

Reforming Catalysts of the PR Family: Scientific Foundations and Technological Advancement

A. S. Belyi

Institute of Hydrocarbon Processing, Siberian Division, Russian Academy of Sciences, Omsk, Russia

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Abstract—Results of investigations of the state of active sites in aluminoplatinum reforming catalysts (RCs) are summarized. Laws governing the formation and the role of platinum ionic species in the adsorption and catalytic conversion of hydrocarbons are presented. Strategies for the design of highly efficient catalysts, the development of catalyst manufacturing technologies, and operation in the production of motor fuels and aromatic hydrocarbons are formulated. Data are reported on the full-scale operation of catalyst PR-51/04 (PR-71), a new RC, and full-scale tests of the Biforming process, a new process for motor fuel production by coprocessing C_3 – C_4 hydrocarbon gases and gasoline fractions.

Catalytic reforming of gasolines continues to be one of the basic processes for preparing high-octane motor fuels, aromatic hydrocarbons, and hydrogen.

The evolution of the process consisted of increasing the conversion depth, hydrocarbon aromatization selectivity, and the operational stability of catalysts. During the 50 years of existence of the Platforming process, the yield of target products (aromatic hydrocarbons and hydrogen) increased by a factor of 1.5, and the cycle duration between regenerations became more than 4 times longer. These achievements, which were mainly due to the development of new catalysts, provided the basis for technological advancement. Progress consisted in the reduction of the working pressure from 4.0 to 0.3 MPa and in the development of a reactor unit with a moving bed and continuous catalyst regeneration (the CCR system).

Chemical reactions of hydrocarbon conversion under the reforming conditions are accompanied by the formation of low-value C_1 – C_4 hydrocarbons with 15–25% yields based on the stock. Improvement of the process selectivity and a search for alternative sources are of paramount importance in view of limited petroleum resources, lowering production rates, and rising costs.

Conventional industrial reforming catalysts (RCs) consist of a fluorine- and chlorine-promoted alumina support and platinum or platinum plus metallic (mainly, rhenium) promoters uniformly distributed over its bulk.

Contemporary views on the organization of platinum RCs are based on the results of numerous studies, which peaked in the 1960s–1980s. Many data were collected to prove that platinum in a nonmetallic state (soluble, electron-deficient, ionic, or oxidized platinum [1–3]) is formed along with disperse platinum metal (Pt^0). All of the platinum states other than Pt^0 were interpreted in terms of strong metal–support interactions. However, no reliable correlations were found until

recently between the electronic state and catalytic properties of platinum.

The efforts of the staff of the Omsk Branch of the Institute of Catalysis (since 2004, the Institute of Hydrocarbon Processing), Siberian Division, Russian Academy of Sciences, for more than two decades were focused on RCs. These efforts culminated in the discovery of an important role of nonmetallic states of platinum (Pt^σ) in the adsorption of reagents and the catalysis of reforming reactions [4]. The investigations were begun with the development of an adsorption method for measuring the densities of surface platinum atoms in different electronic states [5, 6]. The investigation of a large group of catalysts showed that the Pt^0 -to- Pt^σ concentration ratio in an RC is a function of the chemical composition of the catalyst and the preparation process. The results were used to prepare model catalysts with set Pt^0 -to- Pt^σ ratios [7, 8]; these catalysts were characterized using physicochemical methods. It was found that the ionic platinum state Pt^σ is close to the state of platinum(II) in chlorides and that, compared to Pt^0 , it possesses some specific adsorption and catalytic properties [4–11, 14].

Catalytic Properties of Pt^0 and Pt^σ Sites in Hydrocarbon Conversion Reactions

Benzene hydrogenation. It was inferred from kinetic data [12] that Pt^σ is inactive at 100°C and the benzene conversion is dictated by the concentration of Pt^0 sites. The Pt^0 atom catalytic activity is 22–24 mol/atom Pt^0 /s. After reacting with water, the activity of Pt^σ sites in the benzene conversion becomes comparable with the Pt^0 activity. This result was explained by the ligand effect. The electronic structure of Pt^σ changes in the reaction with H_2O ; the bond strength changes as a result, and the rate-controlling stage (desorption of nascent cyclohexane) becomes more rapid [13].

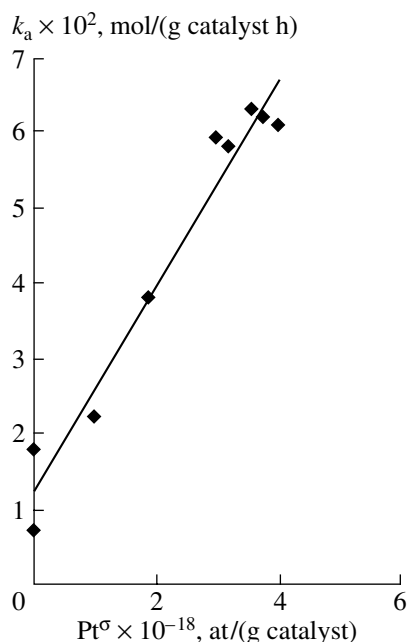


Fig. 1. Rate constant of heptane aromatization k_a at 500°C and $p = 1.0$ MPa vs. the density of Pt^σ atoms.

Cyclohexane dehydrogenation. The catalyst activity at 200–400°C is controlled by the Pt^0 concentration [4], while Pt^σ sites are inactive. At 400–500°C, Pt^σ sites are involved in cyclohexane dehydrogenation. The activation energy in the presence of Pt^σ is 28 kcal/mol (against 19 kcal/mol for metallic platinum). Such a significant change in the energy parameters of the reaction suggests that the dehydrogenation mechanism on Pt^σ is different.

***n*-Heptane aromatization.** A linear correlation was found between the rate constant of aromatization k_a and the amount of Pt^σ atoms in the catalyst (Fig. 1) [4–6]. The atomic catalytic activity of Pt^σ at 500°C and $P_{H_2} = 1.0$ MPa is 3–4 mol/atom Pt^σ /s, which is one order of magnitude higher than the activity of Pt^0 . For these reasons, the selectivity S of the major aromatization reaction expressed through the ratio of k_a to the overall rate constant k_0 of heptane conversion on Pt^σ -containing catalysts is substantially higher (by a factor of 1.6–1.7, Fig. 2), while the alkane C_1 – C_4 formation rate is lower. A high methane concentration in the hydrogenolysis products of *n*-paraffins indicates the preference of C–C bond rupture, which is uncharacteristic of Pt^0 . Pt^σ atoms do not form many-site bonds with adsorbate hydrocarbons (the strength of these bonds affects the degree of hydrogenolysis at internal C–C bonds), and deep dehydrogenation is the reason for the formation of coke precursors on an active surface.

The above results served as the basis to modify the classical bifunctional model of RCs. In terms of this modified model, both Pt^σ and Pt^0 sites exist on the alu-

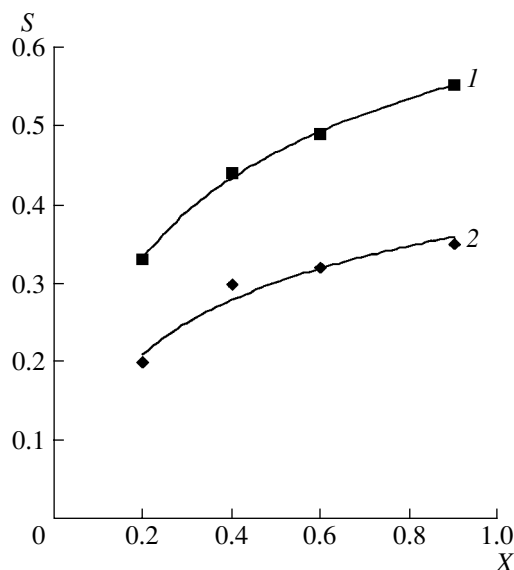


Fig. 2. Heptane aromatization selectivity vs. conversion at $T = 500^\circ\text{C}$ and $p = 1.0$ MPa on (1) $0.5Pt^0 + 0.5Pt^\sigma$ and (2) Pt^0 catalysts.

mina surface. Such a catalytic system has a high activity and promotes the aromatization reaction with a high selectivity.

Medium effects on the properties of Pt^0 and Pt^σ sites in reforming reactions. Long-term stability tests in heptane reforming showed that the steady-state activity A_{st} of Pt^σ -containing catalysts was about 10% lower than the initial activity A_0 . In contrast, Pt^0 sites experience a strong deactivation while achieving the steady-state activity ($A_{st} = 0.7A_0$, Fig. 3). The reforming mechanisms on Pt^0 and Pt^σ sites are apparently different.

Pt^σ sites show a high resistance to poisoning in the conversion of hydrocarbons containing trace sulfur, while Pt^0 sites are subject to strong deactivation.

Reforming Catalysts with Group IVA and VIA Modifiers

Oxygen adsorption at 25°C was studied on reduced (500°C) and modified catalysts with Pt^σ/Pt^0 ratios varying from 0.2 to 2.3 (Table 1). The catalysts were modified as follows: the surface of a reduced catalyst was treated first by a mixture of H_2 with H_2S , H_2Se , H_2Te (400°C), or C_7H_{16} (500°C) and then by hydrogen at 500°C. Sulfur, selenium, tellurium, and carbon were found to interact with Pt^σ ; the manifestation of the interaction was a full loss of the ability of Pt^σ atoms to adsorb oxygen. However, modified Pt^σ atoms increased their activity in cyclohexane dehydrogenation and *n*-alkane dehydrocyclization, and the activation energy increased [4]. These results reflect ligand effects, whose nature is the same in the series of the elements

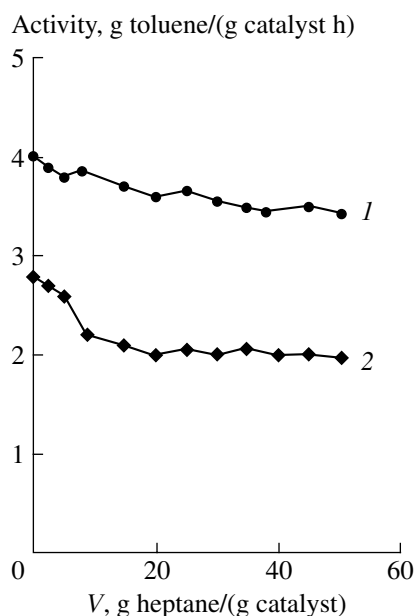


Fig. 3. Catalyst activity in heptane reforming at $T = 520^\circ\text{C}$ and $p = 1.0$ MPa for (1) $\text{Pt}^0 + \text{Pt}^i$ and (2) Pt^0 catalysts.

that interact with Pt^i . The improvement of the catalyst stability as a result of coking inhibition is an essential effect of the modifying.

Pt + Sn + Cl/alumina catalytic system. Investigations using adsorption and physical methods (EXAFS and Mössbauer spectroscopy) showed that, depending on the preparation conditions, one of the following modification mechanisms is operative: either disperse $\text{Pt}^0\text{-Sn}^0$ alloys (intermetallic compounds) are formed, or surface structures are formed in which tin is in the Sn^{2+} and Sn^{4+} states (the $\text{Pt}^i\text{-Sn(II)}$ model) [15, 16]. The second mechanism operates when wet alumina is doped by tin in the form of tin(IV) hydroxochlorides at the plasticization stage of the support preparation. The average oxidation number of tin in such catalysts is two, as derived from adsorption measurements; the platinum state corresponds to the $\text{Pt}^i\text{-Sn(II)}$ model. The existence of surface Sn(II) compounds is a factor in increasing the concentration of Pt^i sites (Table 2) and

changing their properties, in particular, in improving the C_6 dehydrocyclization selectivity and the coking resistance. Most features of the platinum–tin catalysts are due to the electronic effect; this effect is responsible for the reduced activity in reactions that involve strongly adsorbed transition states (hydrocracking, C_5 dehydrocyclization).

$\text{Pt-Re-Cl/Al}_2\text{O}_3$ catalytic system. Investigation of the state of platinum in platinum–rhenium catalysts showed that the role of rhenium is to increase the platinum dispersion and the concentration of Pt^i sites (to 70%). The Pt^i concentration in platinum–rhenium catalysts remains sufficiently high (50–60%), as opposed to $\text{Pt/Al}_2\text{O}_3$ catalysts (where the share of Pt^i sites decreases down to 10–20% as the overall platinum concentration increases to 2.5%).

The product composition and selectivity of paraffin conversion in the presence of platinum and platinum–rhenium catalysts are identical. The rhenium-modified catalysts are distinguished by a high stability (Fig. 4).

Active Site Distribution on an Oxide Support of an RC

The surface area of an active component (AC) in supported catalysts is many tens or hundreds times smaller than the surface area of the support. Therefore, the location of the AC in the pore structure can vary. The AC particle microdistribution (MD) is suitably expressed through the relationship $F_{\text{AC}} = (\Delta S/S_0)_{\text{AC}} / \Delta \log R$, where ΔS is the surface area fraction of the AC located in pores with sizes in the range ΔR [17].

An experimental determination of this type of function was first carried out for Pt/SiO_2 , $\text{Pt}/\alpha\text{-Al}_2\text{O}_3$, $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$, $\text{Pt-Sn/Al}_2\text{O}_3$, $\text{MoS}_2/\text{SiO}_2$, and $\text{MoS}_2/\text{Al}_2\text{O}_3$ systems using a combination of two methods in one experiment, namely, capillary condensation (method 1) and selective chemisorption (method 2), under the condition that catalyst pores were filled with condensed water. Method 1 gives the surface area fraction of the support $(\Delta S/S_0)_{\text{supp}}$ in the pore size range $<R$. Method 2 gives the surface area fraction of the AC $(\Delta S/S_0)_{\text{AC}}$ in the same pore size range [18–22].

Table 1. Oxygen adsorption on $\text{Pt/Al}_2\text{O}_3$ catalysts modified with H_2O , S, Se, Te, or C

Pt wt %	Relative content of Pt species, $\text{Pt}^x/\text{Pt}_s^*$		Oxygen adsorption, O/Pt_s					
	Pt^i	Pt^0	Pt_s	$\text{Pt}_s + \text{H}_2\text{O}$	$\text{Pt}_s\text{-S}$	$\text{Pt}_s\text{-Se}$	$\text{Pt}_s\text{-Te}$	$\text{Pt}_s\text{-C}^{**}$
0.35	0.2	0.8	0.90	0.81	0.80	0.78	0.80	0.60
2.30	0.6	0.4	0.70	0.41	0.39	0.41	0.40	0.31
0.35	0.7	0.3	0.63	0.29	0.30	0.31	0.29	0.20

* Pt_s —overall relative concentration of surface platinum atoms including Pt^i and Pt^0 ; Pt^x —concentration of the surface platinum atoms in a particular electronic state.

** $\text{Pt}_s\text{-C}$ was prepared by treating the catalyst with a $\text{C}_7/\text{H}_2 = 1 : 5$ (mol/mol) mixture at 500°C for 2 h, then by H_2 at 500°C for 1 h.

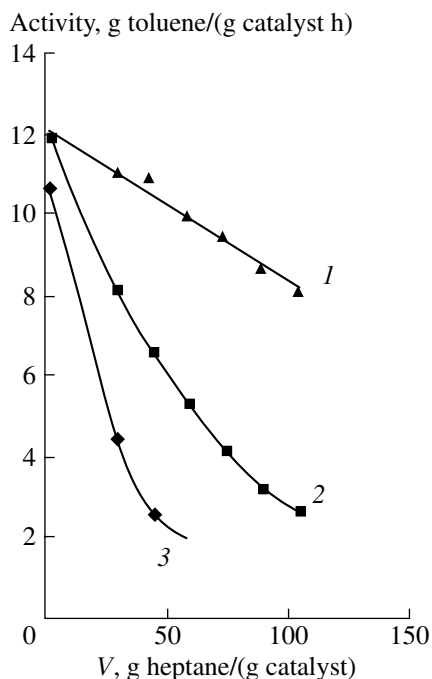
Table 2. State of platinum in catalysts

Catalyst	Content, %		$D, \%$ (Pt_s/Pt) $\times 100\%$	Composition of surface Pt atoms		
	Pt	Sn		Pt_s	Pt^0	Pt^σ
Pt	0.35	—	78	0.78	0.43	0.35
Pt-Sn ₁	0.35	0.22	92	0.92	0.41	0.51
Pt-Sn ₂	0.35	0.45	95	0.95	0.38	0.57

Analysis of MDs in model catalysts showed a selective localization of platinum in the pore structure of the support. In the preparation of adsorption catalysts, the MD is most strongly affected by the sorption conditions of the AC precursor. Rapid sorption of H_2PtCl_6 leads to a circular distribution across the diameter of a support particle and to platinum concentration in large mesopores. A considerable part of the support surface area with $R < 5.0$ nm is practically free of platinum (Fig. 5a).

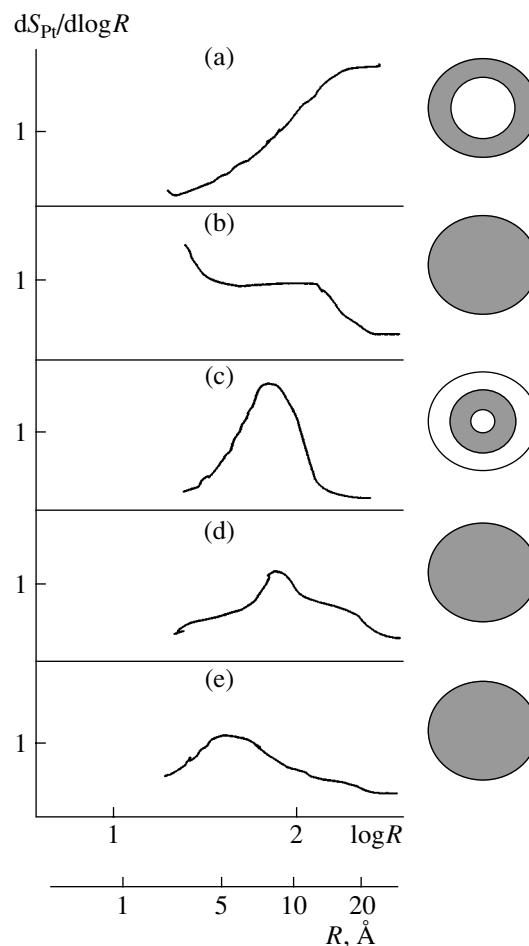
Acid anions that have lower sorption strengths than $PtCl_6^{2-}$ (e.g., excess HCl) provide homogeneous MDs with platinum concentrating in fine mesopores with $R < 5.0$ nm (Fig. 5b).

Compounds whose sorption strengths are comparable to or higher than the sorption strength of $PtCl_6^{2-}$ (such as $H_2C_2O_4$) enable one to vary the platinum MD and to obtain various metal-particle distribution profiles in different pore sizes depending on the competitor (oxalic acid) concentration in the impregnating solution (Figs. 5c–5e).

**Fig. 4.** Catalyst activity in heptane reforming vs. feed flow rate for (1) Pt-Re-S, (2) Pt-Sn-S, and (3) Pt-S catalysts.

The different adsorption properties of Pt^0 and Pt^σ sites, in particular, the selective loss of the ability of Pt^σ sites to absorb oxygen after being modified with sulfur, selenium, or tellurium, were used to estimate the metallic and ionic platinum MDs in RCs simultaneously containing both platinum species (Fig. 6).

A general correlation was derived as a result of the investigation of numerous RCs prepared by various methods. The Pt^σ localization region in all cases shifts (compared to Pt^0) toward smaller mesopore sizes ($R <$

**Fig. 5.** Effects of (a–c) the nature and (c–e) the amount of the competitor on platinum MD for (a) H_2PtCl_6 , (b) $H_2PtCl_6 + HCl$, and (c–e) $H_2PtCl_6 +$ (c) 0.2 N, (d) 0.3 N, and (e) 0.35 N $H_2C_2O_4$.

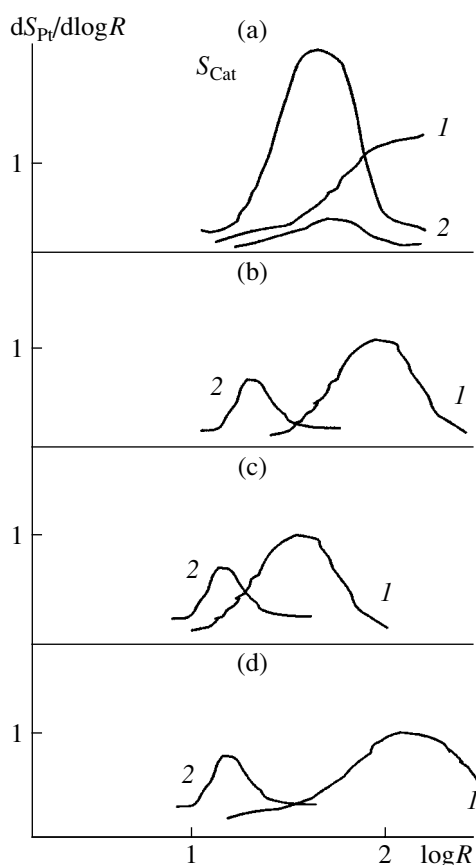


Fig. 6. Effect of the nature of the competitor during H_2PtCl_6 adsorption on the state and MD of (1) Pt^0 and (2) Pt^σ in the Al_2O_3 pore structure: (a) H_2PtCl_6 , (b) $\text{H}_2\text{PtCl}_6 + \text{CH}_3\text{COOH}$, (c) $\text{H}_2\text{PtCl}_6 + \text{H}_2\text{C}_2\text{O}_4$, and (d) $\text{H}_2\text{PtCl}_6 + \text{HCl}$.

5.0 nm). Pt^σ formation is promoted by compounds that displace the platinum sorption front to smaller pore sizes and that can form dynamic coordination bonds with platinum(IV).

A relationship was found between the anchorage mechanism of PtCl_6^{2-} anions on the surface and the state of platinum in an RC. When platinum(IV) complexes are sorbed in a fine pore containing presupported Cl^- and Br^- ions, three to five surface ligands enter the first coordination sphere of the platinum [23, 24]. It was presumed, however, that multiple binding through bridging halide ligands enhances the strong adsorption of the AC precursor on the support and the postreduction formation of Pt^σ states.

General Principles of RC Design

Comprehension of the organization and operation mechanism of RCs provided the basis for substituting a systemic approach, namely, RC design, for the conventional preparation of RCs [24–26].

To design a catalyst means to solve a many-factor problem in which scientific and engineering aspects are interrelated. Design involves finding a complex solution to the following issues:

- (1) synthesis of surface compounds in conformity with the notions of the structure of active sites;
- (2) achievement of an optimal AC topography in the pore structure of the catalyst;
- (3) optimization of the pore structure and chemical composition of the support;
- (4) optimization of the shape, size, and mechanical strength of catalyst particles;
- (5) development of RC production technologies.

Industrial catalysts bearing up to 30% Pt^σ sites were created over the course of more than three decades in the development of catalytic reforming [24–26]. The chemical composition of the catalysts was optimized and Pt^σ concentrations were brought to 70% with the use of a systemic approach to the design of platinum–rhenium catalysts.

Production Technology for New RCs

The composition of the active surface of RCs and its distribution over the pore space of the support served as the basis for the design of catalyst brands PR-42 and ShPR-2 based on the $\text{Pt-Sn-Cl/Al}_2\text{O}_3$ system and brands PR-50, PR-51, and ShPR-5 based on the $\text{Pt-Re-Cl/Al}_2\text{O}_3$ system (here PR denotes a platinum–rhenium catalyst and Sh, a ball (spherical) catalyst).

The research and development work included the following:

- (1) choice of an optimal chemical composition of the catalyst to provide for the selective aromatization of all hydrocarbons contained in the gasoline fraction;
- (2) investigation of the effect caused by the textural characteristics of the support on the properties of the catalyst;
- (3) development of preparation technology for a strong alumina support with designed textural characteristics;
- (4) investigation of the effect of the AC distribution on catalytic properties;
- (5) development of the full-scale catalyst preparation technology as applied to existing production facilities;
- (6) carrying out development work, including full-scale work, to test new technical solutions in catalyst production;
- (7) determination of the operation characteristics of the catalysts in pilot-scale plants on real stocks.

At the commercialization stage (1988–1995), it was found that the facilities (flowsheets and equipment) of the existing catalyst plants did not match the level required to implement the optimal preparation processes for new catalysts. However, implementation

parameters for the key stages of the support and catalyst production were substantiated due to the comprehension of the RC organization.

The commercialization stage consisted of the development, creation, and commercialization of the following technologies:

- (i) continuous deposition during the nitrate process of alumina preparation;
- (ii) plasticizing and molding in support production;
- (iii) production of spherical alumina (the support for ShPR catalysts);¹
- (iv) vacuum wetting and circulation impregnation at the AC application stage; and
- (v) activation and reduction of PR and ShPR catalysts.

Pilot-scale manufacturing of ShPR catalysts was launched. Several pilot-scale batches (200 ton) were produced, and successful full-scale tests were carried out.

Full-scale manufacturing of PR catalysts was launched. The first full-scale batch was produced in 1992. A total of six full-scale batches (200 ton) were produced. The catalysts are operated at five reformers with an overall output of 2.5 million t gasoline per year.

The catalysts are produced under the license of the Institute of Catalysis, Russian Academy of Sciences, at ZAO Promyshlennyye Katalizatory (Industrial Catalysts, Tyumen Oil Company (TNK), Ryazan) and OAO Angarskii Zavod Katalizatorov i Organicheskogo Sinteza (Angarsk Catalysts and Organic Synthesis Plant, YUKOS Company).

Full-Scale Operation Experience of Reforming Catalysts PR-50 and PR-51 [24–29]

The operation development stage involved the optimization of parameters for the key stages of the flow-sheet; implementation of technical support for the charging, launching, performance, and regeneration of the catalyst; development of operational documentation; and fixed runs of reformers.

A 12-year experience of full-scale operation of the new catalysts has been accumulated. The PR catalyst brand demonstrates a higher aromatization selectivity than the conventional catalysts. The reformat yield on the PR catalysts is 3–5 wt % higher, the octane number (ON) is 95–96 versus 90–93, the hydrogen concentration in the recycle gas is 5–8% higher, benzene and toluene concentrations are lower, and aromatic hydrocarbons C₈₊ are higher.

The catalysts demonstrate a high stability (the reaction cycle duration is longer than 17 months) and a high deactivation resistance when the process parameters deviate from their as-designed levels as a result of failure of equipment.

¹ In collaboration with R.A. Shkrabina.

Currently, the catalysts are operated at the following facilities: OAO Ryazanskii NPZ (Ryazan Refinery, two reformers with an output of 900 thousand tons per year); OAO KINEF, Surgutneftegaz Oil Company (Kishinev), one reformer with an output of 300 thousand tons per year); NPK-Galichina (Drogobych (Ukraine), one reformer with an output of 300 thousand tons per year); and OOO LINOS, TNK-BP (Lisichansk (Ukraine), one reformer with an output of 1000 thousand tons per year).

New RCs of the PR Brand

Design of the new catalysts comprised the following stages:

- (i) optimization of the chemical composition of surface Pt^σ compounds with the goal of improving the activity, selectivity, and stability (coking resistance) of the catalysts;
- (ii) achieving an optimal Pt^σ microdistribution on the support surface;
- (iii) optimization of the chemical composition, acid–base properties, and pore structure of the support.

The new catalysts PR-61 and PR-71 were designed as a result [25]. Representative pilot tests of the new catalyst PR-61 against catalyst PR-51 show a higher selectivity in paraffin aromatization (58–60% versus 48–51%) with the same activity. Catalyst PR-71 is more active than PR-51 or PR-61. The RON of the reformat on PR-71 is 95–96 at 464°C and 98–100 at 474°C, which is 6–7 K lower than on catalysts PR-51 and PR-61. The process selectivity on PR-71 is intermediate between the levels provided by PR-51 and PR-61.

The main strengths of the new catalysts PR-61 and PR-71 are a steady-state output of the reformat with RON 98–100 and a longer reaction cycle (1.3 times that on PR-51).

The RC production lines at ZAO Industrial Catalysts have now been modernized to organize the production of the new catalyst brands [26]. This work has been fulfilled in the framework of the State Contract no. 02.190.11.009 (April 11, 2003) “Development and Commercialization of a New Generation of Catalysts and Catalytic Technologies for Motor Fuel Production.”

The first batch of the new catalyst PR-51/04 (an approximate version of PR-71) was produced on these modernized lines in March/April, 2004. The catalyst (43.1 ton) was charged into the R-104 reactor of the reformer LCh-35-11/1000 at the OOO LINOS (TNK-Ukraine), and in June/July, its full-scale high-stiffness tests were carried out (Table 3).

From the full-scale tests, it follows that

- (i) reformed gasolines with RON = 95–96 are produced at integrated average temperatures of 464–465°C, and gasolines with RON = 98–99.5 are produced at 474–475°C;

Table 3. Performance parameters of the reformer LCh-35-11/1000 at OOO Lisichansknefteorgsintez, TNK-BP

Date	June 22, 2004	June 29, 2004	June 30, 2004	July 1, 2004	July 5, 2004	Aug. 6, 2004
Feed rate, m ³ /h	140	140	145	155	145	140
R-104 output pressure, MPa	1.45	1.37	1.38	1.38	1.37	1.36
Input reactor temperature/temperature difference, °C						
R-102	482/51	488/53	488/54	488/56	482/51	476/53
R-103	485/34	492/33	492/33	491/34	485/33	480/32
R-104	488/14	493/13	493/14	492/14	487/13	486/16
Σ difference	−99	−99	−101	−104	−97	−101
Integrated average temperature over the unit	470	476	476	475	470.6	465
HCG* circulation multiplicity, nm ³ /m ³	1400	1450	1400	1290	1400	1450
Hydrogen concentration in HCG, vol %	82.0	80.2	81.0	82.1	83.2	85.5
Reformate RON/MOM	96.6/85.5	98.6/87.0	99.5/88.5	98.5/87.7	96.6/87.0	95.5/86.0
Reformate yield, wt %	87.3	86.5	86.2	86.3	87.3	87.5

Notes: The actual feed composition: BO, 96°C; 10%, 105°C; 50%, 125°C; 90%, 165°C; BE, 181°C (hereafter, BO stands for boiling onset; BE, for boiling end).

Paraffins/naphthens/aromatics = 60 : 27 : 13.

*HCG stands for a hydrogen-containing gas.

(ii) the reformate yield with RON = 96 is 87.5% and that with RON = 99.5 is 86.3% with a hydrogen yield of 2.4–2.6% based on the feed.

The above achievements prove the high activity and selectivity of the new catalyst.

Thus, the full-scale tests of the new catalyst fully confirm the pilot-scale results reported earlier [25].

We should note that in this case fully consistent quality levels were achieved for the laboratory and full-scale production of the catalysts. We believe this to be due to the systemic approach to the preparation and production technology of RCs.

New Production Technologies for Motor Fuels

The analysis of numerous tests of PR catalysts suggested that reactions of hydrocarbon gases (products of cracking of the gasoline components) are responsible, among other reasons, for the high selectivities of the catalysts. During the intense circulation of hydrogen and the cracking products through a catalyst bed in a mixture with C₆–C₁₁ alkanes, light hydrocarbon molecules are adsorbed on the surface, together with heavier molecules; then, they convert into aromatization products. An analysis of the thermodynamic possibility that such reactions will occur confirmed the validity of this suggestion.

Experimental investigations of the conjugate conversion of propane–butane alkanes with paraffins C₇–C₈ and straight-run gasoline fractions highlighted the following tendencies:

(1) Typical high-octane gasolines are formed as a result of the conversion of C₃–C₄ alkanes under the reforming conditions at 480–500°C and H₂ partial pressures from 0.2 to 1.5 MPa;

(2) Improvement of the high-octane gasoline yield as a result of C₃–C₄ hydrocarbon conversion can reach 15–30%.

These data served to develop new processes for the production of high-octane gasolines by means of their coprocessing with low-molecular alkanes.

In the Biforming-1 process, the processing of a mixture of 100 wt % gasoline and 5 wt % C₁–C₄ (a total of 105%) provides the following yields (wt %): H₂, 2.0; C₁–C₂, 9.0; C₃–C₄, 0; and gasolines with RON = 95, 94% (a total of 105%) [30].

In the Biforming-2 process, the processing of 100 wt % gasoline and 5 wt % C₃–C₄ alkanes (a total of 105%) provides the following yields (wt %): H₂, 2.0; C₁–C₂, 9.0; C₃–C₄, 3.0; and gasolines with RON = 95, 91% (a total of 105%) [31].

Both variants of the process can provide a 10–15% improvement in the high-octane gasoline yield over the classic catalytic reforming of gasoline fractions.

In the Cycloalkate variant of the process, the separation of hydrogen from C₁–C₂ alkanes is achieved through catalytic binding of H₂ in the benzene hydrogenation reaction followed by recycling of gaseous hydrocarbons into the reaction zone. The cyclohexane hydrocarbons produced are either used as ecologically sound fuels or directed to dehydrogenation to produce 98–100% pure hydrogen [32].

Table 4. Performance parameters of the reformer L-35–11/300 at the OAO Ryazan Refinery, TNK-BP

Parameter	Reforming	Biforming
Feed rate, ton/day	739.2	739.2
Fluidized gas rate, ton/day	–	31.8
R-4 output pressure, MPa	1.7	1.7
Input reactor temperature/temperature difference, °C		
R-1	482/64	482/64
R-2	488/42	488/42
R-3	490/19	490/19
R-4	492/12	492/12
Σ difference	137	137
HCG circulation multiplicity, nm ³ /m ³	1100	1100
Hydrogen concentration in HCG, vol %	84.5	83.5
Reformate RON/MOM	95.2/85.3	95.3/85.3
Reformate yield, wt %	86.0	89.0

Notes: The actual feed composition: BO, 106°C; 10%, 121°C; 50%, 127°C; 90%, 158°C; BE, 176°C.

Paraffins/naphthens/aromatics = 60.2 : 29.9 : 9.9.

A 3.0 wt % increase in the reformate yield is equivalent to an additional output of 7500 ton gasoline per year on this reformer.

These technologies were tested on a demonstration plant with reactor capacities of 0.1 dm³ and an output of 2.5 dm³/day (based on the feed). The full-scale reformer L-35–11/300 (Ryazan Refinery, TNK-BP) has been modified to implement the Biforming-2 process. Full-scale tests of the Biforming-2 process on catalyst PR-51 (produced in 1998 at ZAO Industrial Catalysts) were carried out in July 2004. The results of fixed runs of the reformer are listed in Table 4.

The full-scale tests of the Biforming-2 process showed that the yield of gasolines with RON = 96 increased from 86 to 89 wt % and the hydrogen yield increased from 2.3 to 2.5 wt % when a fluidized 4.2 wt % C₃–C₄ petroleum gas was fed to the reactor unit. Therefore, this technology is of interest for most of the oil refineries, since petroleum gases are processed into more valuable products and since the yield of high-octane motor fuels increases.

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