CATALYSIS IN CHEMICAL
AND PETROCHEMICAL INDUSTRY

State-of-the-Art in the Industrial Production and Use
of Zeolite-Containing Adsorbents and Catalysts in Russia

O. S. Travkina[a], M. R. Agliullin[a], and B. I. Kutepov[a], *

[a] *Institute of Petrochemistry and Catalysis, Ufa Federal Research Center, Russian Academy of Sciences, Ufa, 450075 Russia*
**e-mail: kutepoff@inbox.ru*

Abstract—The ways for the production of zeolite powders, which are currently manufactuired on an industrial scale, and their conversion into grained zeolite-containing adsorbents and catalysts are studied. Some data on the Russian manufacturers of these materials are presented. A brief overview on the utilization of these materials in adsorption drying, the purification and separation of gaseous and liquid media, and the catalytic processing of hydrocarbons in Russia and worldwide is given.

Keywords: zeolites, adsorbents, catalysts, drying, purification, separation, hydrocarbons, catalysis

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INTRODUCTION

The term zeolites has long described crystalline hydrated group 1 and 2 metal aluminosilicates from whose microporous structure water can be reversibly extracted by moderate heating without destroying the silicon–oxygen framework [1, 2]. To include nonaluminosilicate composites and structures, the term zeolite and zeolite-like materials was introduced for materials whose framework density is 19 to 20 tetrahedrally coordinated framework atoms per 1000 Å^3 [3].

The main fields of natural zeolite application are construction, agriculture, environmental engineering, and the pharmaceutical industry [4–8]. The global production of natural zeolites exceeded 3.5 million t in 2018. The reasons for the wide use of natural zeolites are the availability and low cost of zeolite-rich rock, and the lack of competing minerals and rocks at comparable prices. At the same time, adsorbents and catalysts prepared using natural zeolites are less efficient than their analogs produced using synthetic zeolites, so around 250 zeolites and zeolite-like materials have already been synthesized [9]. For one reason or another, however, few of them (zeolites A, X, Y, L, ferrierite, mordenite, ZSM-5, ZSM-12, ZSM-23, silicalite-1, Beta, MCM-22, Rho, Eu-1, TS-1, SAPO-11, and SAPO-34) have found industrial use [10, 11].

Since the creation of the first synthetic zeolites as a new class industrial materials in 1954, their global production had grown to 1.86 million t in 2014 [12], of which no more than 5000 t were produced in Russia.

The main uses for synthetic zeolites are ion-exchange materials, adsorbents, and catalysts. The greatest (72% in volume) use for synthetic zeolites is detergents [10]. In countries where it is illegal to use sodium tripolyphosphate $Na_5P_3O_{10}$ in synthetic detergents, zeolites A and P are used as cation exchangers to remove hardness cations from water. Their content in synthetic detergents can be as high as 25 wt %. Approximately 1.4 million t of zeolites was used for this purpose in 2014 [12]. Zeolites for synthetic detergents are currently imported to Russia because of the high prices of the raw material (alumina trihydrate) for their production.

The second largest (~17% in volume) users of synthetic zeolites are different zeolite-containing catalysts. In monetary terms, they account for approximately 55% of the total sales of zeolite-containing materials [10]. The global consumption of zeolite catalysts in 2014 was estimated at around 300000 t [10], of which no more than 10000 t were produced in Russia and consisted mainly of oil fraction cracking catalysts.

The use of synthetic zeolites in adsorption processes is diverse and includes the drying and removal of sulfur compounds from, natural, associated, and refinery gases; petrochemical streams (e.g., ethylene and propylene) and refrigerants; the production of adsorbents for insulated glass units; the separation of gas mixtures (e.g., xylenes and normal paraffins); and the production of oxygen via air separation (different variants of pressure swing adsorption). The global production of zeolite adsorbents in 2014 was estimated to be 180000–200000 t [12], of which no more than 2000 t were produced in Russia was and included mainly adsorbents for the drying and removal of sulfur compounds from natural, associated, and refinery gases, and ethylene and propylene [12]. Zeolite-containing

Table 1. Conditions for the crystallization of zeolite powders manufactured in Russia

Zeolite	Conditions of crystallization			Reference
	Composition of reaction mixture	Temperature, °C	Time, h	
A	$(2.0-2.4)Na_2O \cdot Al_2O_3 \cdot (2.0-2.4)SiO_2 \cdot (60-100)H_2O$	60–70	8–12	[1]
X	$(2.0-2.4)Na_2O \cdot Al_2O_3 \cdot (3.0-3.5)SiO_2 \cdot (60-100)H_2O$	90–95	20–24	[1]
Y	$(2.0-2.2)Na_2O \cdot Al_2O_3 \cdot (6.0-6.5)SiO_2 \cdot (150-160)H_2O$	90–95	32–48	[1]
Offretite	$(0.7-0.8)R_2O \cdot (4.5-4.7)Na_2O \cdot (5.6-5.7)K_2O \cdot Al_2O_3 \cdot (25.0-26.0)SiO_2 \cdot (448.0-460.0)H_2O$	96–98	144–150	[22]
Mordenite	$(2.5-3.0)Na_2O \cdot Al_2O_3 \cdot (12-20)SiO_2 \cdot (200-300)H_2O$	125–155	5–8	[23]
ZSM-5	$(2.0-2.2)Na_2O \cdot (2.1-2.3)R^* \cdot Al_2O_3 \cdot (30-60)SiO_2 \cdot (444-750)H_2O$	160–180	48–72	[23]
Beta	$(2.0-2.2)Na_2O \cdot (4.6-9.0)R^* \cdot Al_2O_3 \cdot (15-35)SiO_2 \cdot (400-550)H_2O$	150–160	24–120	[24, 25]

* R is the cation of the structure-forming agent (e.g., tetrabutylammonium bromide or tetraethylammonium hydroxide).

adsorbents for insulated glass units are imported into Russia.

Different problems of the industrial production of zeolite-containing adsorbents and catalysts and their use worldwide were described in detail in [1, 2, 10, 11, 13–21].

1. PRODUCING GRANULATED ZEOLITE-CONTAINING ADSORBENTS AND CATALYSTS

1.1. Ways for the Production of Industrially Important Zeolite Powders

The first stage of the production of granulated zeolite-containing materials is the synthesis of fine zeolites. The efficiency of a certain use of a certain zeolite depends on its chemical and phase composition, its degree of crystallinity, the characteristics of the porous structure, and the crystal size distribution. These characteristics are controlled by the conditions of synthesis. Table 1 presents the compositions, temperatures, and durations of the synthesis of zeolites manufactured in Russia (zeolites A, X, Y, L, mordenite, ZSM-5, and Beta). We can see that each type of zeolite is characterized by its own set of values of the composition of the reaction mixture and other synthesis parameters that are required for successful crystallization. The production of each zeolite is therefore a unique process. Note that the literature contains neither exact values of the parameters of fine zeolite synthesis nor supporting data from the manufacturers.

The main stages of the industrial synthesis of any zeolite are the mixing of the initial components to obtain a reaction mixture of the required composition (see Table 1), low-temperature holding, crystallization proper, washing, filtration, and drying (Fig. 1) [1, 11, 14, 26].

The effect the parameters of the crystallization of fine aluminosilicate zeolites have on the kinetics of crystallization and the physicochemical characteristics of the resulting materials was described in [1, 11, 14]. It should be noted that different features emerge upon moving from the laboratory synthesis of zeolites to their industrial production. In industrial-volume crystallizers, it is difficult to ensure the formation of a uniform gel of a required composition at the stage of mixing of the initial components. This is done by using diluted solutions (which lowers the productivity of each m³ of the interior of the apparatus), changing the order of their mixing, and stirring intensely. If these conditions are changed, zeolite of the required quality fails to crystalize.

The main kinetic parameter of zeolite crystallization is the temperature of crystallization. The durations of the induction period and synthesis are shortened as the temperature of crystallization rises. The process temperature can also determine the equilibrium composition of the crystallization products, so the rate of heating the reaction mixture is also a most important parameter. The reaction mixtures in industrial crystallizers are obviously much more difficult to heat than under laboratory conditions. This problem is solved by directly feeding superheated steam into the reaction mixture, using steam-jacketed crystallizers, or pumping the reaction mixture through heat exchangers. The heat-transfer problem can also arise while cooling large volumes of the mixture after crystallization, when the products can remain in hot solutions longer than is required [11, 26].

An important stage of the production of molecular sieves is separating the crystalline product from the mother liquor with subsequent washing to prepare it for further treatment. The solid and liquid phases are separated via filtration or centrifugation using belt or drum filters, or plate-and-frame presses. Finer zeolites with particles less than 1 μm in size are manufactured internationally using centrifuges of different types [11].

Washing is typically done in filtration equipment. Excessive washing can result in partial decationization
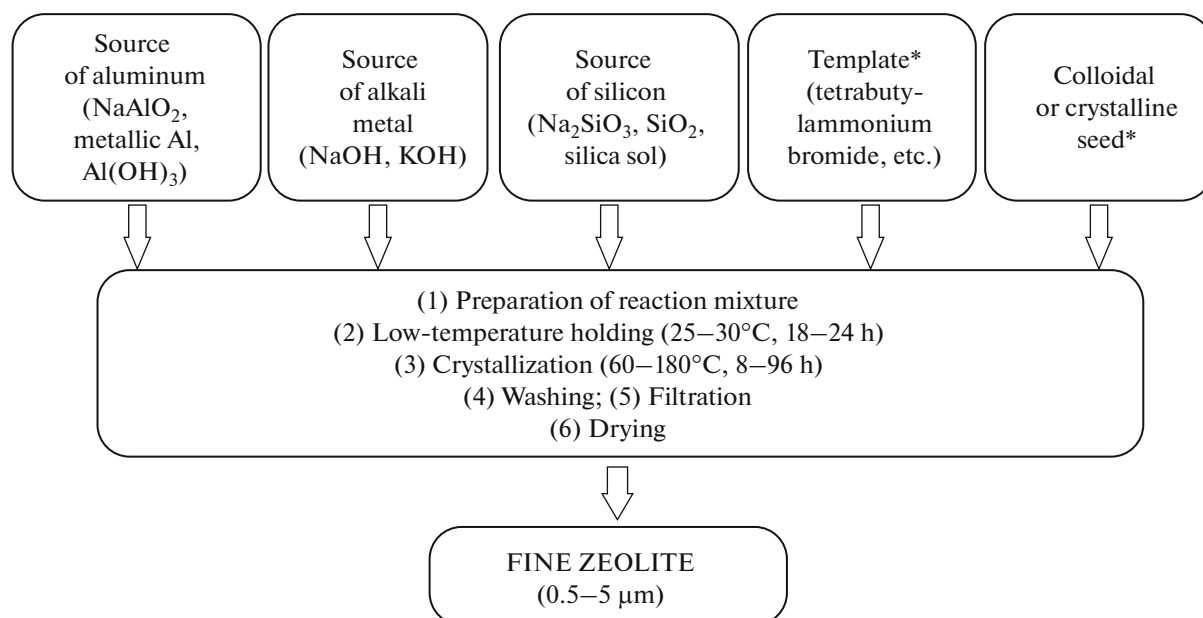
Source of aluminum ($NaAlO_2$, metallic Al, $Al(OH)_3$)	Source of alkali metal (NaOH, KOH)	Source of silicon (Na_2SiO_3, SiO_2, silica sol)	Template* (tetrabuty-lammonium bromide, etc.)	Colloidal or crystalline seed*

(1) Preparation of reaction mixture
(2) Low-temperature holding (25−30°C, 18−24 h)
(3) Crystallization (60−180°C, 8−96 h)
(4) Washing; (5) Filtration
(6) Drying

FINE ZEOLITE
(0.5−5 μm)

Fig. 1. Generalized flowchart for the synthesis of fine aluminosilicate zeolites of different structural types.

of zeolite [11]. This can be a problem in the production of zeolites A and X, which are used to manufacture adsorbents. The cationic composition of zeolite is often crucial for its use in sorption processes. Additional problems can arise if there are acid sites on the surface of a sorbent, since olefins and some aromatic compounds can undergo catalytic transformations during drying, purification, and separation [11].

The synthesized fine zeolite is subjected to postsynthetic treatment for use in the specific adsorption of catalytic process. To use zeolite A in the drying of reactive olefins (e.g., ethylene and propylene), the size of the inlet windows in large voids is reduced to ~0.3 nm by substituting K^+ cations for Na^+ cations [1]. Normal and iso C_{16+} paraffins are separated using adsorbents based on zeolite A, in which Ca^{2+} cations are substituted for Na^+ cations and the size of the inlet windows is therefore increased to ~0.5 nm [1, 2]. The adsorption separation of xylenes is performed using adsorbents that contain zeolite BaX. Other cations are substituted for Na^+ cations via several cation-exchange treatments in aqueous salt solutions [1, 11, 27].

Depending on what zeolite-containing product is manufactured, the ion-exchange stage is conducted on fine zeolite or already granulated zeolite material to facilitate the separation of the liquid and solid phases and further treatment, and to minimize possible losses of the expensive metal-containing components used to prepare bifunctional catalysts.

There are many ways of combining ion exchange, heat treatment in air or steam, acid and alkali treatments, and the deposition of different silicon-containing compounds on the external surface of zeolite when

producing a highly efficient catalyst for a certain catalytic reaction [27].

Table 2 presents data on zeolite powders manufactured in Russia as commercial products: NaA, CaA, NaX, offretite, cesite (ρ), NaM, NaKE, and ultrastable Y in different cation-exchange forms, along with high-modulus zeolites of structural types MFI (TsVM, TsVK, TsVN, IK-17-1, ZSM-4, ZSM-5, ZSM-11) and BEA (β).

1.2. Production of Granulated Zeolite-Containing Adsorbents and Catalysts

Zeolites are synthesized as fine crystalline powders with particle sizes of 0.5 to 5 μm. They are used in granulated form in adsorption and catalysis. Granulated zeolite-containing materials are manufactured in different sizes and shapes, depending on the design of the equipment of an adsorption or catalytic process. Russia produces microspherical (20−150 μm) and coarser-grained zeolite-containing catalysts in the shape of spheres and granules for fluidized- and moving-bed reactors, respectively. Extruded granules with different shapes of cross sections are mainly used in fixed-bed apparatuses.

There are two main approaches to manufacturing granulated zeolite materials [1, 11, 26]. The first is the production of granulated zeolites containing a binder. In the production of adsorbents, the binders are kaolinite and montmorillonite clays. In the production of cracking catalysts, zeolite is contained in a complex composite matrix. Aluminum hydroxide with boehmite or pseudoboehmite is most often used in the production of other refining and petrochemical zeo-

Table 2. Data on zeolite powders manufactured in Russia as commercial products

| Manufacturer	Type of zeolite	Use	Main characteristics
OOO Ishimbaisky spetsializirovannyi khimicheskii zavod katalizatorov (https://kntgroup.ru/ru/production)	Ultrastable zeolite Y	Component of cracking and hydrocracking catalysts	$SiO_2 : Al_2O_3 = 5.1-6.2$ Cell size, Å: 24.24–24.65 Cation form: Na^+, H^+, NH_4^+ Specific surface area, m^2/g: 600–900
	Ultrastable zeolite H–Y	Component of cracking and hydrocracking catalysts	$SiO_2 : Al_2O_3 = 6-18$ Cell size, Å: 24.61–24.35 Cation form: H^+ Na_2O content, %: <0.60 Specific surface area, m^2/g: 600–700
	Zeolite ZSM-5	Component of catalysts of catalytic cracking, hydrocracking, isomerization, alkylation, dewaxing, etc.	$SiO_2 : Al_2O_3 = 30-300$ Cation form: NH_4^+ Na_2O content, %: ≤0.05 Specific surface area, m^2/g: ≥400
ZAO Nizhegorodskie sorbenty (Nizhny Novgorod Sorbents), http://www.nsorbent.ru/products.shtml	NaA, CaA, NaX	Deep drying and fine purification of gases and liquids	Crystal size, μm: 1–10
	NaY, NaM, NaKE, TsVM, TsVK, TsVN, β (beta), ZSM-4, ZSM-5, ZSM-11, ρ (cesite), offretite	Component of catalysts of cracking, hydrocracking, hydrotreatment, hydroisomerization, aromatization, and alkylation	Crystal size, μm: 1–10
PAO Novosibirskii zavod khimkontsentratov (Novosibirsk Chemical Concentrate Plant), http://www.nccp.ru/products/zeolite_catalysts/	Zeolite IK-17-1 (ZSM-5)	Additive for fluid catalytic cracking (FCC) catalysts for octane enhancement of pyrolysis gasolines and increase in olefin content of cracked gases (feedstock for production of alkylate and polypropylene)	Mass fraction of zeolite ZSM-5, %: ≥90 Mass fraction of SiO_2, %: 93.2–95.7 Mass fraction of Al_2O_3, %: 4.3–5.7 Mass fraction of Na_2O, %: ≤0.16 Bulk density, g/cm^3: 0.6–0.8
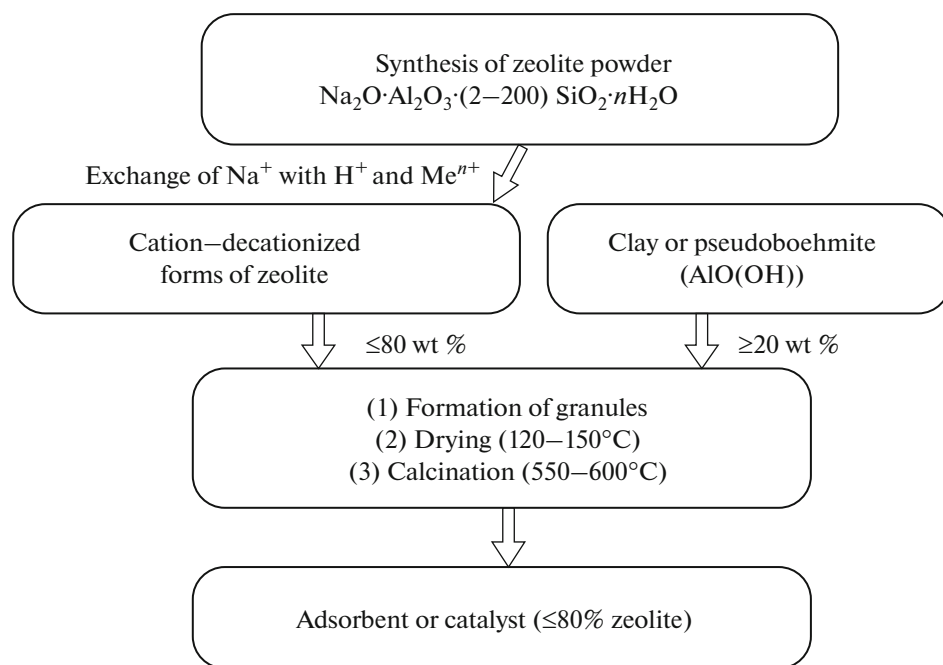
Fig. 2. Ways for the preparation of binder-containing granulated zeolites.

lite-containing catalysts. The aluminum hydroxide is converted to γ-Al_2O_3 during the calcination of formed and dried granules. Ways of producing binder-containing granulated zeolite sorbents and catalysts include stages of the synthesis of fine zeolite of the required structural type, its modification (e.g., ion exchange or dealumination), and subsequent forming in a mixture with a binder into granules of the required size and shape, followed by drying and calcination (Fig. 2).

Extrusion, the forming of spheres, and spray drying are the most widely used ways of producing granulated zeolite materials. In preparing a mixture for forming, zeolite and a binder are loaded in a mixer along with plasticizers and additives that burn away at the calcination stage and create additional porosity in the final product.

Drying and calcination are integral to the production of all granulated zeolite-containing materials. Only after calcination do their final chemical and phase compositions take constant values, along with the characteristics of the porous structure and the mechanical strength. At high temperatures of calcination, the components of a binder can undergo phase transitions to crystalline forms that are sometimes much stronger than the initial amorphous hydrated oxide or hydroxide.

Many stages used in the industrial manufacturing of zeolite adsorbents and catalysts are also used to obtain nonzeolite analogs. The unit operations and equipment that are used can be found in any industry which produces catalysts and adsorbents [26].

The possibility of varying the type and amount of zeolite and a binder, and the introduction of different additives to the mixture to be formed allow us to obtain adsorbents and catalysts with desired consumer properties with no appreciable alteration of the process [11, 26]. Most industrial catalysts are currently produced in this way. However, introducing a binder to the granules reduces the content of zeolite and thus the concentration of catalytically active sites. For such zeolite-containing materials, it is not always possible to obtain the mechanical strength required for long-term operation under industrial conditions because the obtained adsorbent or catalyst granules are a mechanical mixture of zeolite crystals and binder particles.

In another approach to producing granulated zeolite-containing materials, granules containing sources of silicon and aluminum (kaolin in particular), a crystal seed (zeolite), and pore-forming additives are initially subjected to forming and then to heat treatment, crystallization in alkaline aqueous solutions, washing, and drying. Such materials are called binder-free granulated zeolites. In these materials, the content of the zeolite phase can be as high as 90–95%, and the limiting capacity of water vapor adsorption is comparable to that of fine zeolites of the same structural types. The history of research and achievements in this field was described in [28, 29]. Technologies to produce binder-free granulated zeolites are used in Russia by OOO Ishimbaiskii spetsializirovannyi khimicheskii zavod katalizatorov (Ishimbai, Bashkortostan) and OOO Real Sorb Trading (Yaroslavl) to obtain different sorbents (see Section 2). Figure 3 presents a generalized flowchart of the production of granulated zeolites
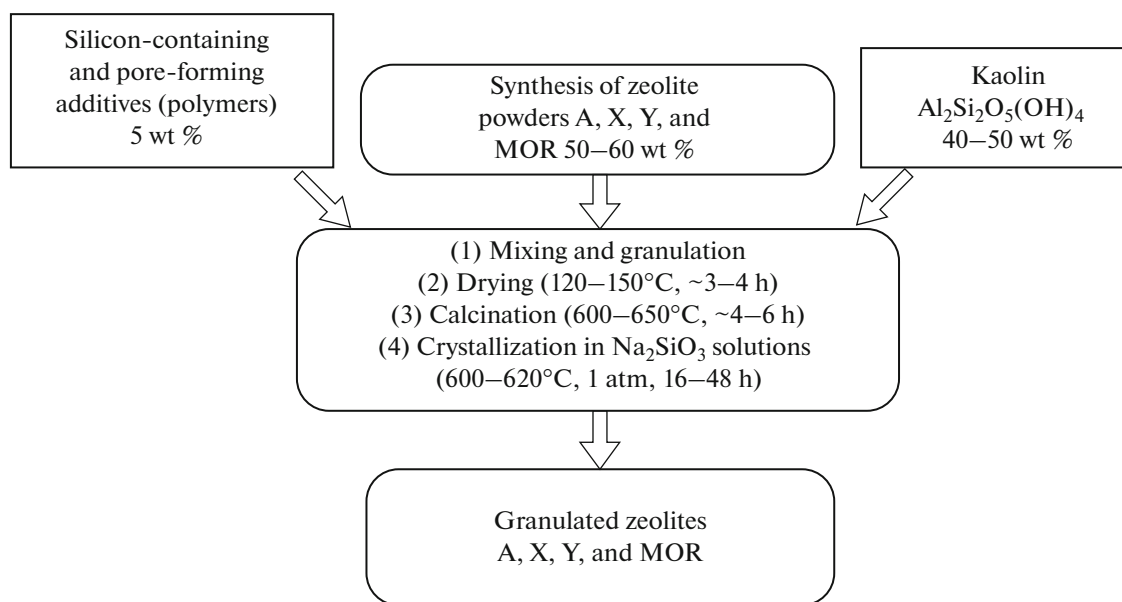
Fig. 3. Generalized flowchart for the production of granulated zeolites with high degrees of crystallinity and a hierarchical porous structure.

A, X, Y, and MOR with high degrees of crystallinity and hierarchical porous structures [29].

This term characterizes the obtained zeolite-containing materials more accurately than *binder-free granulated zeolites*. Table 3 presents the characteristics of these materials.

As with the production of fine zeolites, there are no exact values of the parameters for the synthesis of granulated zeolite-containing adsorbents and catalysts in the literature.

2. ADSORPTION DRYING, PURIFICATION, AND SEPARATION OF GASEOUS AND LIQUID MEDIA ON ZEOLITE-CONTAINING ADSORBENTS

Zeolites are characterized by features of the sorption of molecules of different compounds [1, 2, 34–36]. The primary porous structure of zeolites contains micropores of a certain size (less than 1 nm), in which sorption occurs throughout the micropore space. So while the adsorbate in the bulk phase is in the vapor state, it is in a near-liquid state inside the micropores. The voids of the crystal lattice of zeolites A and X, the ones most widely used in sorption, also hold a fairly large number of cations. This results in additional features of sorption, one of which is the effect the chemical nature and content of exchange cations have on the size of the inlet windows in the voids of zeolites (the molecular sieve effect). Another feature is that the exchange of Na^+ cations with other cations can alter the positions of the latter in voids, which changes the limiting filling volume and hydrophilicity of zeolites. Zeolites therefore primarily sorb water molecules from mixtures of water vapor, CO_2, H_2S, and organic compounds. Yet another feature of zeolites is the specific interaction between adsorbate molecules and exchange cations at low degrees of adsorption space filling.

2.1. Drying and Purification

Drying and purification of gaseous media. The greatest use of zeolite-containing adsorbents in Russia are drying and purification to remove sulfur com-

Table 3. Characteristics of granulated zeolites with high degrees of crystallinity and hierarchical porous structure

Granulated zeolite*	Crystalline phase	V_{micro}, cm^3/g	V_{meso}, cm^3/g	V_{macro}, cm^3/g	Mechanical resistance to end crushing, kg/mm^2	Average granule diameter, mm	Reference
NaA	Zeolite A	0.24	0.10	0.11	≥1.4	1.5–1.6	30
NaX	X	0.28	0.10	0.16	≥1.4	1.5–1.6	30
NaY	Y	0.28	0.15	0.15	≥1.4	1.5–1.6	29, 31, 32
NaMOR	Mordenite	0.15	0.18	0.18	≥1.4	1.5–1.6	29, 33

* Degree of crystallinity is no less than 90 rel %.

pounds and carbon dioxide from natural and associated gases [37−40]. Along with the main hydrocarbon components, these gases contain such undesirable impurities as water vapor, carbon dioxide, hydrogen sulfide, and thiols. Moisture lowers the calorific value of combustible gases and forms ice plugs that clog gas pipelines and disturb plant operation. Hydrocarbon hydrate crystals pose special difficulties created by snowlike solid compounds that form at positive temperatures at high pressures. Hydrogen sulfide and thiols gradually corrode pipeline elements, and carbon dioxide often results in the plugging of low-section pipeline elements.

The content of undesirable impurities in natural or associated gas varies according to the oilfield, for each of which an separate procedure for the drying and purification of gaseous hydrocarbons has been proposed. The final stage is almost always adsorption using granulated zeolites A and X.

Zeolite-containing adsorbents are also used in the refining and petrochemical industries to dry ethylene, propylene, and other gases such as the hydrogen-containing recycled gas from the catalytic reforming of gasoline fractions [34−36].

Drying of liquid media. *Drying of chlorofluorocarbon refrigeration oil.* The reliability and service life of hermetically sealed refrigerating machines depends largely on the purity of refrigerants and lubricants. Moisture accounts for the formation of as much as 80% of the fouling in chlorofluorocarbon refrigerators, corroding the system and ultimately burning out its electric motor.

Drying of transformer oil. Adsorption drying is widely used in the recycling of transformer oils, reducing the dielectric loss of fresh transformer oils, the drying of oil by zeolites, in filters for the continuous recycling of transformer oils, and other purposes.

2.2. Separation of Hydrocarbon Mixtures

The adsorption separation of mixtures is the most efficient option when their components have similar boiling points or are unstable at temperatures of distillation. Adsorption separation is used internationally to separate aromatic hydrocarbons and their derivatives (e.g., isomers of xylene, *para*-diethylbenzene, and cymene), nonaromatic hydrocarbons (e.g., olefin−paraffin and *n*-paraffin−isoparaffin mixtures), and carbohydrates and organic acids (e.g., fructose−glucose mixture, citric acid, and fatty acids). It also used for the fine separation of chemicals and pharmaceuticals (e.g., enantiomers and vitamins), and other purposes [11].

Industrial processes of adsorption separation using zeolites (Parex processes) are used domestically to separate *n*-paraffins from the diesel fraction (OOO KINEF, Kirishi) and *n*-xylene in integrated plants for producing aromatic hydrocarbons (Bashneft-Ufaneft-

ekhim, Ufa, Bashkortostan; AO Gazpromneft-ONPZ, Omsk).

Adsorption separation of $C_{10}−C_{20}$ *n*-paraffins. The feedstock for this process is the hydrotreated diesel fraction (200−320°C) with quality indices ρ_{20} = 0.825−0.845 kg/L; iodine value, ≤1.6; sulfur content, ≤0.05%; content of aromatic hydrocarbons, ≤35%; and paraffins, 18−21%. The products are liquid normal paraffins $C_{10}−C_{20}$ (≥99.1−99.5 wt % pure) used to produce biodegradable surfactants (e.g., sulfonates and higher fatty alcohols) and plasticizers. The dewaxed diesel fraction (denormalization product) has pour points of −60 to −70°C and is used as a component of winter diesel fuel. An adsorbent based on zeolite A in the Ca form is manufactured in Russia for this purpose.

Adsorption separation of xylenes. The adsorption separation of xylenes on zeolites is more efficient and economical than crystallization and extraction [11]. The degrees of separation of *n*-xylene are 60% in crystallization, 80% in extraction, and 98.4% in one-stage adsorption. Xylenes are most often separated on an adsorbent based on zeolite BaX.

2.3. Adsorption Separation of Air

Nitrogen and oxygen are mostly produced via air separation using pressure swing adsorption on zeolite-containing adsorbents. Different variants of this process are the literature [35, 36, 41, 42].

In Russia, zeolite-containing adsorbents for drying, purification, and separation of gaseous and liquid media are manufactured by OOO Ishimbaiskii spetsializirovannyi khimicheskii zavod katalizatorov (Ishimbai, Bashkortostan, https://kntgroup.ru/ru/production/), OOO Real Sorb Trading (Yaroslavl, http://realsorb.com/products), AO Angarskii zavod katalizatorov i organicheskogo sinteza (Angarsk, http://www.kataliz.ru/product.htm), ZAO Nizhegorodskie sorbenty (Nizhny Novgorod, http://www.nsorbent.ru/products.shtml), OOO Salavatskii katalizatornyi zavod (Salavat, Bashkortostan, https://skatz.ru/products/), AO Gazprom-ONPZ (Omsk, https://onpz.gazprom-neft.ru/production/), and PAO Novosibirskii zavod khimkontsentratov (Novosibirsk, http://www.nccp.ru/products/zeolite_catalysts/). The applications and characteristics of the manufactured products can be found on the above websites. Note that the adsorbent characteristics presented there do not always allow us to judge the efficiency of these adsorbents in an adsorption process.

3. CATALYTIC PROCESSES OF HYDROCARBON PROCESSING ON ZEOLITE-CONTAINING CATALYSTS

The possibility of creating acid sites and control their strength and concentration by varying the struc-

Table 4. Industrial catalytic processes of hydrocarbon processing using zeolite-containing catalysts [46]

Zeolite	Catalytic processes
FAU (HY, USY)	Catalytic cracking[R], hydrocracking[R], hydrodearomatization and disproportionation of polyalkylbenzenes[R]
MOR (Mordenite)	Hydroisomerization of C_5–C_6 n-paraffins[R], isomerization of xylenes and diethylbenzenes[R], disproportionation of toluene[R], transalkylation of C_{9+} aromatic hydrocarbons[R]
MFI (ZSM-5)	Catalytic cracking (additive)[R], hydrocracking[R], hydrodewaxing[R], disproportionation of toluene[R], oligomerization of C_3–C_4 olefins[R], gas-phase alkylation of benzene with ethylene[R], aromatization of olefins
BEA (Beta)	Hydrocracking[R], alkylation of benzene with propylene, disproportionation of polyalkylbenzenes[R], oligomerization of C_3–C_4 olefins, acylation
MTT (ZSM-23)	Isodewaxing of diesel fuel and oils[R]
LTL (L)	Aromatization of gasoline fraction
MWW (MCM-22)	Liquid-phase alkylation of benzene with ethylene or propylene[R]
AEL (SAPO-11)	Hydroisomerization of oils and waxes[R]
CHA (SAPO-34)	Synthesis of lower olefins from methanol (MTO)
MFI (TS-1)	Liquid-phase oxidation of phenol with hydrogen peroxide, epoxidation of propylene with hydrogen peroxide
MFI (Silicalite-1)	Gas-phase isomerization of cyclohexanone oxime to caprolactam

Superscript R denotes industrial catalytic processes implemented in Russia.

tural type, chemical composition (decationization; Si : Al ratio; presence of other atoms, such as Ti, Ga, Fe, B, etc., in the crystal lattice), unique molecular-sieve properties, and thermal stability of a number of synthetic zeolites mean it is now hard to imagine the catalytic processing of organic substances without using zeolite-containing catalysts. The history of the industrial production of catalysts based on synthetic zeolites dates back more than half a century. Today we use catalysts that contain not only aluminosilicate zeolites, but silicoaluminophosphates (e.g., SAPO-11 and SAPO-34 [43, 44]) and titanosilicates (e.g., TS-1) as well [45].

The world's largest-volume catalytic processes that use zeolite-containing catalysts are now fluidized-bed catalytic cracking (~95% zeolite-containing catalysts), hydrocracking, and isomerization [46]. However, the industrial use of zeolite-based catalysts goes beyond these processes. Table 4 lists molecular sieves that are currently used as components of large-volume catalytic refining and petrochemical processes.

We can see that catalytic systems based on zeolite materials are widely used in Russia. Of the molecular sieves listed in Table 4, there is industrial-scale production of zeolites HY, USY, and ZSM-5 (see Table 2) and microspherical (OOO Ishimbaiskii spetsializirovannyi khimicheskii zavod katalizatorov and AO Gazpromneft-ONPZ) and granulated (OOO Ishimbaiskii spetsializirovannyi khimicheskii zavod katalizatorov and OOO Salavatskii katalizatornyi zavod) zeolite-containing cracking catalysts based on them; catalysts of the hydroskimming and hydrodewaxing of oil fractions, and conversion of olefin-containing refinery

off-gases and low-octane straight-run oil or gas-condensate gasoline fractions to high-octane component of motor gasolines (AO Angarskii zavod katalizatorov i organicheskogo sinteza); catalysts of the hydrodewaxing of diesel and oil fractions, aromatization of gaseous hydrocarbons, processing of alcohol-containing feedstock, and gasoline upgrading (ZAO Nizhegorodskie sorbenty); and catalysts of production of high-octane gasoline, diesel fuel, and C_3–C_4 liquified gas from gas condensates and middle oil distillates, and aromatization of propane–butane fraction (PAO Novosibirskii zavod khimkontsentratov). The characteristics of these manufactured catalysts can be found on the websites of the above plants. Note that the characteristics of both adsorbents and catalysts presented on the websites do not allow us to judge the effectiveness of their use in a catalytic process or compare them to imported analogs.

CONCLUSIONS

A number of fine zeolites are currently produced on an industrial scale worldwide for the manufacturing of adsorbents and catalysts: A, X, Y, L, ferrierite, mordenite, ZSM-5, ZSM-12, ZSM-23, silicalite-1, Beta, MCM-22, Rho, Eu-1, TS-1, SAPO-11, and SAPO-34. Based on these zeolites, granulated zeolite-containing adsorbents and catalysts of different sizes and shapes are produced with or without added binders.

The largest-volume applications of zeolite-containing adsorbents are drying and purification to remove sulfur compounds and carbon dioxide from different gaseous and liquid media. Zeolite-contain-

ing adsorbents are also used for the separation of aromatic hydrocarbons and their derivatives (e.g., isomers of xylene, *para*-diethylbenzene, and cymene), nonaromatic hydrocarbons (e.g., olefin−paraffin and *n*-paraffin−isoparaffin mixtures), and carbohydrates and organic acids (e.g., fructose−glucose mixture, citric acid, and fatty acids); the fine separation of chemicals and pharmaceuticals (e.g., enantiomers and vitamins); and the production of oxygen via air separation.

In Russia, zeolite-containing products are manufactured by OOO Ishimbaiskii spetsializirovannyi khimicheskii zavod katalizatorov, OOO Salavatskii katalizatornyi zavod, OOO Real Sorb Trading, PAO Novosibirskii zavod khimkontsentratov, ZAO Nizhegorodskie sorbenty, AO Gazprom-ONPZ, and AO Angarskii zavod katalizatorov i organicheskogo sinteza. As commercial products, these plants manufacture zeolite powders zeolites NaA, CaA, NaX, offretite, cesite, NaM, NaKE, and ultrastable Y in different cation-exchange forms; high-modulus zeolites of the structural types of MFI (TsVM, TsVK, TsVN, IK-17-1, ZSM-4, ZSM-5, ZSM-11) and BEA; and adsorbents and catalysts based on them. The total production of these plants does not exceed 5−7% of the global production.

The largest-volume applications of zeolite-containing adsorbents in Russia are drying and purification to remove sulfur compounds and carbon dioxide from natural and associated gases. Zeolite-containing adsorbents are used in the refining and petrochemical industries to dry ethylene, propylene, and other gases., and to dry the hydrogen-containing recycled gas from the catalytic reforming of gasoline fractions.

Domestic adsorbents have been fully substituted for imported ones in the above applications. The industrial processes of separating *n*-paraffins from the diesel fuel fraction and separating *n*-xylene in integrated plants for producing aromatic hydrocarbons use both international and domestic adsorbents. Zeolite-containing adsorbents for insulated glass units are imported.

In Russia, zeolite-containing catalysts are used in 14 industrial catalytic processes of conversion of organic substances (see Table 4). Only the demand for catalysts at plants of the catalytic cracking of vacuum gas oil, the hydroisomerization of C_5−C_6 *n*-paraffins, and the oligomerization of C_3−C_4 olefins is currently fully met with catalysts produced in Russia that are on par in performance with imported analogs. Imported catalysts are used in the rest of the processes listed in Table 4.

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