al$_2$O$_3$, Mo$_2$O$_3$/Al$_2$O$_3$, etc.). The catalytic properties of these substances are determined by the presence in transition metal atoms of several degrees of oxidation, which in the conditions of catalysis are easily changed by the transfer of an electron from an atom of another agent. For example, Mo in the oxides can have oxidation degrees Mo$^{2+}$, Mo$^{3+}$, Mo$^{4+}$, Mo$^{5+}$ and Mo$^{6+}$, so it is easily oxidized and reduced during the heterogeneous catalysis, thus providing a catalytic cycle.

To oxide catalysts belong natural materials (bauxite, diatomaceous earth, clays). Natural catalysts are cheap, the technology for their preparation is relatively simple. Natural clays are most widely used in industrial catalysis. They represent a mixture of various aluminosilicates and their isomorphous substitution products, and also contain sand, limestone, iron oxides, mica, feldspar and other impurities. Some natural aluminosilicates such as kaoline, have a relatively high catalytic activity in reactions of the acid-base catalysis in their natural form, after drying and calcination. Most others require more in-depth pre-treatment.

**Metallic catalysts.**

Metals are usually much more active than oxides and have a more universal catalytic activity, although generally they are less selective. The most versatile are metals of the VIII group of the periodic table, especially Pt and Pd, which catalyze various oxidation, hydrogenation, dehydrogenation, etc. reactions at low temperatures. The catalytic activity is determined by the electron configuration and the symmetry of the d-orbitals of surface atoms.

Metals that are at the end of the transitional periods have in the d-shell holes (the absence of electrons), which facilitates their participation in the catalytic transformation. Metals in the beginning of the period, usually form a strong bond with the molecules of the reactants. This leads to the formation of phases (surface or bulk) of oxides, hydrides, etc., which reduce the catalytic activity of a metal. Thus, Ni is active in the hydrogenation reactions, and copper is inactive.

The industry widely uses fine metal catalysts deposited on carriers (SiO$_2$, Al$_2$O$_3$, aluminum silicates, activated carbon, diatomaceous earth, etc.). This increases the surface of the catalyst, reduces its consumption and prevents the particles from sintering.

In addition, the industry widely uses metal catalysts produced in the form of wire, foil, plates, discs, tapes, etc.

One of the most common skeletal catalysts is the Raney nickel. The catalyst is prepared by the treatment of the alloy of nickel and aluminum by an alkali solution. Aluminum is leached from the alloy in the form of aluminate and nickel is partially converted into nickel hydride.

The resulting catalyst has a specific porous structure (a skeletal catalyst) and contains a large amount of adsorbed hydrogen and nickel hydride.
Along with nickel catalysts a widespread use have platinum and palladium catalysts. The use of these catalysts is limited by their high cost. The most frequently used are platinum and palladium catalysts with a high degree of dispersion in the form of so-called platinum or palladium black. Widely used are also platinum and palladium catalysts obtained by the deposition of metals, their chlorides and oxides to carriers - charcoal, pumice, silica, silica gel.

**Sulfide catalysts**

Sulfides of molybdenum, tungsten (MoS₂ and WS₂), etc. are stable and relatively cheap industrial catalysts. On these catalysts very large volume processes - hydrotreating and hydroforming of petroleum fractions - are performed. These processes involve the removal of impurities from the various oil fractions, the improvement of the quality and performance characteristics of fuels, oils; and the removal of raw materials of a secondary origin, which are obtained by the destructive processing of heavy petroleum fractions. The role of these processes is steadily increasing due to stringent environmental requirements for the fuel quality, which are introduced in all developed countries.

**Metal complex and organometallic catalysts**

The best known type of metal complex catalysts are the Ziegler-Natta catalysts - catalytic complexes formed by interaction of transition metal compounds [TiCl₄, TiCl₃, VOCl₃, (C₅H₅)₂TiCl₂, etc.] with alkyl derivatives and other compounds of metals of groups I-III (AlR₃, AlR₂Cl, LiR, MgRCl, ZnR₂, etc.). These catalysts are used in the olefin polymerization.

The Ziegler-Natta catalysts may be of heterogeneous and homogeneous types. Among the heterogeneous catalysts the most important are Ti-Mg-, V-Mg- and organometallic chromocene catalysts. The first two are widely used in the synthesis of stereoregular polypropylene and polyethylene in a suspension and a gas-phase modes. The catalysts are halides of Ti and V, attached to the substrates containing MgO, MgCl₂ or polyethylene with grafted fragments of MgR and MgCl. Chromocene catalytic systems are used in the production of polyethylene in the gas phase in a fluidized bed.

A common type of heterogeneous catalysts is immobilized catalysts in which active sites are fixed on the carriers - organic or inorganic materials (alumina, silica, various polymers). The increased stability is characteristic for gel-immobilized catalytic systems, in which the active site, including the transition metal compound, is not only on the surface but also inside the gel, which is a specific type of rubber or some other macromolecular compound.

To homogeneous catalysts belong complexes (C₅H₅)₂TiCl₂, (C₅H₅)₂VC₁₂ or TiOR₄ with organoaluminum compounds, widely used for the dimerization and polymerization of ethylene. Homogeneous zirconocene catalysts, representing a set of cene, for example pentadienyl or indenyl, zirconium compounds with methylaluminoxane [A₁(CH₃)O]ₙ, allow to obtain polyethylene and other polyolefins. With their help, in particular, it is possible to produce polypropylene with a different stereospecificity, including the isotactic, polyisotactic, fully or partially syndiotactic structure that gives the polymer a number of valuable properties (e.g., impact resistance).
The stereospecificity of these catalysts is determined by the nature of the transition metal, a ligand environment of the central atom, a lattice type of a catalyst, etc.

By their activity and specificity the Ziegler-Natta catalysts are close to the enzyme catalysts, which makes it possible to conduct catalytic polymerization processes with a high yield and a selectivity for the main product.

**Mixed catalysts**

In the reactions of the acid-base type (cracking, dehydration, isomerization, etc.) the high activity have catalysts, consisting of several substances - metal oxides with a different cation charge, amorphous aluminosilicates and zeolites, heteropolyacids, sulfates, phosphates, etc.

Mixed catalysts are distinguished by the fact that almost all their ingredients are in a commensurate quantity and are active for this reaction. The components of the mixed contact mass during their formation may react with each other to form a new, more active compound. Supported catalysts are a widely used type of complex contact masses.

It is just the surface of the mixed systems, where it is easier to form reactive charged particles.