CATALYSIS IN PETROLEUM REFINING INDUSTRY

Development of Catalysts for Hydroprocesses in Oil Refining

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Abstract—The review presents an analysis of the scientific and technical level and tendencies in the development of modern imported and Russian catalysts for the main hydroprocesses of oil refining—hydrocracking of vacuum gas oil and hydrotreatment of various distillates (catcracked gasoline, diesel fuel, vacuum gas oil). Forecasts were made on prospects for the industrial production and mass use of Russian catalysts for hydroprocesses.

INTRODUCTION

More than 90% of industrial oil refining technologies are based on catalytic processes. The catalysts of oil refining is the second largest segment (29%) of the world market of catalysts, estimated at $23.4–24.6 billion in 2014 [1]. According to data from various sources, the market size varied from $5.4 billion in 2014 (Fig. 1a) [2] to $6.8 billion in 2015 [3] and 2017 [4]. The differences in the values and estimates of its annual growth rates until 2020−2022 from 2.8 to 4.1% may be explained by the difference in the types of processes included in these calculations. The majority of the most popular types of oil refining catalysts are produced by approximately 10 leading companies, with more than 50% of the market provided by BASF SE (18.1%), WR Grace (7.0%), Johnson Matthey (5.9%), Albemarle (9.3%), Haldor Topsøe (3.0%), and Honeywell (9.8%) [3].

The total demand of Russia for oil refining catalysts in 2015 was ~80 thousand tons with growth prospect of 1.8%/year [3, 4]. The data on changes in the market of catalysts for the main processes until 2022 are shown in Fig. 1b [4].

The growing demand for motor fuels under conditions of changing sources and quality of feedstocks and stricter environmental requirements is provided with the appearance of new processes and catalysts for deep processing of vacuum gas oils (VGOs) and heavier
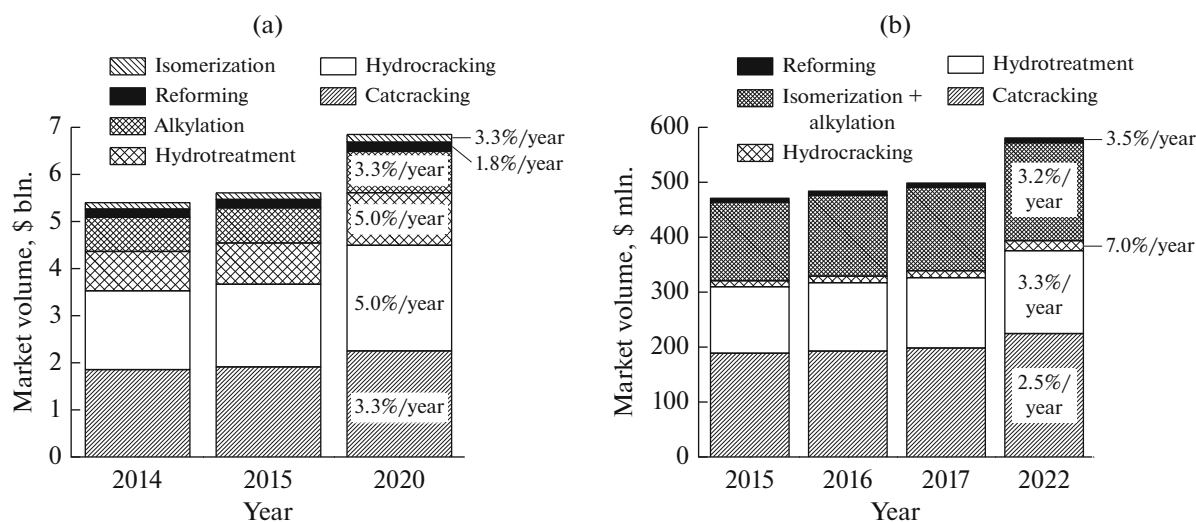

Fig. 1. (a) World and (b) Russian markets of catalysts for the major oil refining processes for 2020−2022.

Table 1. Composition of HC catalysts for the synthesis of various desired products [16]. The number of "+" signs corresponds to the frequency of use of the given component

Desired product	Process configuration	Hydrogenating function			Acid function		
		Pt, Pd	NiW	NiMo	zeolite	amorphous aluminosilicate	Al$_2$O$_3$
Gasoine	One-stage		+	+	++		
	Two-stage	++			++		
Kerosene	One-stage		+	++	++		
	Two-stage	+	+	+	+	+	
DF	One-stage		+	++	++	+	
	Two-stage	+	+		+	+	
Oils	One-stage		+	+	+	+	+

fractions and improvement of the existing ones. Catalytic cracking (CC) and hydrocracking (HC) are the main processes developed specifically for this purpose. Hydrotreating (HT) processes, consisting in the removal of various impurities and compounds from processed distillates, are designed to increase the service life and efficiency of CC and HC catalysts and to bring the quality of diesel or gasoline fractions to the level determined by the environmental standards. That is why the catalysts of CC, HC, and HT are dominant on the world market in terms of both mass (71−78%) and cost (69−80%) in any forecast [2]. The need for these catalysts in Russia is also constantly growing (Fig. 1b), and the growth rates for catalysts of HC and HT are significantly higher than the average rates in both absolute and value terms. However, the demand for CC catalysts is satisfied by more than 50% due to the Russian brands, while the share of imported catalysts of hydroprocesses is 90−95%. In this review, we analyzed the main characteristics and development trends of modern catalysts for hydroprocesses, including HT of various distillate fractions and the production of low-freezing fuels and HC. The scientific and technical level of research and development in this area performed in Russia over the past 10 years was evaluated, and prospects for providing oil refineries with Russian catalysts were determined.

1. CATALYSTS OF HYDROCRACKING OF VACUUM GAS OIL

1.1. Main Factors Governing the Activity, Selectivity, and Stability of Hydrocracking Catalysts

The catalysts used in the HC of VGO should have two combined functions: hydrogenation−dehydrogenation and cracking. The first function is performed by nanosized layered structures of molybdenum or tungsten sulfides promoted by nickel sulfide [5, 6], or noble metals (Pt, Pd) [7, 8]. Systems based on supported transition metal sulfides are most widely used due to their high stability against sulfur and nitrogen compounds contained in raw materials. Noble metals have a higher hydrogenating activity, but these catalysts are much more expensive and strongly poisoned by any sulfur and organonitrogen compounds [9]. Therefore, their application is limited to the second stage of hydrocracking.

The cracking function is performed by the acid sites of the catalyst support, which contains alumina, amorphous aluminosilicate [10, 11], and/or zeolite [8, 12, 13]. The choice of the composition of the support depends on many factors: characteristics of feedstock, process configuration, desired products, etc. The presence of strong acid sites in zeolites promotes secondary cracking, which forms gasoline fraction hydrocarbons and gases [9]. Dealumination of the zeolite matrix, leading to a decrease in the number of acid sites, an increase in the distance between them, and formation of mesopores as a result of severe hydrothermal treatment, makes it possible to vary the selectivity of hydrocracking from gasoline toward middle distillates: kerosene and diesel fuel [14]. In this respect, they approach amorphous aluminosilicates in their characteristics. On the other hand, the lower activity of catalysts based on amorphous aluminosilicates [5] requires higher temperatures of the process, which leads to a decrease in the quality of the hydrocracking product and a decrease in the catalyst service life [15]. Low-acid alumina catalysts are effective only in mild hydrocracking, but can be used for hydroprocessing of heavy oil residues. Table 1 shows the preferable combinations of the two functions of the hydrocracking catalyst for different variants of the process [16].

In industrial catalysts for HC of VGO, ultrastable Y type zeolite is used [15−17], whose acid characteristics and lattice parameter are controlled by thermal-vapor and/or acid dealumination. Despite the great number of publications on other types of zeolites as components of hydrocracking catalysts (β, IZM-2, ZSM-5, ITQ-21, etc.), their large-scale use for the production of industrial catalysts has not yet been confirmed.

The relationship between the cracking and hydrogenation functions is an important parameter that determines the activity, selectivity, and stability of HC catalysts. Secondary cracking processes can occur on catalysts with low relative contents of hydrogenating

Table 2. Maximum yields of desired products on modern HC stacked-load catalyst configurations in a fixed bed [31, 32]

Desired product	Processing conditions		Yield of desired product, wt %
	T, °C	feedstock consumption, h^{-1}	
One-stage HC*			
Middle distillates/DF	>410	0.7−1.0	75−80/40
	<410	0.7−1.0	60−65
Two-stage HC			
Naphtha (65−177°C)	365−380	1.5−2.0	65
Middle distillates	390−410	0.7−1.0	70−80
Product flexibility			
Naphtha/middle distillates	−	−	30−40/45−55
Middle distillates/naphtha	−	−	60−65/15−20

*Most probably, one-stage HC with recycling of the residue.

centers or at their low activity. As a result, light hydrocarbons are formed, and coke is deposited on acid sites, which leads to quick deactivation of catalysts. At the same time, when the hydrogenating activity is dominant, the cracking is suppressed, and isomerization of hydrocarbons predominantly proceeds. This relationship can be regulated by the distance between the hydrogenation−dehydrogenation centers and acid sites [18−22], the strength of centers, and their quantitative ratio [15, 23, 24].

In addition to the required chemical composition, the catalyst supports should have textural characteristics that provide:

—uniform distribution of the supported catalytically active components and their possibly smallest particle size;

—good availability of active sites for high molecular weight reagents; and

—facilitated diffusion of products, which minimizes the secondary cracking and polycondensation of aromatic compounds and (dehydro-)cyclization of high molecular weight olefins, which ultimately lead to the formation of coke and catalyst deactivation.

Minimization of polycondensations and (dehydro-)cyclizations is especially important when processing vacuum residues. For this purpose, hierarchical porous materials are used in the preparation of supports and catalysts, including zeolites, which have a developed "transport" network of meso- [25−28] and/or macropores [29, 30] in addition to micropores.

1.2. Industrial Catalysts of Hydrocracking and Trends in their Development

Chevron Lummus Global (CLG)−Advanced Refining Technologies (ART), Honeywell UOP, Axens, Criterion Catalysts & Technologies, Haldor Topsøe A/S, and Sinopec Corporation are the world's leading manufacturers of HC catalysts. The compa-

nies generally offer catalysts for all stages of HC, including guard bed, pre-hydrotreatment of HC feedstock, and HC proper. In addition, for each desired product (gasoline/kerosene, middle distillates, diesel fuel (DF), base oils), its own brands of hydrocracking catalysts are offered. New generations of catalysts, characterized by higher selectivity and/or activity, are introduced on the market every 5−10 years. This provides an increase in the yield of desired products and/or lifetime of catalysts between regeneration cycles, and processing of heavier feedstock becomes possible. According to the data of [31, 32] (Table 2), in single-stage HC on the best stacked-load catalyst configurations based on amorphous aluminosilicates, the yield reaches 75−80% for middle distillates and ~40% for DF. However, because of the high process temperature at the start of the cycle (>410°C), the catalyst cycle length is very low. The addition of zeolites to the support increases the activity of the catalyst layer, but the yield value does not exceed 60−65% because of lower selectivity.

In two-stage HC, the highly active stacked-load catalyst configurations designed for obtaining the maximum yield of the light gasoline fraction (C_5−C_7 hydrocarbons) with a low octane number further sent to reforming generally completely convert VGO at space velocities of 1.5−2.0 h^{-1} and temperatures of 365−380°C. The yield of the desired product is 65%. On packages with a lower overall activity, the yield of middle distillates, as in the case of single-stage HC, does not exceed 70−80%. The products can be directly used for the preparation of jet kerosene and qualified DF with high cetane number and low contents of sulfur and aromatic compounds.

Some manufacturers also offer packages on which it is possible to obtain products with different fractional compositions depending on the process conditions. Thus, when using the HC-140LT catalyst recently announced by UOP, in different modes the dominant product can be naphtha (30−40 wt % yield

Table 3. Catalytic characteristics of the KGK-2ST pilot catalyst (IC, SB RAS) and its industrial analogues in HC in the mode of the second stage of the process (content in feedstock: $S < 5$ ppm, $N = 5$ ppm) [32]

Characteristic	KGK-2ST (IC, SB RAS)	Analogue
VGO conversion	57.8	55.4
Product yield, wt %		
Gas	2.0	2.3
Naphtha	9.3	8.0
Middle distillates (kerosene + DF)	46.6	45.3
HC residue	42.2	44.6

with 45–55 wt % middle distillates) or middle distillates (60–65 wt % yield with 15–20 wt % naphtha) [31]. The Criterion company offers a similar catalyst (Zeolyst Z-FX10) [34]. As is known, highly aromatic heavy naphtha or pure fuel products (diesel fuel CN-V or its mixture with jet fuel) can be obtained on the FC-32 (SINOPEC) catalyst with high selectivity. Stable operation of this catalyst during the processing of feedstocks of various compositions, including those with high nitrogen contents, is possible due to the formation of an open system of pores with a wide size distribution [31, 33]. The product flexibility provided by this catalyst allows adaptation to quickly changing market requirements without reactor reloading.

In the long term, the decrease in the demand for DF in the United States and China, the ban on the use of diesel cars in many cities, and the announced rejection of internal combustion engines in motor cars in Europe can lead to a decrease in the demand for the key products of HC [33]. In this case, those catalysts will get advantage that provide for high yield of jet kerosene, heavy naphtha with high contents of aromatic compounds used for the production of hydrocarbons of the benzene–toluene–xylene (BTX) fraction, and feedstock for high-quality oils. In particular, a significant increase (by 6.7 million tons/year from 2018 to 2020) in the production of oils of the second and third groups and an increase from 30 to 50% in their share in the total volume are caused by more stringent requirements for engine emissions and fuel efficiency. The development of catalysts with stable and selective work with feedstocks of various compositions is an especially important challenge. The patent landscape over the last 5 years given in [33] fully confirms the observed trends in the development of research on HC catalysts. The integration of HC with reforming in order to obtain high-octane gasoline or the involvement of HC products in petrochemical processing (pyrolysis, production of BTX) at modern refineries under construction has stimulated the development of catalysts for these purposes by Chevron (ICR 214, ICR 215) [35], Albemarle (KC 2715), Axens (Craken-Flex series), Criterion (Z-863), and Haldor Topsøe (TK-971). One of the latest new-generation catalysts HC-320 from UOP allows variation of the product composition in the range from feedstock for ethylene production by pyrolysis and jet fuel A-1/kerosene to high-quality feedstock for base oils [33].

1.3. Studies and Development of HC Catalysts in Russia

At present, there is no industrial production of HC catalysts in Russia. Several publications reported on methods for the preparation of various zeolites used in HC catalysts developed at Moscow State University [36, 37] and the Institute of Petrochemistry and Catalysis, Russian Academy of Sciences (Ufa) [38, 39]. Systematic studies of HC catalysts and methods for their preparation are underway at the Institute of Catalysis, Siberian Branch, Russian Academy of Sciences (Novosibirsk) [32, 40–50] within the framework of the project for the development of catalysts by Gazprom Neft.

Detailed studies of the effect of the micro-mesoporous structure formed as a result of postsynthetic treatment of zeolite Y [47, 48] and its acid characteristics [46] on the composition of the products of hexadecane and VGO HC on NiMo/Y-Al$_2$O$_3$ catalysts were used as the basis for the development of formulations for real catalysts. The pilot samples of NiMo/Y-Al$_2$O$_3$ catalysts have catalytic characteristics comparable to those of the industrial samples used under the single-pass cracking conditions (Fig. 2). The developed hydrocracking catalyst for the second stage of the process is also comparable in activity and selectivity to its modern industrial analogue (Table 3) [32]. The characteristics estimated based on the results for the two-stage HC with recycling allow us to predict the yield of middle distillates (up to 80 wt %) with minimal (2–3 wt %) gas generation.

The technological capabilities for industrial production of ~3,000 tons of HC catalysts capable of satisfying the demand of nine existing VGO HC units (total feed capacity is ~14 million tons) and 17 units under construction (35 million tons/year) for HC in a fixed bed are available at Novokuibyshevsk Catalyst Plant (owned by NK Rosneft) and the catalyst production plant currently constructed by Gazprom Neft (Omsk). This makes it possible to predict the industrial application of domestic catalysts for the next five years.
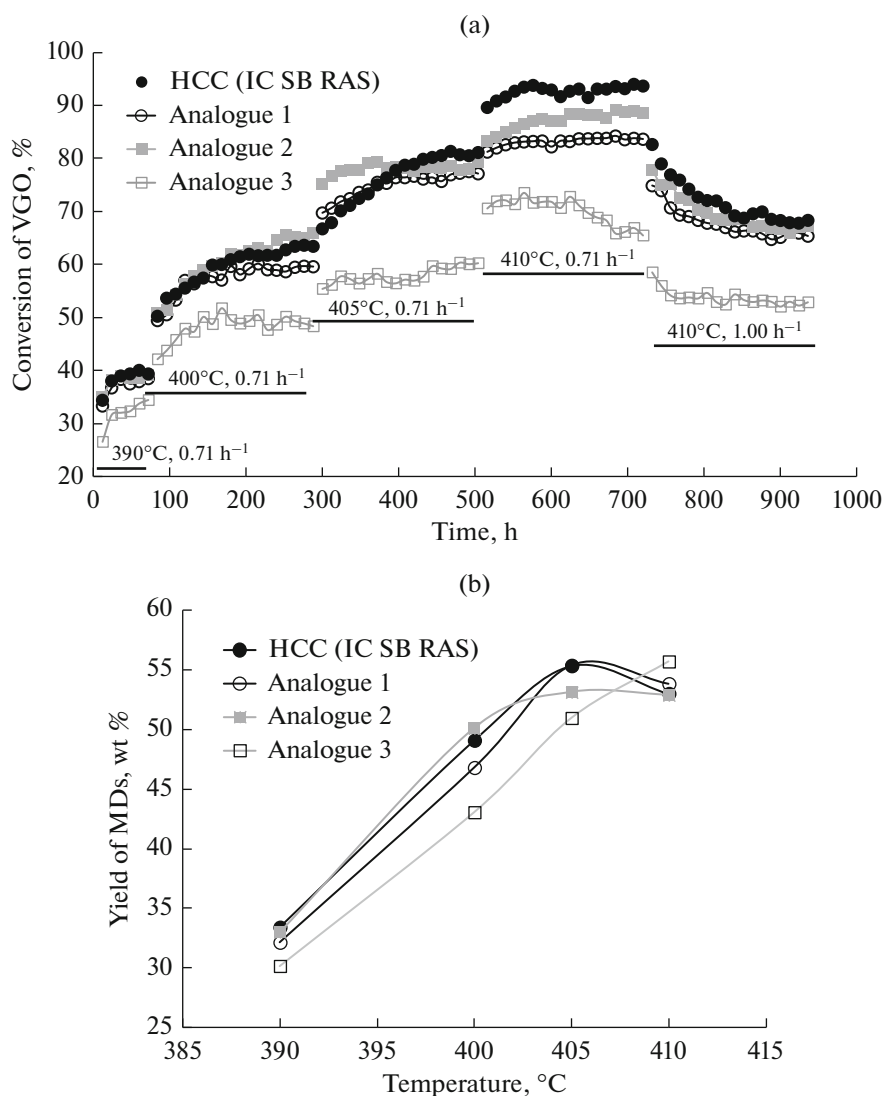
Fig. 2. (a) Conversion of VGO and (b) yield of middle distillates (MDs) per pass on the pilot stacked-load catalyst configuration of IC SB RAS and industrial imported catalysts (analogues 1−3). 390−410°C, 16.0 MPa, H_2/feed = 1500 normal L/L, 0.7−1.0 h^{-1} (per catalyst package). Feedstock: a mixture of straight-run VGO and heavy coker gas oil (S = 0.85 wt %, N = 0.19 wt %) [32].

2. HYDROTREATMENT CATALYSTS FOR VARIOUS FRACTIONS OF HYDROCARBON FEEDSTOCK

The constant toughening of requirements for the contents of harmful and undesirable impurities in fuel and engine emissions (primarily sulfur, aromatic hydrocarbons, olefins, nitrogen oxides) in countries with the highest gasoline and diesel fuel consumption dictates the development of hydrotreatment (HT) of various hydrocarbon fractions over the last 10 years.

2.1 Catalysts for Hydrotreatment of Gasoline Fractions

2.1.1. Main trends in the development of HT catalysts of for catcracked gasolines (CCGs). In motor gasolines, the main source of sulfur (≈95% and more) are gasolines obtained during catcracking. The concentration and type of sulfur-containing compounds in CCGs depend on the feedstock and the presence or absence of hydrotreatment step for CC feedstock at the oil refinery. The research octane number (RON) of CCGs at the level of 92−93 is provided by olefins that concentrate in light fractions, and its decrease during HT should be minimised. The CCG is also characterized by significant (several wt %) content of diene compounds. Their polymerization under HT conditions leads to increased pressure drop and decreased catalyst activity.

To achieve the required level of sulfur in motor gasoline (10 ppm), the conversion of sulfur-containing compounds in CCG should generally exceed 98%. In accordance with the peculiarities of its composition, the overwhelming majority of industrial processes that

Table 4. Main industrial technologies for HT of CCG [51−55]

HT strategy	Technology (company)	Decrease in ON, units	Number of units/volume of feedstock or market share	
			World	Russia
Selective HT	Prime G + (Axens/IFP)	1−2	>190/50%	6/≈6.5 mln t/year
	Prime G + (Axens/IFP)+ OATS™(BP)	0−2	3/−	−
	SCANfining II (ExxonMobil)	5	43/68 mln t/year	−
	SCANfining I + Zeromer	1.5		−
	Select-Fining (UOP)	2.5	19/−	−
	RSDS-II (RIPP/Sinopec)	1.8−2.1	19/9.3 mln t/year	−
	RSDS-III ((RIPP/Sinopec)	1.0		−
	HOT™ (Haldor Topsøe)	<4	No data	−
	CDHydro + CDHDS (CB&I)	~0.4−0.5*	40/−	2/−
Nonselective HT (deep HT, compensation of the decrease in ON by isomerization or HC)	Octgain (Exxon Mobil)	2.5−3.0	2/−	−
	ISAL (UOP, INTEVEP (PDVSA))	No data	5/−	−

*At 100 ppm sulfur in the feedstock.

afford products with less than 20 ppm sulfur at a minimum decrease in ON (Table 4) [51−55] use a selective HT strategy and work according to the schemes including:

—preliminary hydrogenation of diene hydrocarbons under mild conditions on a Pd(Ni)/support catalyst; and

—separation of CCG into light/heavy or light/medium/heavy fractions and separate purification of the obtained fractions.

For desulfurization of the light fraction ($T_b \leq$ 70°C), the industry often uses extraction, in particular, the well-known alkaline purification methods with conversion of mercaptans into disulfides (Merox and Minalk processes at UOP (United States) or Sulfrex, Sweet'nK, and Sweet'nG at Axens (France)), as well as oxidative processes that do not affect the olefin content. Attempts to use ionic liquids based on alkylimidazole cations and various anions (hexafluorophosphate, tetrafluoroborate, ethyl sulfate, octyl sulfate, diethyl sulfate, etc.) for selective removal of various higher-boiling thiophene derivatives, which are very difficult to remove from CCG, have failed. This is explained by the insufficient efficiency of extraction of thiophenes and easy decomposition of many ionic liquids in the presence of moisture, leading to a release of HF and other halogen-containing wastes, and also by their high cost.

Therefore, selective hydrogenation of higher-boiling thiophenes is performed on Co-Mo/Al$_2$O$_3$ systems; hydrogenation of the most stable sulfur-con-

taining compounds is performed under conditions with H$_2$ deficiency on Co(Ni)-Mo/Al$_2$O$_3$ catalysts.

The main problem with the use of Co−Mo/Al$_2$O$_3$ catalysts is that olefins are also hydrogenated on the coordinatively unsaturated Mo sites that are active in the hydrogenolysis of the sulfur-containing components of feedstock. Numerous studies showed that in catalysts that are optimum from the viewpoint of the activity : selectivity ratio, the particles of the active CoMoS phase are characterized by a Co : Mo molar ratio of 0.3, the stacking degree of MoS$_2$ is ≥2, and the average length of slab is 3 or 4 nm [16, 56, 57]. The active component particles having uniform composition and required morphology and interacting with the support to a minimum extent are usually obtained by impregnation with solutions containing precursors of active metals in the presence of chelating agents. The acid-base properties of the support, which determine the stability of the catalyst against coke formation, in turn, also affect the characteristics of the active component. They are most often varied by addition of MgO, various hydrotalcite-like compounds, aluminosilicates, alkali metals, P, and B [16].

All the suppliers of HT technologies generally offer their own highly selective Co(Ni)Mo/Al$_2$O$_3$ catalysts. Axens (Prime G+ process) developed catalysts of the composition Co−Mo/Al$_2$O$_3$ with a specific surface area of 150−300 m^2/g (HR 806, HR 846) and Ni−Mo/Al$_2$O$_3$ with a surface area of 50−150 m^2/g (HR 841). ExxonMobil uses Albemarle's RT-225™ and RT-235™ catalysts with an MCM-41 type support based on aluminosilicates with low acidity and ordered meso-

porous structure in its SCANfining II and ZEROMER processes.

In recent years, progress in solving the problem of decreased CCG octane number has been achieved mainly due to the removal of mercaptans from the fraction with $T_b < 100-130°C$ by converting them into higher boiling sulfur-containing compounds by reactions with (di-)olefins simultaneously with or immediately after hydrogenation of dienes. This allows the fractionation temperature between the light and middle CCG fractions to be shifted to higher values, thus minimizing the hydrogenation of olefins. On the Axens HR 845 catalysts with a proposed composition of Ni-Mo/Al$_2$O$_3$, some part of mercaptans are converted into higher-boiling thiophenes as a result of the reaction with (di-)olefins [58, 59]. Mercaptans and thiophenes are alkylated with C$_7$–C$_{15}$ olefins in the absence of H$_2$ within the framework of the Prime G+ (Axens) and OATS™ (BP) joint technology on the TA801 catalyst based on ion-exchange resins. The resulting high-boiling ($T_b > 200°C$) alkyl-(benzo)thiophenes are concentrated in the heavy fraction of naphtha [58, 60]. As a result of the use of these catalysts, the decrease in the CCG octane number after HT does not exceed 2 units. Simultaneously with hydrogenation of dienes, the TK-703™ catalyst (Haldor Topsøe) converts light mercaptans into heavy high-boiling sulfides, which are separated from gasoline by fractionation [61, 62]. It cannot be ruled out that the insignificant (≈1 unit) decrease of ON in the hydrotreated CCG after the RSDS-III process (Sinopec) related to optimization of fractionation conditions, which makes it possible a significant part of olefins to get into the light naphtha fraction [63], is also achieved using such catalysts.

2.1.2. Research and development of CCG hydrotreatment in Russia. The annual demand of Russian refineries for CCG hydrotreatment was ~130 t/year in 2017, including more than 77 t/year for the Prime G+ process. For 2020 and beyond, the demand for Axens catalysts will increase to 143 t/year as units are commissioned at the Angarsk Petrochemical Complex and Ryazan Refinery (Prime G+ process). At present, there is no industrial production of Russian brands.

Currently, several groups are engaged in the development of the CCG hydrotreatment catalysts. The most active studies are underway at Samara State Technical University on the effect of the composition and morphology of the CoMo phase and preparation procedures on the catalyst activity and selectivity used in conventional processes [64–69]. This research group patented CoMo/γ,δ-Al$_2$O$_3$ modified with K and P(B) [70, 71] and (Ni–Fe)W/Al$_2$O$_3$ [72] catalysts, and a method for their activation [73]. An increase in the selectivity of the CoMo/γ,δ-Al$_2$O$_3$ catalysts (at close extents of feedstock desulfurization, ON decreases by 2 units instead of 4.5) is achieved due to the predominant suppression of the hydrogenating activity when using K$_2$MoS$_4$ as an additives containing both the

modifier (K) and the active metal (Mo). To form sites not affected by the modifier, on which hydrodesulfurization predominantly proceed, a Co–Mo bimetallic complex and stabilizing organic modifier are used.

In 2019, the Rosneft company patented diolefin hydrogenation catalysts consisting of a highly porous cellular material with a grafted γ-Al$_2$O$_3$ layer on which bimetallic Co(Ni)Mo complexes are deposited [74]. There is no information on the production and use of Russian CCG hydrotreatment in open sources.

At the Boreskov Institute of Catalysis, CoMo/ASA–Al$_2$O$_3$ systems (ASA is amorphous silica–alumina) were proposed for use as promising catalysts for hydrotreatment of the entire CCG flow without separation into fractions. The high efficiency of hydrogenolysis of sulfur-containing compounds and isomerization of linear terminal olefins on such systems makes it possible to achieve the required sulfur content in the product (Fig. 3) [75, 76]. The addition of Mg, especially at the stage of support formation, leads to the formation of finely dispersed particles of the active component with the maximum number of layers in the package. This significantly increases the degree of desulfurization and further reduces the decrease in ON as a result of a decrease in the rate of hydrogenation of olefins [77]. The authors patented this catalyst, a method for its preparation, and a method for performing the process using this catalyst [78–80]. The process parameters using this catalyst provide HT of CCG to residual sulfur of less than 10 ppm with minimum reconstruction of the currently available equipment at Russian refineries [75].

Process capabilities for the industrial production of such catalysts are available both at the operating catalyst plants and the catalyst plant under construction at Gazpromneft (Omsk).

2.2. Diesel Fuel Hydrotreatment Catalysts

2.2.1. Main requirements and development trends for diesel fuel hydrotreatment catalysts. The main trends in the development of DF purification processes and catalysts over the past 10 years were determined by:

—the sharp increase in the market demand for DF, including winter and arctic brands, which is over 30% of its total consumption in Russia;

—stricter requirements for the contents of sulfur in DF (<10 ppm in EURO-5, -6); polycyclic aromatic hydrocarbons (PAHs) (<11 wt % for Euro-5 and <8 wt % for Euro-6); and nitrogen oxides in vehicle emission (<0.18 g/km for Euro 5 and <0.08 g/km for Euro 6);

—constant increase in the amount of secondary distillates involved in the processing, such as cat-cracked light gas oils (CCLGs) and light coker gas oils (LCGOs) characterized by increased contents of alkyl-substituted thiophenes, which are difficult to convert; nitrogen-containing heterocyclic com-
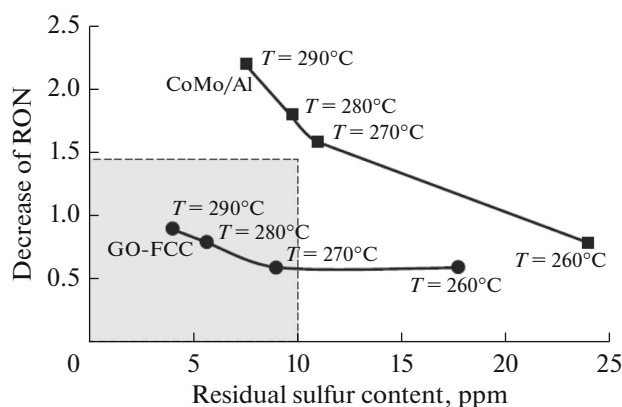
Fig. 3. Reduction of RON after HT of CCG on a commercial catalyst (CoMo/Al) and the catalyst developed at Boreskov Institute of Catalysis (GO-FCC) [75].

pounds; and PAHs; and by lower cetane numbers (CNs) than for straight-run fractions.

In the early 2000s, all major licensors of HT processes/catalysts (Haldor Topsøe, Grace, Axens, UOP) performed studies on the use of various sorbents (including ionic liquids) for selective extraction/adsorption of polar nitrogen-containing compounds from gas oil fractions, which could protect basic HT catalysts, especially in the case of processing heavier feedstock and feedstock with secondary distillates. However, this method has not become widespread because of significant loss of hydrocarbons due to low selectivity of adsorption and the unresolved problem of regeneration of sorbents and extractants.

Accordingly, the characteristics of modern diesel fuel hydrotreatment catalysts should provide increased activity in denitrogenation and hydrogenation of aromatic and unsaturated hydrocarbons in addition to desulfurization reactions. Therefore, the industry uses both conventional $CoMo/Al_2O_3$ catalysts of hydrogenolysis and systems based on NiMo with HT predominantly occurring via preliminary hydrogenation of aromatic compounds depending on the composition of feedstock. With high interdependence of all reaction rates and different routes of purification reactions from S and N on the Co(Ni)-Mo active component [81], however, it is rather problematic to combine all the necessary functions in one catalyst. Therefore, to obtain DF with the required characteristics, many companies suggest stacked-load catalyst configurations. The choice of catalysts for each reactor zone (or each reactor) and their ratio are based on clear understanding of the reactivities of various sulfur- and nitrogen-containing feedstocks [81–84]. Accordingly, companies usually offer different catalysts characterized by the maximum activity in each of the target reactions. A separate group is dewaxing catalysts required to obtain low freezing fuels.

Modern diesel fuel deep hydrotreatment catalysts from the leading manufacturers on the market including Albemarle (STARS series), Criterion (Centinel/Centinel Gold, Ascent/AscentPlus, Centera), and Haldor Topsøe (BRIM/HyBRIM series) are characterized by [81, 85–94]:

—close chemical compositions of the active component (10−15% Mo, 3−4% Co or Ni), which forms completely sulfidized Co(Ni)−Mo−S phases of types II and III;

—the use of γ-Al_2O_3 modified with B or P as a support;

—uniform particle distribution of the Co(Ni)−Mo−S phase of the required shape, size, and crystal morphology (the average length is no more than 5 nm; no more than 2.5 layers) over the support surface;

—specific surface area of 150−200 m^2/g with an average pore diameter of 8−11 nm and total pore volume of at least 0.35 cm^3/g.

Further increase in the catalyst activity is considered by manufacturers to be associated with:

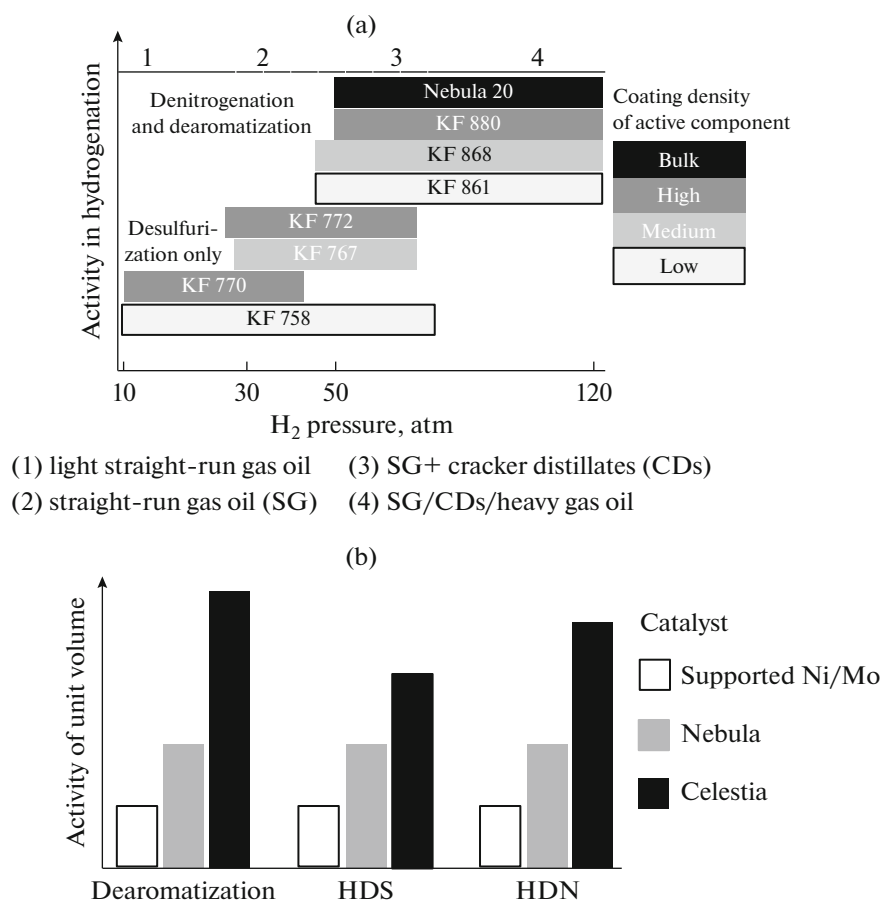—an increase in dispersion of particles of the sulfide active component,

—optimization of the texture and acid-base characteristics of the support,

—an increase in the coating "density" of the active component.

According to the data of Criterion, a sequential decrease in the length of sulfide particles from 4−4.5 nm (Centinel, Acsent series) to 3−3.5 nm (Centinel Gold, Acsent Plus series) and ultimately to 2.5−3.5 nm (Centera) resulted in a decrease in the starting temperature of HT by 10°C and a twofold increase in the catalyst cycle length [90, 95]. Haldor Topsøe noted the importance of further reducing the number of layers in a stack of active particles [96]. Regarding an increase in the coating density, Albemarle implies the deposition of a larger amount of the active component with the required particle size of Co(Ni)MoS (KF770, KF772, KF880), including the use of Nebula and Celestia bulk NiMo catalysts [97, 98] (Fig. 4a) characterized by the maximum activity in all target reactions (Fig. 4b). Studies on optimization of support texture are aimed at obtaining a monomodal pore structure with a narrow size distribution determined by the size of the largest molecules of the feedstock and by the requirements to minimization of accumulation of carbon deposits.

2.2.2. Level of production for the diesel fuel hydrotreatment catalysts in Russia. The demand for DF HT catalysts in 2015 in Russia was ~2000 t/year with 40% growth prospects by 2020. Of these, the volume of grades that can be used for HT of feedstocks with a heavy composition and/or with addition of secondary distillates (primarily, CCLGs and LCGOs) can amount to 1100 t/year. Imported catalysts were used at all HT units until 2019. In 2018, the Ht-100RN cata-

(1) light straight-run gas oil (3) SG+ cracker distillates (CDs)
(2) straight-run gas oil (SG) (4) SG/CDs/heavy gas oil

Fig. 4. (a) Activity of catalysts with different contents of the active component (coating density); (b) specific activity of the unit volume of the best supported (NiMo) and bulk catalysts Nebula and Celestia in hydrodesulfurizations (HDSs), hydrodenitrogenations (HDNs), and hydrogenations of aromatic hydrocarbons.

lyst developed at the Joint Research and Development Center of Rosneft oil company (RN-TsIR) was successfully tested in a pilot reactor and then in an industrial reactor at Bashneft-Ufaneftekhim; the catalyst provides the production of diesel fuel of Euro-5 standard even when using up to 40% of components of secondary origin in HT. The Russian-made catalyst enables stable work at temperatures 5−10 degrees lower than its imported analogues and is characterized by longer (two to three times) run duration. Its industrial batch was produced at AZKiOS [99−101]. As the available capacities of RN-Kat for the production of hydrotreatment catalysts amount to 4 thousand t/year, Rosneft is ready to start export deliveries in 2020 [100]. Gazpromneft is creating new production of HT catalysts with a capacity of 4 thousand t/year. It will use the developments of the Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences. The catalysts for HT of middle distillates make it possible to obtain a product fully complying with the Euro-5 standard and have successfully passed industrial tests at Gazpromneft-Omsk Refinery.

2.2.3. Catalysts for the production of winter/arctic fuel. Today winter/arctic diesel fuel is obtained by catalytic dewaxing of previously hydrotreated feedstock. There are two variants of dewaxing, which are based on mild hydrocracking of heavy and resinous paraffins or hydroisomerization of normal paraffins to obtain iso-paraffins. Hydroisomerization allows higher yields of the desired product (DF) without any significant decrease in its CN (Tables 5 and 6) [102, 103]. The use of catalysts operating under the mild HC principle may be recommended when processing feedstocks with increased end boiling points. In addition, due to their higher resistance to the presence of sulfur and nitrogen in the feedstock, they can be introduced at the inlet or in the middle zone of the HT reactor, which facilitates the HT and allows variation of product composition over a wide range.

Both reactions proceed on bifunctional catalysts containing hydrogenating metals (Ni, Pt, Pd) supported on the acid component—medium-pore zeolite (ZSM-22, ZSM-23) or silicoaluminophosphates (SAPO-11, SAPO-41, SAPO -31) with a one-dimensional pore system available mainly for normal paraf-

Table 5. Composition of the final products of catalytic dewaxing on the Criterion catalysts working based on different principles at 20°C cloud point improvement [102]

Yield (fractions)	wt %	
	Mild hydrocracking (SDD-800)	Hydroisomerization (SDD-821)
C_1–C_4	4.3	0.2
From C_5 to the fraction with T_b = 177°C (naphtha)	9.2	5.9
Diesel fraction	86.7	94.5
Total	100.2	100.6

Table 6. Product composition for the summer and winter (with the MIDW^{TM} catalyst of HT (ExxonMobil) modes of operation of the HT unit [103]

	S, ppm	CN	T cloud, °C	Yield of naphtha, vol %
Summer mode				
Feedstock	2500	49.5	−10	
Product	1.6	52.2	−10	3.3
Difference, units		2.7	0	
Winter mode				
Feedstock	4800	48.6	−8	
Product	0.5	51.2	−27	6.9
Difference, units		2.6	−19	

fins. To further increase their selectivity with respect to normal and weakly branched molecules, chemical passivation or modification of acid sites located on the outer surface of pores/channels and support particles is often performed [104]. The predominant occurrence of mild hydrocracking or hydroisomerizations in these catalysts is determined by the ratio between their hydrogenating and acidic characteristics.

The main manufacturers of hydroisomerization catalysts on the market are Albemarle and Criterion. The Albemarle's MIDW™ catalysts based on Ni(Co)−W(Mo) or Pt(Pd) supported on beta zeolite with modulus 30 and higher are used in the Unionfining (UOP) [105] and HDT/MIDW processes (Exxon Mobil) [103, 106, 107]. The SDD-821 (Criterion) catalysts with a composition Pt(Pd)/zeolite [104] are used in Shell's Catalytic Dewaxing technology. In recent years, these catalysts appeared in SCCorp (South Korea) and Haldor Topsøe (TK-920 D-wax™, TK-930 D-wax™) [108]. The catalysts operating under the selective mild HC principle are produced by Topsøe (TK-928, TK-932 for the HDS/DW process), Criterion (SDD-800; Catalytic Dewaxing technology, Shell), and Clariant (HYDEX-G, for Axens processes).

The demand for dewaxing catalysts in 2015 in Russia was estimated at ~100 t/year, and the imported selective cracking catalysts SDD-800 and Hydex-G were used in the overwhelming majority of cases. They drove the SGK-1 and SGK-5 dewaxing catalysts from the market, which were developed at VNIINP [109]

due to their higher activity, stability, and the yield of the diesel fraction. In recent years, publications have appeared on the development of hydroisomerization catalysts based on Pt(Pd)/ZSM-23/Al$_2$O$_3$ at IC SB RAS [110, 111] and VNIINP [112]. An analysis of the patents of Rosneft [113, 114] and Gazpromneft−ONPZ [115] showed that one of the main components (up to 60 wt %) of these catalysts are also zeolites with a one-dimensional pore system (ZSM-23 or ZSM-12), whose production in Russia is absent. It is logical to believe that the appearance of hydroisomerization catalysts on the market in the near future will become possible only after the launch of industrial production of zeolites and silicoaluminophosphates of the required types in Russia.

2.3. Catalysts for HT of Vacuum Gas Oils (VGOs)

VGO and heavy VGO, as well as their mixtures with heavy coker gas oils and asphalt-free-oil, which serve as the main feedstock for CC and HC processes, are characterized by higher contents of high-boiling organic compounds of S and N and PAHs compared to those in atmospheric gas oils. These distillates also contain metals (mainly Ni and V), which are part of porphyrin structures that form aggregates with resins and asphaltenes, as well as Fe, Si, As, and Na. A decrease in the contents of N, PAHs, and above-mentioned impurities in feedstock supplied for further processing increases the activity and slows down the deactivation of the CC and HT catalysts. In CC, the

involvement of unhydrotreated VGO in the processing leads to a significant decrease in the yield of CCG and an increase in the content of hard-to-remove sulfur in it. A decrease in the content of basic nitrogen-containing compounds and PAHs is especially important if the resulting CCLG is then used for purification in a mixture with straight-run DF.

The efficient occurrence of principally different reactions, which is necessary to obtain feedstock with the required characteristics for HC and CC, necessitates the use of multi-tiered loading of catalysts. In this case, the characteristics of catalysts in the every layer are optimized to achieve the maximum activity of the HT reactor depending on the conditions and goals of the process and the composition of the initial gas oil distillates. The composition of the upper layers of catalysts should be suitable to remove the metals and asphaltenes, while the composition of the main layer of the HT catalyst is optimum for deep hydrogenolysis of sulfur- and nitrogen-containing compounds and hydrogenation of aromatic compounds. The idea of using multi-tiered loading of different HT catalysts responsible for the decomposition of nitrogen-containing compounds and the removal of aromatics (mainly NiMo) and hydrodesulfurization (depending on H_2 pressure, Co(Ni)Mo) is used by Albemarle [54, 116, 117]; Criterion (Centera series) [85, 118]; Sinopec [119]; Axens (catalysts with high activity in hydrodenitrogenations (HDN) and hydrodesulfurizations (HDS) of the HR 504, 508, 544 series and the new Impulse™ HR 1058 catalyst, additionally capable of catalyzing the HDAr reaction of VGO) [120]; and also Topsøe (catalysts of the HyBRIM™ series: TK565, TK569, TK609, TK611) [121].

Some common characteristics of modern VGO hydrotreatment catalysts are as follows. The optimum metal content in them varies in the range 8−12 wt % Mo and 2−5 wt % Co(Ni) [122−124]; further increase in the concentration leads to deterioration of the texture characteristics of the catalyst and dispersion of the active component particles. In this case, all the deposited metals are mainly in the form of the CoNiMoS phase of types II and III, represented by particles up to 3 nm long with up to two layers in a stack and the maximum fraction of Co(Ni) atoms localized in the upper part of the edges of MoS_2 particles. The diameter of the main pores of the catalyst varies from 5−8 nm for HT of VGO [125] to 10−20 nm for HT of asphalt-free-oil with low metal (<27 ppm) and asphaltene (<1%) contents [126] and of heavy feedstock with high metal or asphaltene (≈120 ppm) contents [127]). At sufficiently high specific surface area of the catalyst the diffusion of reactant molecules and removal of reaction products are ensured by minimizing the contents of bottle-shaped, blind, or slit-like pores. The ongoing studies on methods for the preparation of supports and catalysts are aimed at providing the optimum combination of these characteristics.

In 2017, the annual demand for the catalysts for the hydrotreatment of VGO derived from CC feedstocks in Russia exceeded 800 t/year with growth prospects of more than 1100 t/year by 2030. If all the planned fixed bed HC units are commissioned, the demand for HT catalysts for them can reach 2000 t/year. Studies aimed at the development of technology for the production of a complete package of VGO hydrotreatment catalysts are underway at the Institute of Catalysis and are performed together with Gazpromneft. In addition to the VGO hydrotreatment support and catalyst, as well as methods for their preparation and for performing the process using these catalysts [131−138] reported in scientific publications [128−130] and patents, catalysts for the guard layer [32, 139, 140] and demetallization [32] have also been actively developed in recent years. Life tests of a laboratory sample catalyst for HT of HC feedstocks (straight-run VGO+heavy coker gas oil) on a pilot plant showed that a product containing 15 ± 5 ppm nitrogen can be obtained at temperatures 3−6°C lower than on the commercial analogue [32].

Patents for the P-modified catalyst for deep hydrotreatment of VGO based on $NiMoW/Al_2O_3$ and a method for its preparation [141], demetallization catalyst [142], and a package of protective layer catalysts designed to reduce the deposits of asphaltenes, organometallic compounds, resins, PAHs, and other coke precursors in the upper layer of the catalyst for HT of atmospheric residue or a mixture of VGO and heavy coker gas oil [143] were obtained at Samara State Technical University [141] and VNIINP [142, 143].

As the feedstock base and methods for the preparation of supports, VGO and DF hydrotreatment catalysts, and guard layer are basically similar, it is realistic to expect a relatively quick (~5 years) launch of their industrial production.

CONCLUSIONS

The present analysis of the scientific and technical level of modern imported and Russian catalysts for hydroprocesses used to obtain the desired products (Table 7) allows us to draw the following conclusions and make predictions:

(1) The chemical compositions of hydroprocess catalysts are similar for the majority of manufacturing companies; their catalytic properties significantly depend on the characteristics of the porous supports used (alumina, zeolites, aluminosilicates, etc.).

(2) For the industrial production of HC and hydroisodewaxing catalysts in Russia, it is necessary to develop technology for the synthesis of synthetic zeolites, primarily, zeolites of the types USY, ZSM-23, SAPO-41, and ZSM-12.

(3) The level of research and development in Russia allowed the Rosneft and Gazpromneft companies

Table 7. Estimation of the development levels of modern competitive catalysts of the hydrocracking and hydrotreatment of various oil distillates. Prospects for supplies of base catalysts for oil refineries of Russia

Catalyzed process	Consumption by 2030 (planned), t/year	Development level			Potential manufacturers
		scientific developments	runs of pilot/commercial batches	industrial production	
Hydrocracking	≈2700	Institute of Catalysis–Gazprom Neft, RN-TsIR (Rosneft–KNT Group)	—	—	RN-cat, Gazprom Neft production under construction
Hydrotreatment of CCGs	130	Samara State Technical University, Institute of Catalysis–Gazprom Neft, RN-TsIR	—	—	RN-cat, Gazprom Neft production under construction, Nizhny Novgorod Sorbents (Nizhegorodskie sorbenty)*
Hydrotreatment of DF	2700	RN-TsIR, Institute of Catalysis–Gazprom Neft	Bashneft–Ufaneftekhim, Gazprom Neft–Omsk Refinery	AZKiOS	
Hydrotreatment of VGO	1100	Institute of Catalysis–Gazprom Neft	—	—	
Production of winter (arctic) fuels	130–150	RN-TsIR, VNIINP, Institute of Catalysis–Gazprom Neft	Gazprom Neft–Omsk Refinery	VNIINP	—

*For the case of winter (arctic) fuels, this is potential manufacturer after the start of industrial production of zeolites and silica–aluminophosphates of the required brands in Russia.

to perform successful pilot and industrial tests of competitive catalysts for hydrotreatment of mixed DFs with different contents (10−20%) of secondary distillates.

(4) The creation of a joint venture between Rosneft and KNT Group (RN-Kat) and the completion of the construction of a new catalyst production facility in Omsk in the near future have created good prospects for the transition of Russian refineries to the mass use of Russian catalysts for DT HT within 3 or 4 years.

(5) Research and development of VGO hydrocracking and hydrotreatment catalysts, including those in mixtures with secondary heavy gas oils, allow the start of production of grand lots and pilot plant tests of these catalysts. The results will determine the rate of further development of the production of the VGO hydrocracking and hydrotreatment catalysts in Russia. In the upside case, the start of mass use of Russian-made catalysts is estimated at 4 or 5 years.

(6) Taking into account the climatic features of Russia, there is high demand for motor fuels and oils of winter and arctic brands. The current trend in the development of catalysts for the production of these products is the use of hydroisodewaxing and catalytic systems based on ZSM-23 and SAPO-41 zeolites. The domestic demand for Russian catalysts for this purpose seems to be quite possible taking into account the available scientific developments, and will depend on the activity of industrial manufacturers of catalysts.

(7) The Russian CCG hydrotreatment catalysts are about ready for pilot and industrial plant tests; the results can be expected in the next 2 or 3 years.

(8) Research in the field of control over the physical and chemical properties of alumina as a catalyst support and the development of methods for the synthesis of zeolites are considered priority directions in research on catalysts for hydroprocesses in oil refining.

(9) The introduction of newly developed catalysts for hydroprocesses in industry requires the development of methods for predicting the process characteristics based on methods of mathematical modeling and catalytic models of oil refining processes.

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REFERENCES

1. Subramanian, V., *Global Markets for Catalysts: Focus on Catalyst Regeneration (CHM046C),* Wellesley, MA: BCC Research, 2015.

2. McWilliams, A., *Catalysts for Environmental and Energy Applications (CHM020E),* Wellesley, MA: BCC Research, 2015.

3. Tanmay, J., *Refinery Catalysts: Technologies and Global Markets (CHM078),* Wellesley, MA: BCC Research, 2017.

4. Refinery Catalysts Market. Markets & Markets Official Website. https://www.marketsandmarkets.com/Market-Reports/refinery-catalyst-advanced-technologies-and-global-market-84.html. Cited April 16, 2021.

5. Ward, J., *Fuel Process. Technol.,* 1993, vol. 35, pp. 55−85.

6. Gosselink, J.W., in *Transition Metal Sulphides: Chemistry and Catalysis,* Weber, Th., Prins, R., and van Santen, R.A., Eds., Springer: Dordrecht, 1998, pp. 311−355.

7. Reinhoudt, H.R., Troost, R., van Schalkwijk, S., van Langeveld, A.D., Sie, S.T., van Veen, J.A.R., and Moulijn, J.A., *Fuel Process. Technol.,* 1999, vol. 61, nos. 1−2, pp. 117−131.

8. Landau, M.V., Vradman, L., Valtchev, V., Lezervant, J., Liubich, E., and Talianker, M., *Ind. Eng. Chem. Res.,* 2003, vol. 42, no. 12, pp. 2773−2782.

9. Maxwell, I.E., *Catal. Today,* 1987, vol. 1, no. 4, pp. 385−413.

10. US Patent 9387466, 2016.

11. US Patent 9669396, 2017.

12. US Patent 9079174, 2015.

13. Hassan, A., Ahmed, S., Ali, M.A., Hamid, H., and Inui, T., *Appl. Catal., A,* 2001, vol. 220, nos. 1−2, pp. 59−68.

14. Rigutto, M.S., van Veen, R., and Huve, L., *Stud. Surf. Sci. Catal.,* 2007, vol. 168, pp. 855−913.

15. Choi, W.S., Lee, K.H., Choi, K., and Ha, B.H., *Stud. Surf. Sci. Catal.,* 1999, vol. 127, pp. 243−250.

16. *Catalysis by Transition Metal Sulphides. From Molecular Theory to Industrial Application,* Toulhoat, H. and Raybaud, P., Eds., Paris: Technip, 2013.

17. Martínez, C. and Corma, A., *Coord. Chem. Rev.,* 2011, vol. 255, nos. 14−13, pp. 1558−1580.

18. Cornet, D., Qotbi, M.E., and Leglise, J., *Stud. Surf. Sci. Catal.,* 1999, vol. 106, pp. 147−156.

19. Francis, J., Guillon, E., Bats, N., Pichon, C., Corma, A., and Simon, L.J., *Appl. Catal., A,* 2011, vols. 409−410, pp. 140−147.

20. Camblor, M.A., Corma, A., Martínez, A., Martínez-Soria, V., and Valencia, S., *J. Catal.,* 1998, vol. 179, no. 2, pp. 537−547.

21. Corma, A., Lopez, C., and Martinez, A., *Stud. Surf. Sci. Catal.,* 2004, vol. 154, pp. 2380−2386.

22. Shimada, H., Sato, K., Honna, K., Enomoto, T., and Ohshio, N., *Catal. Today,* 2009, vol. 141, nos. 1−2, pp. 43−51.

23. Weitkamp, J. and Ernst, S., in *Zeolites in Guidelines for Mastering the Properties of Molecular Sieves,* Barthomeuf, D., Derouane, E.D., and Hölderich, W., Eds., New York: Plenum Press, 1990, pp. 343−354.

24. Henry, R., Tayakout-Fayolle, M., Afanasiev, P., Lorentz, C., Lapisardi, G., and Pirngruber, G., *Catal. Today,* 2014, vols. 220−222, pp. 159−167.

25. Klemt, A. and Reschetilowski, W., *Chem. Eng. Technol.,* 2002, vol. 25, no. 2, pp. 137−139.

26. US Patent 8882993, 2014.

27. US Patent 9580328, 2017.

28. US Patent 9662640, 2017.

29. US Patent 10301184, 2019.

30. US Patent 8778171, 2014.

31. Peng, C., Fang, X., and Zeng, R., *Catalysis,* 2016, vol. 28, pp. 86−118.

32. Kazakov, M.O., Abstract of Papers, *Trudy Tret'ei ezhegodnoi konferentsii "PRO Kataliz Forum: Rossiiskie katalizatory—status AKTIVEN"* (Proc. Third Annual Conf. "PRO Catalysis Forum: Status ACTIVE"), St. Petersburg, 2019.

33. Christensen, P., Hearn, A., and Yeung, T., *PTQ,* Q1 2018, pp. 1−5. https://www.digitalrefining.com/article/1001430/the-future-for-hydrocracking-part-1. Cited April 17, 2021.

34. Al-Somali, F., Maas, E., and Visser, T., *PTQ,* Q2 2016, pp. 1−7. www.digitalrefining.com/article/1001273. Cited April 17, 2021.

35. Torchia, D. and Howard, N., *PTQ,* 2016, pp. 1−4. http://www.digitalrefining.com/article/1001258. Cited April 17, 2021.

36. Ivanova, I.I., Kolyagin, Yu.G., Kasyanov, I.A., Yakimov, A.V., Bok, T.O., and Zarubin, D.N., *Angew. Chem., Int. Ed.,* 2017, vol. 56, no. 48, pp. 15344−15347.

37. Ponomareva, O.A., Knyazeva, E.E., Shkuropatov, A.V., Ivanova, I.I., Gerzeliev, I.M., and Khadzhiev, S.N., *Pet. Chem.,* 2017, vol. 57, no. 12, pp. 1147−1150.

38. Travkina, O.S., Agliullin, M.R., Filippova, N.A., Khazipova, A.N., Danilova, I.G., Grigor'eva, N.G., Narender, N., Pavlov, M.L., and Kutepov, B.I., *RSC Adv.,* 2017, vol. 7, no. 52, pp. 32581−32590.

39. Agliullin, M.R., Danilova, I.G., Faizullin, A.V., Amarantov, S.V., Bubennov, S.V., Prosochkina, T.R., Grigor'eva, N.G., Paukshtis, E.A., and Kutepov, B.I., *Microporous Mesoporous Mater.,* 2016, vol. 230, pp. 118−127.

40. RF Patent 2607908, 2015.

41. RF Patent 2662234, 2017.

42. RF Patent 2662239, 2017.

43. RF Patent 2662232, 2017.

44. RF Patent, 2603776, 2015.

45. RF Patent 2607905, 2015.

46. Dik, P.P., Danilova, I.G., Golubev, I.S., Kazakov, M.O., Nadeina, K.A., Budukva, S.V., Pereyma, V.Y., Klimov, O.V., Prosvirin, I.P., Gerasimov, E.Yu., Bok, T.O., Dobryakova, I.V., Knyazeva, E.E., Ivanova, I.I., and Noskov, A.S., *Fuel,* 2019, vol. 237, pp. 178−190.

47. Kazakov, M.O., Nadeina, K.A., Danilova, I.G., Dik, P.P., Klimov, O.V., Pereyma, V.Y., Paukshtis, E.A., Golubev, I.S., Prosvirin, I.P., Gerasimov, E.Yu., Noskov, A.S., Dobryakova, I.V., Knyazeva, E.E., and Ivanova, I.I., *Catal. Today,* 2019, vol. 329, pp. 108−115.

48. Kazakov, M.O., Nadeina, K.A., Danilova, I.G., Dik, P.P., Klimov, O.V., Pereyma, V.Y., Gerasimov, E.Yu., Dobryakova, I.V., Knyazeva, E.E., Ivanova, I.I., and Noskov, A.S., *Catal. Today,* 2018, vol. 305, pp. 117−125.

49. Dik, P.P., Pereima, V.Y., Nadeina, K.A., Kazakov, M.O., Klimov, O.V., Gerasimov, E.Yu., Prosvirin, I.P., and Noskov, A.S., *Catal. Ind.,* 2018, vol. 10, no. 1, pp. 20−28.

50. Dik, P.P., Nadeina, K.A., Kazakov, M.O., Klimov, O.V., Gerasimov, E.Yu., Prosvirin, I.P., and Noskov, A.S., *Catal. Ind.,* 2018, vol. 10, no. 1, pp. 29−40.

51. Stratiev, D.S., Shishkova, I.K., and Dobrev, D.S., *Fuel Process. Technol.,* 2012, vol. 94, no. 1, pp. 16−25.

52. Huang, A., Benoit, A., Cheng, G., and Riley, B., *Catalagram,* 2017, no. 120, pp. 8−20.

53. Sadeghbeigi, R., *Fluid Catalytic Cracking Handbook,* Amsterdam: Elsevier, 2012.

54. Anderson, G., *ALBEMARLE Catal. Cour.,* 2015, no. 84, pp. 22−24.

55. Andonov, G., Petrov, S., Stratiev, D., and Zeuthen, P., *PTQ,* Q1 2006, pp. 1−7. www.digitalrefining.com/article/1000152. Cited April 18, 2021.

56. Miller, J.T., Reagan, W.J., Kaduk, J.A., Marshall, C.L., and Kropf, A.J., *J. Catal.,* 2000, vol. 193, no. 1, pp. 123−131.

57. Qiherima, Yuan, H., Li, F.H., Zhang, Y.H., and Xu, G.T., *Chin. Chem. Lett.,* 2011, vol. 22, no. 3, pp. 366−369.

58. US Patent 7052598, 2006.

59. Axens Official Website. www.axens.net/product/catalysts-a-adsorbents/103/hr-845.html. Cited February 21, 2020.

60. Axens Official Website. www.axens.net/product/catalysts-a-adsorbents/165/ta-801.html. Cited February 21, 2020.

61. Haldor Topsøe Official Website. www.topsoe.com/products/tk-703-hyoctanetm. Cited February 20, 2021.

62. Rasmussen, H., FCC naphtha posttreatment, https://refiningcommunity.com/wp-content/uploads/2017/02/FCC-Naphtha-Post-treatment-Rasmussen-Haldor-Topsoe-FCCU-Galveston-2017-.pdf. Cited April 18, 2021.

63. Qu, J., Xi, Y., Li, M., Pan, G., Jin, X., Gao, X., and Nie, H., *China Pet. Process. Petrochem. Technol.,* 2013, vol. 15, no. 3, pp. 1−6.

64. Ishutenko, D., Nikulshin, P., and Pimerzin, A., *Catal. Today,* 2016, vol. 271, pp. 16−27.

65. Nikulshin, P.A., Ishutenko, D.I., Mozhaev, A.A., Maslakov, K.I., and Pimerzin, A.A., *J. Catal.,* 2014, vol. 312, pp. 152−169.

66. Ishutenko, D., Anashkin, Yu., and Nikulshin, P., *Appl. Catal., B,* 2019, vol. 259. https://doi.org/10.1016/j.apcatb.2019.118041

67. Pimerzin, Al.A., Ishutenko, D.I., Mozhaev, A.V., Kapustin, V.M., Chernysheva, E.A., Maximova, A.V., Pimerzin, A.A., and Nikulshin, P.A., *Fuel Process. Technol.,* 2017, vol. 156, pp. 98−106.

68. Ishutenko, D., Minaev, P., Anashkin, Yu., Nikulshina, M., Mozhaev, A., Maslakov, K., and Nikulshin, P., *Appl. Catal., B,* 2017, vol. 203, pp. 237−246.

69. Nikulshin, P., Ishutenko, D., Anashkin, Yu., Mozhaev, A., and Pimerzin, A., *Fuel,* 2016, vol. 182, pp. 632−639.

70. RF Patent 2557248, 2013.

71. RF Patent 2705397, 2019.

72. RF Patent 2676260, 2016.

73. RF Patent 2655030, 2016.

74. RF Patent 2714139, 2019.

75. Nadeina, K.A., Pereima, V.Yu., Klimov, O.V., Koryakina, G.I., Noskov, A.S., Kondrashev, D.O., Kleymenov, A.V., Vedernikov, O.S., Kuznetsov, S.E., Galkin, V.V., and Abrashenkov, P.A, *Catal. Ind.,* 2017, vol. 9, no. 3, pp. 230–238.

76. Nadeina, K.A., Klimov, O.V., Pereima, V.Yu., Koryakina, G.I., Danilova, I.G., Prosvirin, I.P., Gerasimov, E.Yu., Yegizariyan, A.M., and Noskov, A.S., *Catal. Today,* 2016, vol. 271, pp. 4–15.

77. Nadeina, K.A., Klimov, O.V., Danilova, I.G., Pereyma, V.Yu., Gerasimov, E.Yu., Prosvirin, I.P., and Noskov, A.S., *Appl. Catal., B,* 2018, vol. 223, pp. 22–35.

78. RF Patent 2575637, 2016.

79. RF Patent 2575639, 2016.

80. RF Patent 2575638, 2016.

81. Stanislaus, A., Marafi, A., and Rana, M.S., *Catal. Today,* 2010, vol. 153, nos. 1–2, pp. 1–68.

82. Battiston, A., *Catal. PTQ,* 2016, pp. 1–7. http://www.digitalrefining.com/article/1001243. Cited April 18, 2021.

83. Battiston, A., *ALBEMARLE Catal. Cour.,* 2016, no. 85, pp. 10–14.

84. Rogers, M., Paper presented at the American Fuel and Petrochemical Manufacturers Annual Meeting, March 2015; paper AM-15-24.

85. Rasmussen, H.W., Abstract of Papers, *Proc. Am. Fuel Petrochem. Manuf. Annu. Meet. Q&A Technol. Forum,* 2016, p. 4.

86. Topsøe, H., *Appl. Catal., A,* 2007, vol. 322, pp. 3–8.

87. Eijsbouts, S., van den Oetelaar, L.C.A., and van Puijenbroek, R.R., *J. Catal.,* 2005, vol. 229, no. 2, pp. 352–364.

88. Marafi, M., Stanislaus, A., and Furimsky, E., *Handbook of Spent Hydroprocessing Catalysts,* Amsterdam: Elsevier, 2010.

89. Song, C., *Catal. Today,* 2003, vol. 86, nos. 1–4, pp. 211–263.

90. Carlson, K., *Catal. PTQ,* 2010, vol. 15, no. 2, pp. 21–23. https://www.digitalrefining.com/article/1000472/active-site-developments-for-improved-productivity. Cited April 17, 2021.

91. Fujikawa, T., Kimura, H., Kiriyama, K., and Hagiwara, K., *Catal. Today,* 2006, vol. 111, nos. 3–4, pp. 188–193.

92. Klimov, O.V., *Oil Gas J. Russ.,* 2013, no. 3, pp. 71–75.

93. Eijsbouts, S., in *Synthesis of Solid Catalysts,* de Jong, K.P., Ed., Weinheim: Wiley-VCH, 2009, pp. 302–330.

94. Klimov, O.V., Leonova, K.A., Koryakina, G.I., Gerasimov, E.Yu., Prosvirin, I.P., Cherepanova, S.V., Budukva, S.V., Pereyma, V.Yu., Dik, P.P., Parakhin, O.A., and Noskov, A.S., *Catal. Today,* 2014, vol. 220–222, pp. 66–77.

95. Manna, U., Abstract of Papers, *Proc. Int. Conf. on Refining Challenges and Way Forward,* New Delhi, 2012.

96. Zeuthen, P., Abstract of Papers, *Proc. Int. Symp. on Advances in Hydroprocessing of Oil Fractions (ISAHOF 2013),* Acapulco, Mexico, 2013, p. 7.

97. ALBEMARLE Official Website. www.albemarle.com. Cited February 20, 2020.

98. Transformative performance. Boost your margins and flexibility with Celestia™ hydroprocessing catalyst. https://www.albemarle.com/storage/wysiwyg/celestia-fact-sheet_rev_002.pdf. Cited February 20, 2020.

99. Rupec Official Website. www.rupec.ru/news/38799/. Cited January 16, 2020.

100. Oil Capital Official Website. https://oilcapital.ru/news/export/27-12-2019/rosneft-nachinaet-eksport-katalizatorov-gidroochistki-diztopliva. Cited March 15, 2020.

101. Rosneft Official Website. https://www.rosneft.ru/press/news/item/199247/. Cited January 16, 2020.

102. http://www.criterioncatalysts.com/news-technical-papers/literature/_jcr_content/par/textimage.stream/1481793167354/5a0905b16d36818a51ad8c19b1307427344bbfd3e26ce1d53293786eb3151b0f/dewaxing-factsheethires.pdf. Cited March 15, 2018.

103. Hou, Z., Hilbert, T., and Kalyanaraman, M., Abstract of Papers, *Proc. 7th Ref. Chin. Conf.,* Beijing, 2013.

104. Szynkarczuk, R., Paper presented at the American Fuel and Petrochemical Manufacturers Annual Meeting, Orlando, FL, March 2014; paper AM-14-74.

105. Hilbert, T., Kalyanaraman, M., Ravella, A., Acharya, M., Smith, R., and Thakkar, V., MIDW™ technology enables premium distillate production. Commercially proven integrated technology solutions for low-cloud/high cetane diesel. http://cdn.exxonmobil.com/~/media/global/files/catalyst-and-licensing/conference_2013-1912-midw_technology_enables_premium_distillate_production.pdf. Cited March 10, 2017.

106. Pappl, D.A. and Hilbert, T.I., *PTQ,* 1996, pp. 35–41.

107. Kalyanaraman, M., Smyth, S., Hilbert, N., and Acharya, M., Paper presented at the International Refining and Petrochemical Conference, Verona, 2014.

108. Hydrotreating. Diesel hydrotreating. Haldor Topsøe Official Website. www.topsoe.com/processes/hydrotreating/diesel-hydrotreating. Cited February 25, 2020.

109. Kiseleva, T.P., Aliev, R.R., Posokhova, O.M., and Tselyutina, M.I., *Neftepererab. Neftekhim.,* 2016, no. 1, pp. 3–7.

110. Uvarkina, D.D., Piryutko, L.V., Danilova, I.G., Budukva, S.V., Klimov, O.V., Kharitonov, A.S., and Noskov, A.S., *Russ. J. Appl. Chem.,* 2015, vol. 88, no. 11, pp. 1827–1838.

111. Smirnova, M.Yu., Piryutko, L.V., Brester, Yu.S., Parfenov, M.V., Kaichev, V.V., Klimov, O.V., and Noskov, A.S., *Pet. Chem.,* 2020, vol. 60, no. 2, pp. 212–218.

112. Kiseleva, T.P., Gizetdinova, A.F., Aliev, R.R., and Skornikova, S.A., *Mir Nefteprod.,* 2015, no. 4, pp. 17–24.

113. RF Patent 2627770, 2016.

114. RF Patent 2616003, 2016.

115. RF Patent 2662934, 2017.

116. Anderson, G., *PTQ,* Q1 2016, pp. 1–5. https://www.digitalrefining.com/article/1001201/

overcoming-clean-fuels-challenges. Cited April 17, 2021.

117. World Refining Association Official Website. http://www.wraconferences.com/wp-content/uploads/2016/11/Albemarle-Paper_ERTC-2016.pdf. Cited May 25, 2020.

118. Chua, K. and Zhil, G., *Catal. PTQ,* 2016, http://www.digitalrefining.com/article/1001255. Cited May 25, 2020.

119. Hu, D., Yang, Q., Dai, L., and Zhao, X., *China Pet. Process. Petrochem. Technol.,* 2013, vol. 15, no. 2, pp. 1−5.

120. Catalysts and adsorbents. Product Listing. Axens Official Website. www.axens.net/document/874/catalysts-a-adsorbents-catalogue/english.html. Cited May 25, 2020.

121. FCC pretreatment catalysts. Improve your FCC pretreatment using BRIM(tm) technology. https://autodocbox.com/Diesel/77532165-Fcc-pretreatment-catalysts.html. Cited April 18, 2021.

122. Ling, T.-R., Wan, B.-Z., Lin, H.-P., and Mou, C.-Y., *Ind. Eng. Chem. Res.,* 2009, vol. 48, no. 4, pp. 1797−1803.

123. Klimov, O.V., Nadeina, K.A., Dik, P.P., Koryakina, G.I., Pereyma, V.Yu., Kazakov, M.O., Budukva, S.V., Gerasimov, E.Yu., Prosvirin, I.P., Kochubey, D.I., and Noskov, A.S., *Catal. Today,* 2016, vol. 271, pp. 56−63.

124. Ma, X., Sakanishi, K., and Mochida, I., *Ind. Eng. Chem. Res.,* 1996, vol. 35, no. 8, pp. 2487−2494.

125. Eurecat Official Website. www.eurecat.com. Cited February 20, 2018.

126. Núñez, M. and Villamizar, M., *Appl. Catal., A,* 2003, vol. 252, no. 1, pp. 51−56.

127. Stanislaus, A., Absi-Halabi, M., and Khan, Z., *Stud. Surf. Sci. Catal.,* 1996, vol. 100, pp. 189−197.

128. Danilevich, V.V., Stolyarova, E.A., Vatutina, Y.V., Gerasimov, E.Yu., Ushakov, V.A., Saiko, A.V., Kli-mov, O.V., and Noskov, A.S., *Catal. Ind.,* 2019, vol. 11, no. 4, pp. 301−312.

129. Nadeina, K.A., Kazakov, M.O., Danilova, I.G., Kovalskaya, A.A., Stolyarova, E.A., Dik, P.P., Gerasimov, E.Yu., Prosvirin, I.P., Chesalov, Y.A., Klimov, O.V., and Noskov, A.S., *Catal. Today,* 2019, vol. 329, pp. 2−12.

130. Vatutina, Y.V., Nadeina, K.A., Klimov, O.V., Kazakov, M.O., Danilova, I.G., Cherepanova, S.V., Khabibulin, D.F., Gerasimov, E.Yu., Prosvirin, I.P., Dik, P.P., and Noskov, A.S., *Catal. Today* (in press). 2020.
https://doi.org/10.1016/j.cattod.2020.03.046

131. RF Patent 2629358, 2017.

132. RF Patent 2626402, 2017.

133. RF Patent 2626401, 2017.

134. RF Patent 2633968, 2017.

135. RF Patent. 2633967, 2017.

136. RF Patent 2626398, 2017.

137. RF Patent 2626399, 2017.

138. RF Patent 2626400, 2017.

139. Nadeina, K.A., Kazakov, M.O., Kovalskaya, A.A., Danilova, I.G., Cherepanova, S.V., Danilevich, V.V., Gerasimov, E.Yu., Prosvirin, I.P., Kondrashev, D.O., Kleimenov, A.V., Klimov, O.V., and Noskov, A.S., *Catal. Today,* 2020, vol. 353, pp. 53−62.
https://doi.org/10.1016/j.cattod.2019.10.028

140. Nadeina, K.A., Kazakov, M.O., Kovalskaya, A.A., Danilevich, V.V., Klimov, O.V., Danilova, I.G., Khabibulin, D.F., Gerasimov, E.Yu., Prosvirin, I.P., Ushakov, V.A., Fedotov, K.V., Kondrashev, D.O., Kleimenov, A.V., and Noskov, A.S., *Catal. Today,* 2019, vol. 329, pp. 53−62.

141. RF Patent 2694370, 2017.

142. RF Patent 2691069, 2018.

143. RF Patent 2699225, 2018.

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