Petroleum and Coal

Article **Open Access**

INDUSTRIAL OPERATION ANALYSIS OF Pt-Re REFORMING CATALYST AT THE INDUSTRIAL UNIT BY PREDICTIVE MODELLING METHOD

Emilia D. Ivanchina[1], Ekaterina S. Chernyakova[1], Inna V. Pchelintseva (Yakupova)[1], Gajni Zh. Sejtenova[2], Rizagul' M. Dyusova[2]*

[1] *Tomsk Polytechnic University, Russia*
[2] *S. Toraighyrov Pavlodar State University, Kazakhstan*

Received February 5, 2018; Accepted April 27, 2018

Abstract

Analysis of the PR-51 catalyst operation effectiveness of the reforming process was conducted with mathematical modelling method using. The main characteristics of PR-51 reforming catalyst were calculated. It was found that the catalyst has proven to be appropriate in operation and ensure high selectivity. It is shown that the product yield increases by 3-5%mass with octane number 96-97.

Keywords*: catalytic reforming; Pt-Re catalyst; kinetic and instrumental methods; mathematical modelling method; product yield.*

1. Introduction

The main characteristics of the yield of catalytic naphtha reforming process depend strongly on the catalyst properties. Catalytic reforming catalyst is quite expensive component, so the big practical importance has detailed study of all process with its participation [1-3].

The efficiency of petroleum products production is mostly determined by the level of the process technology, its technological and economic productivity. Increasing the level of reforming efficiency directly leads to the production costs reduction [4]. In the modern production, the solution of this kind of problem becomes possible due to a detailed study of the processes taking place in rectors on the catalyst, and without these the chemical process is not feasible. Investigation, development and introduction of new catalysts in the industry, improvement of production equipment (reactors, heat exchangers, etc.), technological schemes - all these aspects directly influence the resource efficiency of catalytic reforming [1].

Nowadays catalytic naphtha reforming process is one of the most important processes in oil-refining, and it requires in constant control and enhancement, which could be realized by carrying out of continuous monitoring and analysis of catalyst operation. Based on this kind of data it could be argued about resource efficiency of catalysts and oil raw materials on any oil-refinery [5].

Activity, stability and selectivity are the most important indicators of catalyst operation [6-7]. During operation, the catalyst undergoes physiochemical changes, which is contribute to decrease in the initial activity [8-10].

Catalyst activity depends on its composition, preparation method, physical conditions of metal and acid function [11-14]. Polymetallic catalysts containing 3 and more metals are the most active ones [15-19].

Activity and selectivity decreasing could be caused by [20-21]:

- coke deposition;
- poisoning due to chemisorption of some impurity (such as heavy metals);
- loss of active substances (chlorine);
- erosion and breakage;

- hydrothermal aging, that is, loss of surface area (metallic area and support area).

At industrial operation of catalysts it should carry out investigations, which allow determining its composition, structure, containing of impurities and develop methods of its activity regeneration.

The aim of this study is analysis of industrial reforming catalyst PR-51 by predictive modelling method. This catalyst has shown high performance during 17 years of its operation.

2. Object and method of research

Catalytic reforming unit LG-35-8/300B is an important object of Ltd «Kinef» in Russia and intended for obtaining of individual aromatic hydrocarbons of benzene and toluene. In contra-distinction to other catalytic reforming units, working for the production of high-octane components, the reforming unit LG-35-8/300B the next technological blocks for [22]:

- selective hydrogenation of unsaturated hydrocarbons;
- extraction with solvent regeneration;
- rectification of the extract to individual aromatic hydrocarbons.

A distinctive feature of PR-51 catalyst is presence of active centers, containing pairs of Lewis acid sites of different strengths. These pairs are surface platinum complexes PtClxOyLz (Ptσ-Lz), where platinum ions (Ptσ) act as soft Lewis centers, Lz act as rigid Lewis centers and are cations Al^{3+} of crystal lattice Al_2O_3 [23]. The main physio-chemical characteristics are shown in Table 1.

Table 1. Main characteristics of catalysts PR-51 and AP-10 [21-23]

Indicator/Catalyst	Unit	PR-51	AP-10
Pt	%mass	0.25	0.10
Re	%mass	0.30	-
Cl(F)	%mass	1.0	-
Fe	%mass	0.02	0.017
Na_2O	%mass	0.02	0.02
Diameter	mm	2.8 (1.6)	2.6-3.0
Bulk density	kg/dm^3	0.67-0.68	0.6-0.8

Description and control of catalyst operation main criteria realize by measurement of elementary stages rates of catalytic process and reaction under different parameters changing, which have influence on the rate of reaction (concentration of reacting substances, temperature, etc.). This kind of catalyst properties research is called «kinetic» and explains formalized mechanism of reaction opens physio-chemical mechanism of concrete processes up and allows getting initial data for optimal management by the whole industrial process, determining kinetic parameters of reactions occurring.

However despite of all possibilities of kinetic method, it is not possible to realize its comprehensive application. First of all, relations of process rate and its separate stages from different technological parameters represent complicated dependencies of exponential functions, which could be solved with specialized computer program using only. And secondly, real processes are always accompanied by processes of mass and heat transfer, which could misrepresent information about catalytic process rate.

That's why for comprehensive analysis of catalyst operation beside kinetic methods of study instrumental ones have also been using. This group of methods allows determining the structure of catalyst surface (where chemical reaction occurs), activation form of reacting substances, and explaining the surface reaction mechanism on the concrete platinum contact.

Type of instrumental method is chosen depending on catalyst characteristic demanding. There is a variety of instrumental methods (Table 2).

Thus, the most complete representation about catalyst operation and processes on its surface could be obtained only at cooperative analysis with instrumental and kinetic methods. Of course, the results of these analyses represent a big array of integrated complementary data. That is why the solution of such problems becomes possible only with the development

of mathematical models, based on totality of data obtained by kinetic and instrumental methods.

Table 2. Instrumental methods of catalysts study and control [20]

Catalyst characteristic	Method of study	Catalyst characteristic	Method of study
Chemical composition	X-fluorescence	Structure of catalyst chemical compounds	Thermogravimetric analysis
	Neutron diffraction		Differential thermal analysis
	Atomic-emission spectroscopy		Mössbauer spectroscopy
	Atomic adsorption	The texture of catalysts and carriers (porosity, specific surface, etc.)	BET theory
Structure of catalyst chemical compounds	Nuclear magnetic resonance spectroscopy		Porosimetry
	X-ray crystallography		Chemisorption
	Infrared spectroscopy		X-ray crystallography

Mathematical model using allows avoiding of complicated and expensive experiences [24-27]. Results obtained with mathematical model can optimize catalyst composition for its characteristics improving: activity, selectivity and stability.

The conditions of catalyst operation are not constant: technological conditions at oil-refinery could be changed for a number of reasons [5]. Besides, the composition of raw material is not fixed and could be different depending on oil-field.

Mathematical modelling method allows carrying out a comprehensive analysis of the catalytic reforming unit operation, what helps to increase product yield and decrease production costs.

Improving the stability and selectivity of the catalyst as well as reducing catalyst deactivation is a vital issue for enhancing the efficiency and yield of the catalytic naphtha reforming process. Thus, mathematical modelling method based on physio-chemical regularities of the process is the most objective one for catalyst operation assessment. That is why this method was used for monitoring of industrial unit LG-35-8/300B Ltd «Kinef» and the comprehensive analysis of catalyst operation has been done.

3. Experimental

In June 1999 in three reactors P-2, P-3, P-4 of reforming block the fresh catalyst PR-51 was loaded in quantity of 24433 kg and in 2009 the amount of 873 kg was made in reactor P-2. The total amount of catalyst is 25306 kg. During the repair period in 2009 in reactor P-5 the catalyst AP-10 was loaded in quantity of 7000 kg (Table 3).

Table 3. AP-10 catalyst operation data

№	Regeneration data	The amount of recycled raw materials, t	№	Regeneration data	The amount of recycled raw materials, t
1	06.2000	296 435	8	07.2012	1 127 210
2	06.2001	300 000	9	11.2012	707 71
3	07.2002	294 028	10	02.2014	545 224
4	06.2003	270 028	11	04.2015	473 032
5	06.2004	294 826	12	07.2015	23 100
6	08.2006	727 208	13	till 13.04.2016	236 073
7	07.2009	1 234 061			

The total amount of recycled raw materials PR-51 catalyst (from load till 13.04.2016) using is 5 891 996 ton. Main indicators of reforming block operation are performed in Table 4.

Table 4. Main indicators of reforming block operation with PR-51 catalyst using conditions: Pressure – 1.35 MPa, hydrogen-rich gas circulation ratio– 1200-1300 Nm^3/m^3

Name/Number of cycle	I (1999-2000)	V (2003-2004)	VI (2004-2006)	VII (2006-2009)	VIII (2009-2012)	XIII (2015-2016)
Consumption of raw materials, m^3/h	55	60	60	62	64	62
Fractional composition of raw material, IBP/50 %/EBP, °C	71/81/103	71/82/102	71/81/98	71/80/94	71/78/92	71/77/96
The average temperature at the reactor inlet	486	486	486	482	482	482
Hydrogen concentration in HRG, % vol.	81.6	83.9	86.5	86.5	86.5	79.9
Stable reformate yield, % mass.	82.6	84.8	87.2	87.0	88.0	87
Aromatic compounds output after extraction block, % mass., including	33.2	33.7	33.6	31.5	30.8	35.07
Benzene	13.8	14.0	16.7	17.0	17.1	19.4
Toluene	17.7	17.8	15.5	13.1	12.6	14.6
Aromatic compounds output after reforming block, % mass.	36.5	36.2	36.0	34.0	33.5	32.5
Cycle duration, months	12	12	24	34	36	24*

**Data of October 2016*

According to the results of laboratory studies, the reforming catalyst PR-51 has proven to be appropriate in operation. The aromatic hydrocarbons concentration in a stable catalyst corresponds to 35.07 %mass., with the norm not less than 35 %mass. Hydrogen concentration in hydrogen-rich gas is at the level of 79.9 %vol. In general, the decrease in hydrogen concentration by 5 % is observed in comparison with the previous (84.9 % vol. at 22.07.15).

Based on industrial operation data and laboratory studies computer modelling system «Aktivnost» using the monitoring of PR-51 catalyst was done. The results are performed in Table 5.

Table 5. The monitoring of PR-51 catalyst

Date	13.04.16	17.05.16	25.05.16	07.06.16	29.06.16	27.07.16	23.08.16
Activity	1.02	1	0.99	0.87	0.88	0.94	0.75
Recycled raw material, t	236073	272387	280939	289762	305352	334725	349302
Reactors inlet temperature. °C	482	482	482	482	482	482	477
Consumption of raw materials. m^3/h	62.5	63	63	40	42	62	32
Aromatics, %mass	34.53	33.12	32.58	33.87	32.34	29.74	27.98
Hydrogen output, %	1.57	1.43	1.41	1.34	1.35	1.26	1.06
Coke, %mass.	2.4	2.75	2.83	2.89	3	3.25	3.3
Hydrogen, %	79.9	79.1	79.1	83.6	78.8	79.4	79.6
Product yield	90.4	91.26	91.19	89.87	89.58	92.33	91.73
Par/(Naft+Arom) in feedstock	1.44	1.45	1.46	1.43	1.57	1.48	1.62
n-Par/i-Par in feedstock	0.9	0.92	1	0.93	0.97	1.02	1.01

Analyzing the results. it could be concluded that the catalyst has shown the effective operation.

4. Conclusions

More than 20 years of industrial operation experience of naphtha reforming catalysts PR-51. PR-71 and PR-81 has shown that catalysts of PR family ensure high activity and selectivity. It is shown in product yield increasing by 3-5%mass. with octane number 96-97. Hydrogen

concentration increasing by 3-5%vol. in circulating gas. benzene and toluene content decreasing in with a general increase in the aromatic hydrocarbons content.

Acknowledgements

The research is carried out at National Research Tomsk Polytechnic University and within the framework of National Research Tomsk Polytechnic University Competitiveness Enhancement Program grant.

References

[1] Chernyakova ES. Ivanchina ED. Yakupova IV. Vinidiktova MV. Seytenova GZ. Coke formation reduction in the cataltic reforming reactors at the optimal catalyst activity. Pet. Coal, 2016; 58(2): 746-752.

[2] TregubenkoVY. Udras IE. Zatolokina EV. Smolikov MD. Kir'yanov DI. Arbuzov AB. Gulyaeva TI. Belyi AS. The synthesis and investigation of the reforming catalysts for the reduced aromatics content gasoline obtaining. Procedia Eng., 2015; 113: 144-151.

[3] Elsayed HA. Menoufy MF. Shaban SA. Ahmed HS. Heakal BH. Optimization of the reaction parameters of heavy naphtha reforming process using Pt-Re/Al_2O_3 catalyst system. Egypt. J. Pet., 2017; 26: 885-893.

[4] Koksharov AG. Faleev SA. Chernyakova ES. Ivanchina ED. Yakupova IV. Chuzlov VA. Bifunctional pt-re reforming catalysts properties modelling. Pet. Coal, 2016; 58(7): 726-731.

[5] Zbarsky VL. Gilin VF. Toluene and its nitroderivatives. Editorial URSS. Moscow. 2000: 272.

[6] Barrientos J. Montes V. Boutonnet M. Jaras S. urther insights into the effect of sulfur on the activity and selectivity of cobalt-based Fischer–Tropsch catalysts. Catal. Today, 206; 275: 119-126.

[7] Simson A. Farrauto R. Castaldi M. Steam reforming of ethanol/gasoline mixtures: Deactivation. regeneration and stable performance. Appl. Catal., B. 2011; 106: 295-303.

[8] Barbarias I. Artetxe M. Lopez G. Arregi A. Bilbao J. Olazar M. Influence of the conditions for reforming HDPE pyrolysis volatiles on the catalyst deactivation by coke. Fuel Process. Technol., 2018; 171: 100-109.

[9] Dong XJ. He YJ. Shen JN. Ma ZF. Multi-zone parallel-series plug flow reactor model with catalyst deactivation effect for continuous catalytic reforming process. Chem. Eng. Sci., 2018; 175: 306-319.

[10] Sharma YC. Kumar A. Prasad R. Upadhyay SN. Ethanol steam reforming for hydrogen production: Latest and effective catalyst modification strategies to minimize carbonaceous deactivation. Renewable Sustainable Energy Rev., 2017; 74: 89-103.

[11] Mang T. Breitscheidel B. Polanek P. Knözinger H. Adsorption of platinum complex on silica and alumina: Preparation of non-uniform metal distributions within support pellets. Appl. Catal. A: General, 1993; 106: 239-258.

[12] Shelimov B. Lambert JF. Che M. Didillon B. Initial Steps of the Alumina-Supperted Platinum Catalyst Preparation: A Molecular Study by 195Pt NMR. UV-Visible. EXAFS. and Raman Spectroscopy.J. Catal., 1999; 185: 462-478.

[13] Shelimov BN. Lambert JF. Che M. Didillon B. Molecular-level studies of transition metal-support interactions during the first steps of catalysts preparation: platinum speciation in the hexachloroplatinate/alumina system. J. Mol. Catal. A: Chem., 2000; 158: 91-99.

[14] Marceau E. Carrier X. Che M. Impregnation and Drying. in: K.P. de Jong (Ed.). Synthesis of Solid Catalysts. Wiley-VCH. Weinheim. 2009; 59-82.

[15] Kolesnikov IM. Catalysis and catalysts production. «Tehnika». TUMA GRUPP. Moscow. 2004; p.400.

[16] Moroz EM. Zyuzin DA. Tregubenko VYu. Udras IE. Belyi AS. Likholobov VA. Effect of structural defects in alumina support on the formation and catalytic properties of the active component of reforming catalysts. Reac. Kinet.Mech. Cat., 2013; 110: 459-470.

[17] Jiao WQ. Yue MB. Wang YM. He MY. Synthesis of morphology-controlled mesoporous transition aluminas derived from the decomposition of alumina hydrates. Microporous Mesoporous Mater., 2012; 147: 167-177.

[18] Kul'ko EV. Ivanova AS. Litvak GS. Kryukova GN. Tsybulya SV. Preparation and Microstructural and Textural Characterization of Single-Phase Aluminum Oxides. Kinet. Catal., 2004; 45: 714-721.

[19] Vicerich MA. Especel C. Benitez VM. Influence of gallium on the properties of Pt-Re/Al2O3 naphtha reforming catalysts. Appl. Catal. A: General., 2011; 407: 49-55.

[20] Rahimpour MR. Jafari M. Iranshahi D. Progress in catalytic naphtha reforming process: a review. Appl. Energy. 2013; 109C: p.83
[21] Belyj AS. Pashkov VV. Kir'yanov DI. Smolikov MD. Golinsky DV. Udras IE. Experience of commercial production and operation of new reforming catalysts of PR family. Russian Chemical Journal. 2007; 51: 60-68
[22] E-Him. Petrochemical technologies. http://e-him.ru/.
[23] Smolikov MD. Kir'yanov DI. Kolmagorov KV. Udras IE. Zatolokina EV. Belyj AS. Experience of commercial production and operation of new reforming catalysts PR-81 and SHPR-81. Catal. Ind., 2013; (6): 36-41.
[24] Chsherbakova Y. Dolganova I. Belinskaya N. Benzene alkylation with ethylene process mathe-maical modeling. Proceedings - 2012 7th International Forum on Strategic Technology. IFOST 2012, 2012; Article Number 6357494.
[25] Ivashkina E. Nazarova G. Ivanchina E. Belinskaya N. Ivanov S. The Increase in the Yield of Light Fractions During the Catalytic Cracking of C-13-C-40 Hydrocarbons. Curr. Org. Synth., 2017; 14 (3): 353-364.
[26] Novaes LR. Resende NS. Salim VM. Secchi AR. Modeling. simulation and kinetic parameter estimation for diesel hydrotreating. Fuel, 2017; 209: 184-193.
[27] Ancheyta J. Mederos FS. Mathematical modeling and simulation of hydrotreating reactors: Cocurrent versus countercurrent operations. Appl. Catal. A, 2007; 332: 8-21.

To whom correspondence should be addressed: Dr. Emilia D. Ivanchina. Department of Fuel Engineering and Chemical Cybernetics. Tomsk Polytechnic University. 30. Lenin Avenue. Tomsk. 634050. Russia; tel.: (+7-3822) 60-63-33; fax: (+7-3822) 56-38-65; e-mail: ied@tpu.ru