ISSN 0023-1584, Kinetics and Catalysis, 2008, Vol. 49, No. 4, pp. 562–567. © MAIK “Nauka/Interperiodica” (Russia), 2008.
Original Russian Text © A.S. Belyi, 2008, published in Kinetika i Kataliz, 2008, Vol. 49, No. 4, pp. 587–591.

Design of Reforming Catalysts: Development of New Technologies for the Manufacture of Motor Fuels on This Basis

A. S. Belyi

Institute of Hydrocarbon Processing, Siberian Branch, Russian Academy of Sciences, Omsk, 644040 Russia
e-mail: belyi@ihcp1.oscsbras.ru

Received October 5, 2007

Abstract—The results of studies on the state of platinum in alumina–platinum reforming catalysts performed at the Institute of Hydrocarbon Processing, Siberian Branch of the Russian Academy of Sciences, in the past 20 years are summarized. The main result is the determination of the important role of the nonmetallic states of platinum (Pt^{σ}) in adsorption and catalysis. The main principles of the development of highly efficient catalysts and technologies for their manufacture are formulated. Data on the industrial applications of new reforming catalysts at seven commercial reforming plants under conditions of reforming gasoline production (about 3 million tons per year) with research octane numbers of 96–100 are given. The applicability of new catalysts to the combined conversion of C_3–C_4 and C_{5+} alkane mixtures into high-octane motor fuel components is demonstrated. The results of the development of three modifications of a new technology for the manufacture of environmentally safe high-octane gasoline with the selectivity of formation of the target product close to 100% are presented.

DOI: 10.1134/S0023158408040162

INTRODUCTION

The current concepts of the structure of active sites in reforming catalysts are based on the results of studies performed over many years. The authors of these studies repeatedly noted the occurrence of platinum in the catalysts both as platinum metal (Pt^0) and in nonmetallic or ionic states. However, the role of these states in reforming had remained unclear until recently.

The low platinum content (<0.5 wt %) of reforming catalysts poses major problems for the use of physical investigation techniques.

In 1986, Belyi et al. developed a chemical adsorption method for the quantitative determination of metallic and ionic platinum species simultaneously present in catalysts containing <0.25 wt % Pt [1, 2].

It was found that, unlike Pt^0 atoms, platinum ions form strong σ-donor bonds with water. Duplyakin et al. [2] designated ionic platinum as Pt^{σ}.

It was found that the properties of these states are noticeably different (Table 1) in terms of the stoichiometry of oxygen and hydrogen adsorption [3]; the vibration frequency of adsorbed carbon monoxide [4, 5]; the

Table 1. Physicochemical properties of platinum in Pt/Al_2O_3 catalysts

	Pt^0	Pt^{σ}
1. Interaction and chemical bond formation with σ-donor H_2O molecules	no	yes
2. Chemisorption stoichiometry:		
oxygen O/Pt	1	0.5
hydrogen H/Pt	1	2.0
3. Vibration frequency of adsorbed CO, cm^{-1}	2080	2147
4. Pt $4d_{5/2}$ binding energy, eV (XPS)	315	317.5
5. Oxidizability with oxygen at 473–573 K	no	yes
6. Thermal stability	no	yes
7. Activity in benzene hydrogenation (T = 573 K)	yes	no
8. Activity in cyclohexane dehydrogenation, molecule (Pt_s atom)$^{-1}$ s^{-1} at T = 573 K	24	no
9. Activity in heptane aromatization, molecule (Pt_s atom)$^{-1}$ s^{-1} at T = 773 K	0.3	3.1–4.2

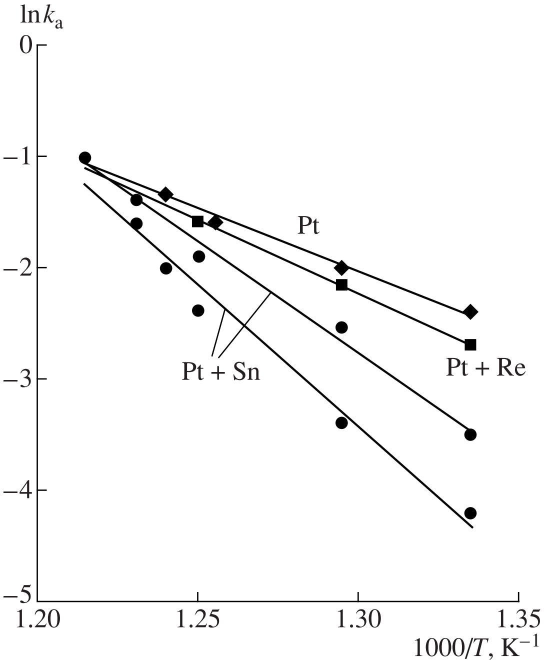

Fig. 1. Comparison between the activities of Pt, Pt + Sn, and Pt + Re catalysts in heptane aromatization (P = 10 atm; H_2/C_7 = 5 mol) (data obtained in samples with different Pt/Sn ratios are given for the platinum–tin catalysts) [13].

Pt $4d_{5/2}$ binding energy (XPS), whose value in $Pt^σ$ is close to the binding energy of bivalent platinum in chlorides [2, 6]; the thermal stability and oxidizability with oxygen [4, 7, 8]; and the atomic activity in hydrogenation, dehydrogenation, and dehydrocyclization reactions [9–11].

$Pt^σ$ is inactive in the reaction of benzene hydrogenation, but it is much more active than Pt^0 (by a factor of ~10 [2]) in n-heptane aromatization.

Selectivity, expressed by the ratio of the rate constant of the aromatization reaction to the overall rate constant of n-heptane conversion, was much higher for $Pt^σ$. Ring closure occurred at terminal carbon atoms in the molecule with the formation of weaker bonds with $Pt^σ$, as compared with Pt^0; this is the reason for the higher selectivity of $Pt^σ$ sites [12, 13].

Based on the experimental data, a model for the surface of reforming catalysts was proposed [11, 14]. According to this model, the role of Pt^0 consists in the acceleration of cracking, isomerization, and C_5-dehydrocyclization reactions, whereas the role of $Pt^σ$ consists in the acceleration of direct C_6 cyclization and the dehydroisomerization of five-membered naphthenes to aromatic hydrocarbons.

Interesting effects were found by studies of reforming catalyst modification with low-valence rhenium and tin ions [9, 10, 14]. The introduction of these modifiers resulted in an increase in the activation energy of alkane aromatization and, very importantly, in a considerable increase in the stability of catalysts (Fig. 1). These effects were explained based on a change in the electronic state of $Pt^σ$ caused by the interaction with a second metal ion [15].

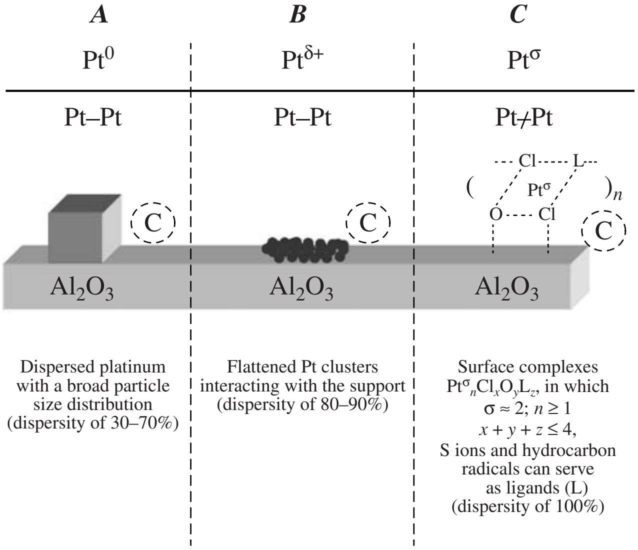

Fig. 2. Models of the states of platinum in reforming catalysts [17].

In the course of our studies, a procedure was developed for the adsorption measurement of the distribution of Pt^0 and $Pt^σ$ active sites in pores with different sizes. The procedure consists in the measurement of the number of Pt sites at various degrees of pore filling with condensed water and the determination of the differential change in the number of sites as a function of pore radius (microdistribution function). It was found [15–18] that, in the majority of cases, the distribution of platinum in pores with different sizes was nonuniform. It was strongly affected by the conditions of hexachloroplatinate adsorption in the course of supporting onto alumina, in particular, the presence and nature of competitor acids (hydrochloric, acetic, or oxalic acid) [16]. Based on these data, methods for regulating the distribution of platinum were developed and a common feature was found [13]: the locus of $Pt^σ$ sites was always shifted to smaller pores.

A relationship between the mechanism of hexachloroplatinic acid adsorption and the state of platinum in reduced catalysts was established [13]. It was found using NMR spectroscopy that the sorption of platinum on a support modified with halogens was accompanied by the occurrence of five to six surface bromine ligands in the coordination sphere of Pt [19]. It was hypothesized that multiple bonds through bridging halogen ligands during the sorption of a precursor in fine pores enhanced the strength of the platinum–support interaction and, consequently, the formation of ionic platinum species in the catalysts (Fig. 2) [17].

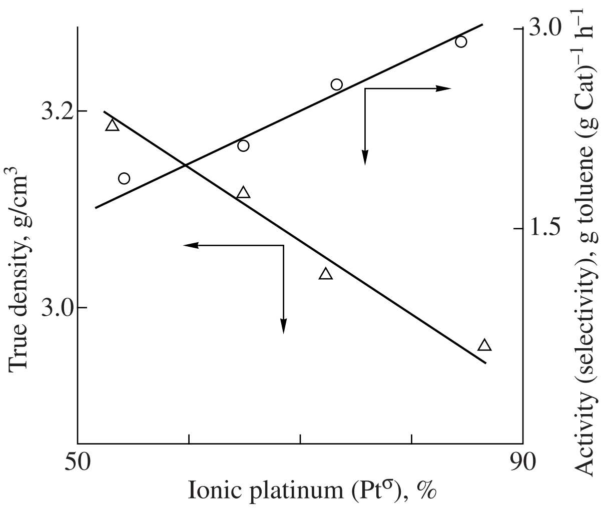

Fig. 3. Dependence of the true density and activity of Pt/Al_2O_3 in heptane dehydrocyclization on the number of Pt^σ sites.

The generalization of previous results [9, 17] allowed us to simulate the active surface of catalysts as a superposition of the following three states:

State ***A*** includes platinum metal particles with an extent of dispersion of 50 to 80% with the localization of a halogen on the support.

Table 2. Industrial output of commercial catalysts from the PR and RU-125 series

	Catalyst weight, t
PR-50 and PR-51	
1992, Ryazan Petroleum Refinery, Russia	25
1994, Ryazan Petroleum Refinery, Russia	40
1998, Ryazan Petroleum Refinery, Russia	30
1999, Kirishi Petroleum Refinery, Russia	25
2001, Galichina Petroleum Processing Factory, Ukraine	25
PR-71	
2005, LCh-35-11/1000 Lisichansk Petroleum Refinery, Ukraine	80
2005, L-35-11/300 Saratov Petroleum Refinery, Russia	25
2005, LCh-35-11/600 Ryazan Petroleum Refinery, Russia	40
2005, LG-35-11/300 Galichina Petroleum Processing Factory, Ukraine	25
RU-125	
2006, LG-35-11/300 Ryazan Petroleum Refinery, Russia	25
2007, L-35-11/300 Ryazan Petroleum Refinery, Russia	30
Total tons	370
Gasoline processing output on PR catalysts, million tons per year	3.5

State ***B*** includes platinum clusters with a higher extent of dispersion (80–90%) exhibiting electron-deficient properties as a result of interactions with alumina.

State ***C*** includes Pt^σ active sites as surface platinum complexes—the products of strong interactions with the crystal structure defects of the support. The limiting extent of dispersion, the ionic state of platinum, the occurrence of ligands bound to the support, the absence of the Pt–Pt bond, and the high resistance to agglomeration are characteristic of the Pt^σ state. State ***C*** exhibits a set of advantages in the reaction of reforming; therefore, methods for the target-oriented synthesis of these surface complexes should be developed.

Later studies allowed one to develop methods for the generation of defects on the surface of primary support particles. These defects are cationic and anionic vacancies and coordinatively unsaturated aluminum cations on the surface of alumina. The true density measured using a helium pycnometer is a defect structure test. The occurrence of defects increased the fraction of the Pt^σ state in the preparation of catalysts and enhanced the activity and selectivity of the catalysts in alkane aromatization reactions (Fig. 3).

A systemic approach to the preparation of reforming catalysts was developed; it involves the end-to-end solution of the following problems:

(i) synthesis of surface compounds in accordance with the concepts of the structure of active sites;

(ii) optimization of the pore structure and chemical composition of the support, as well as the topography of the active component in the pore structure of the catalyst;

(iii) optimization of the shape, size, and strength of catalyst grains;

(iv) development of a reforming catalyst technology.

With the use of scientific knowledge of the optimum properties of reforming catalysts, a technology was developed for the manufacture of these catalysts and three batches of new catalysts were produced at ZAO Promkataliz in Ryazan (Table 2). The PR-50 and PR-51 catalysts manufactured in the period 1992–2001 have been found to be industrially advantageous. Since 2004, an improved catalyst from this series of the PR-71 brand was manufactured and placed in commercial operation. Finally, the RU-125 catalyst, which integrates all of the advantages of the previous PR-51 and PR-71 catalysts and REF catalysts developed at NPP Neftekhim (Krasnodar, Russia), began to be produced in 2006. The RU-125 catalyst is a result of the generalization of experience accumulated at two research centers in Omsk and Krasnodar.

About 370 tons of new catalysts were manufactured. More than 3.5 million tons of gasoline are currently processed with the use of these catalysts at nine industrial plants in Russia and Ukraine.

Table 3. Performance characteristics of reforming catalysts for the 85–180°C fraction*

Average European level	PR-51, PR-71	RU-125
Yield of reforming products, wt %		
82–85	86–88	90
Yield of hydrogen, wt %		
1.6–2.0	2.4–2.6	2.8
Hydrogen concentration in the hydrogen-containing gas, vol %		
73–80	83–86	86
Average integral temperature, °C		
480	470	465
Research octane number		
95–98	95–98	98–100

* Feed: paraffins, 60 wt %; naphthenes, 30 wt %; and aromatic hydrocarbons, 10 wt %.

Table 3 summarizes the results of the operation of new catalysts obtained in the last 15 years. Much higher yields of high-octane gasoline (research octane number of 98–100), hydrogen, and aromatic hydrocarbons were obtained on these catalysts at much lower process temperatures.

The above properties of catalysts were responsible for an increase in the efficiency of commercial semiregenerative reforming plants [20–22].

A possible reason for the high activity of new catalysts is that light hydrocarbon gases formed in the course of reforming are converted into high-octane C_{5+} hydrocarbons upon repeated circulation.

Belyi [13] performed representative studies of the combined conversion of *n*-butane and gasoline fractions on pilot reforming plants (Fig. 4) and found that light gases entered into secondary reactions with the formation of C_7–C_9 isoparaffins and aromatic hydrocarbons under process conditions; the conversion of *n*-butane depended on pressure and the amount of gas supplied for processing; the conversion of *n*-butane into C_{5+} products was ≥50 wt %; the increase in the yield of valuable C_{5+} products was as high as 20–30 wt %, as compared with the reforming process.

With the use of these data, the Biforming process—the combined conversion of C_3–C_4 gases and gasoline fractions into high-octane gasoline—was developed [23, 24]. This process consists in that C_3–C_4 hydrocarbons formed in the course of reforming are continuously recycled by mixing with liquid raw material. Moreover, these hydrocarbons enter into the reaction zone from an external source.

Upon the addition of no more than 15 wt % gases to the feed, the yield of the high-octane component increased by 3–8 wt %.

Table 4. Material balances for reforming and Biforming processes (industrial tests at the L-35-11/300 plant)

Process characteristics	Reforming	Biforming-2
Supplied, wt %:		
fraction of 105–180°C	100	100
liquefied gas (C_1–C_4 alkanes)	–	4.3
Produced, wt %:		
stable reforming products	86.0	89.0
including benzene	1.0	0.8
hydrogen-containing gas	10.7	11.7
dry gas	2.2	2.5
hydrogen (in H_2-containing and dry gases)	2.4	2.5
Loss, wt %	1.1	1.1
Octane number of stable products of catalysis (motor octane/research octane)	85.2/95.3	85.2/95.2

From 2000 to 2004, in cooperation with Ryazan Petroleum Refinery, a commercial reforming plant was reconstructed into a Biforming process plant, and a pilot run was performed in July 2005 (Table 4) [10]. As 4.3 wt % of liquefied gases was supplied to the process, the yield of high-octane catalysis products increased by 3.0 wt %, the yield of hydrogen increased, and the yield of benzene decreased. Thus, the industrial test of the technology completely supported the results of preliminary studies in pilot plants.

The development and commercialization of new catalysts made a considerable contribution to an increase in the efficiency of reforming on the industrial level. According to our estimations, the new Biforming process will allow one to implement the next stage in the development of the process involving the conversion of light hydrocarbon gases.

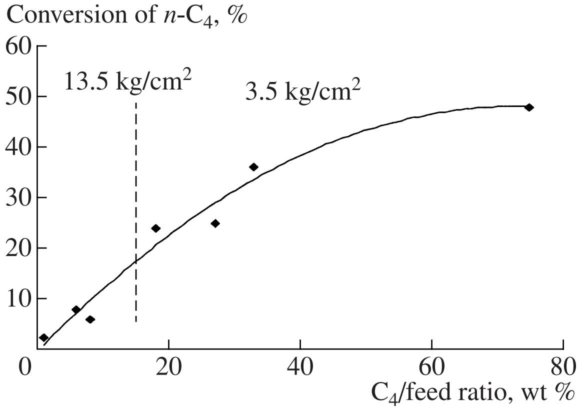

Fig. 4. Combined processing of butanes and C_7–C_{11} paraffins (pilot plant; $P = 3.5$ and 13.5 kg/cm^2; $T = 500$°C).

Table 5. Compositions of feed, Biforming products, and hydrogenation products (Ecoforming process)

Characteristics	Feed fraction 90–185°C	Products	
		biforming	ecoforming
Hydrocarbon type content, wt %:			
isoparaffins	33.8	23.1	22.6
n-paraffins	25.1	9.4	9.3
naphthenes	29.5	2.5	23.1
arenes	11.5	65.0	45.0
Research octane number	56.8	98.5	93.1
Yield of C_{5+} products, wt % on a Biforming feed basis	100	95.0	97.1
Octane-tons per ton of feed	56.8	94.5	90.4
Yield (consumption) of hydrogen, wt %	–	3.4	–2.1

In recent years, the Biforming process has been improved toward a decrease in the aromatic hydrocarbon content of gasoline. Table 5 summarizes the experimental results on the hydrogenation of liquid reaction products with the use of hydrogen-containing Biforming gas. In this case, the arene content was decreased from 65 to 45%. The octane numbers remained at an industrially acceptable level because of an increase in the concentration of naphthene hydrocarbons. Moreover, the yield of a liquid product that can be assigned to the category of environmentally friendly fuel was increased by the addition of hydrogen to arenes. This process was referred to as Ecoforming.

In the near future, research and development work on the nature of active sites in Biforming and Ecoforming catalysts (the formation of surface defects in oxide supports and the optimization of strong metal–support interaction effects on this basis) for the subsequent improvement of the catalysts to solve the problem of efficient hydrocarbon material processing will be undertaken at the Institute of Hydrocarbon Processing, Siberian Branch, Russian Academy of Sciences.

ACKNOWLEDGMENTS

Along with the staff members of this institute, research teams from the Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences (Novosibirsk); Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences (Moscow), ZAO Promkataliz (Ryazan); Petroleum Refinery (Ryazan); AZKiOS (Angarsk); etc., participated in this work.

REFERENCES

1. Belyi, A.S., Smolikov, M.D., Fenelonov, V.B., Gavrilov, V.Yu., and Duplyakin, V.K., *Kinet. Katal.*, 1986, vol. 27, no. 6, p. 1414.
2. Duplyakin, V.K., Belyi, A.S., Ostrovskii, N.M., Smolikov, M.D., Chalganov, E.M., and Nizovskii, A.I., *Dokl. Akad. Nauk SSSR*, 1989, vol. 305, no. 3, p. 648.
3. Belyi, A.S., Kiryanov, D.I., Smolikov, M.D., Zatolokina, E.V., Udras, I.E., and Duplyakin, V.K., *Reac. Kinet. Catal. Lett.*, 1994, vol. 53, no. 1, p. 183.
4. Smolikov, M.D., Zaitsev, A.V., Khabibislamova, N.M., Belyi, A.S., Borovkov, V.Yu., Duplyakin, V.K., and Kazanskii, V.B., *React. Kinet. Catal. Lett.*, 1994, vol. 53, no. 1, p. 169.
5. Smolikov, M.D., Zaitsev, A.V., Zatolokina, E.V., Belyi, A.S., Borovkov, V.Yu., Duplyakin, V.K., and Kazanskii, V.B., *Kinet. Katal.*, 1992, vol. 33, no. 3, p. 625.
6. Belyi, A.S., Smolikov, M.D., Ostrovskii, N.M., Kolomytsev, Y.N., and Duplyakin, V.K., *React. Kinet. Catal. Lett.*, 1988, vol. 37, no. 2, p. 457.
7. Duplyakin, V.K. and Belyi, A.S., *2nd Eur. Congr. on Catalysis*, Maastricht, 1995, p. 725.
8. Belyi, A.S., Udras, I.E., Smolikov, M.D., and Kiryanov, D.I., *2nd Eur. Congr. on Catalysis*, Maastricht, 1995, p. 714.
9. Belyi, A.S., Smolikov, M.D., Kir'yanov, D.I., Proskura, A.G., Udras, I.E., Duplyakin, V.K., Lugovskoi, A.I., Loginov, S.A., and Vashchenko, P.M., *Katal. Prom–sti.*, 2003, no. 6, p. 3.
10. Belyi, A.S., *Kinet. Katal.*, 2005, vol. 46, no. 5, p. 728 [*Kinet. Catal.* (Engl. Transl.), vol. 46, no. 5, p. 684].
11. Ostrovskii, N.M., *Kinetika dezaktivatsii katalizatorov* (Catalyst Deactivation Kinetics), Moscow: Nauka, 2001.
12. Belyi, A.S. and Lugovskoi, A.I., *Khim. Prom–st.*, 1996, no. 3, p. 35.
13. Belyi, A.S., *Doctoral (Chem.) Dissertation*, Novosibirsk: Boreskov Inst. of Catalysis, 2002.
14. Ostrovskii, N.M. and Belyi, A.S., *Khim. Prom–st.*, 1999, vol. 8, p. 522.

15. Smolikov, M.D., Belyi, A.S., Udras, I.E., and Kir'yanov, D.I., *Ross. Khim. Zh.*, 2007, vol. 51, no. 4, p. 48.
16. Smirnova, I.E., Belyi, A.S., Smolikov, M.D., and Duplyakin, V.K., *Kinet. Katal.*, 1990, vol. 31, no. 3, p. 687.
17. Belyi, A.S., Smolikov, M.D., Kir'yanov, D.I., and Udras, I.E., *Ross. Khim. Zh.*, 2007, vol. 51, no. 4, p. 38.
18. Udras, I.E., Kiryanov, D.I., Smolikov, M.D., and Belyi, A.S., *4th Eur. East–West Conf. & Exhibition on Materials and Processes*, St. Petersburg, 1993, vol. 1, p. 25.
19. Duplyakin, V.K., Doronin, V.P., Tsymbal, T.V., Al't, L.Ya., and Belyi, A.S., *Dokl. Akad. Nauk SSSR*, 1985, vol. 281, no. 1, p. 89.
20. Belyi, A.S., *Katal. Prom–sti.*, 2003, no. 2, p. 11.
21. Kir'yanov, D.I., Smolikov, M.D., Pashkov, V.V., Proskura, A.G., Zatolokina, E.V., Udras, I.E., and Belyi, A.S., *Ross. Khim. Zh.*, 2007, vol. 51, no. 4, p. 60.
22. Belyi, A.S., *III Int. Conf. on Catalysis: Fundamentals and Application*, 2007, vol. 1, p. 121.
23. RF Patent 2144992, 2000.
24. RF Patent 2144056, 2000.