

Reduction of Coke Formation on Pt–Re Gasoline Reforming Catalysts

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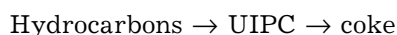
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Abstract

The catalytic activity fluctuations upset the equilibrium in reactions of the hydrogenation of carbon depositions and causes increased coke formation. We propose a method of estimation of the Pt–Re catalysts activity, which allows keeping track of the activity enhancement, and hence provides prolongation of the catalyst service cycle by 20–30 %. The method is based on keeping the catalytic activity at an optimum level using the developed computer system.

The estimation of an optimum catalytic activity is one of the main problems in the analysis of catalysts at plants. The optimum activity is determined by a ratio of target reforming reaction rates and the equilibrium between the reactions of coke structure formation and its hydrogenation.

The mechanism of coke formation on the metal catalytic center of bifunctional catalysts can be shown as a scheme of consecutive reactions:



where UIPC – unsaturated intermediate products of consolidation. Parent materials for generation of UIPC are aromatic hydrocarbons and five-cycle naphthenes. The UIPC are generated by the mechanism of diene synthesis as a result of reactions of consolidation and condensation (Fig. 1).

Quantitatively, the equilibrium of coke formation is determined by three major factors: by a hydrogenating ability of Pt catalyst; by a raw material component structure; by technological modes. Apparently, the hydrogenating activity of Pt catalyst is functionally determined by the nature and quantity of electronic and structural promoters, therefore, the value of the optimum activity is characteristic

for each type of industrial catalysts. The activity changing has fluctuation nature. The catalytic activity fluctuations upset the equilibrium in reactions of the hydrogenation of carbon depositions and causes increase of the coke formation. We propose a method of estimation of the Pt–Re catalysts activity, which allows keeping track of the activity enhancement, and hence provides prolongation of the catalyst service cycle by 20–30 %. The algorithm of activity regulation is given in the Appendix. For confirmation of these conclusions the assessment of operation R-56 catalyst unbalanced by Re at Omsk Oil Refinery Factory (ORF) (Fig. 2) and that of mixed type KR-108U and RB-22Y catalysts at Angarsk ORF (Fig. 3) was

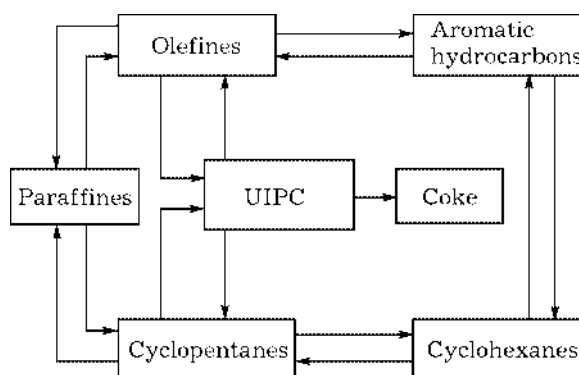


Fig. 1. Scheme of reactions of coke formation.

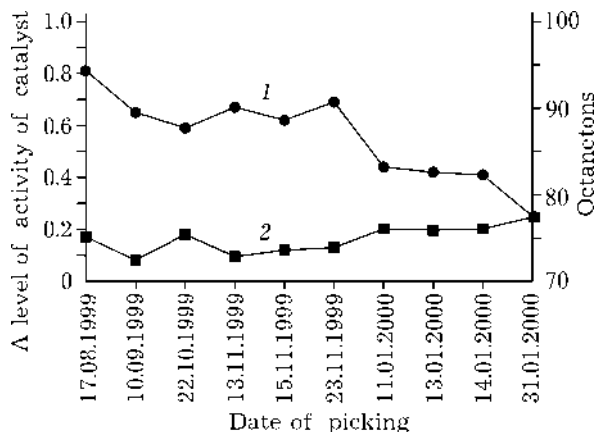


Fig. 2. The results of calculation of activity of Pt-Re catalyst R-56 in unit L-35-11/1000 Omsk ORF.

conducted. Rapid deactivation and coking of the catalyst (see Fig. 2) is due to considerable fluctuation of the activity. In Fig. 3 the operation of plant L-35-11/1000, regulated with our program is shown. The activity is held at an optimum level, therefore decreasing of the activity proceeds slowly.

The numerical evaluation by the mathematical model of a fixed catalytic activity level a_{opt} is executed, which is determined by total amount and structure of coking depositions on the catalyst surface.

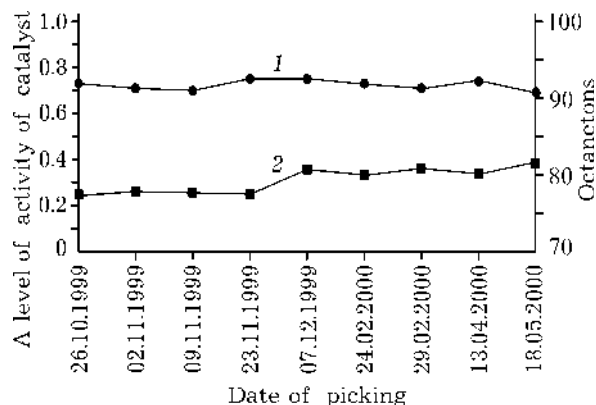


Fig. 3. The results of calculation of activity of Pt-Re catalyst RB-22U, KR-108U in unit L-35-11/1000 Angarsk ORF.

The change of relative catalytic activity ($a = r_A / r_A^0$, where r_A^0 is rate of aromatization on fresh catalyst) can be represented in the following way:

$$a = r_A / r_A^0 = 1 - \theta_C$$

$$dA / dG = -\alpha(a - a_{opt})$$

$$a_{opt} = \frac{k_r P_{H_2}}{k_c Y_n}$$

where G – a quantity of transformed feed stock; A – catalytic activity; θ_C is fraction of

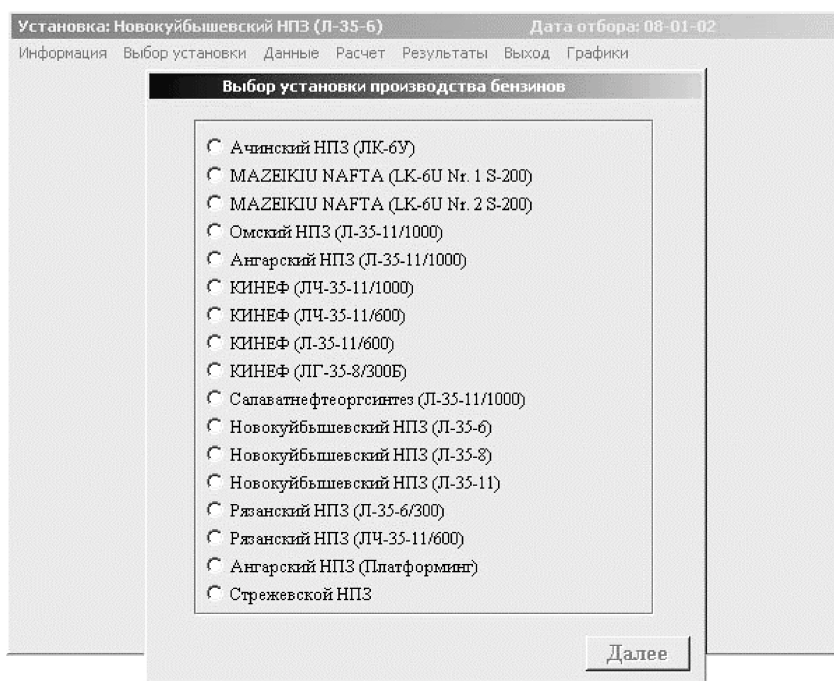


Fig. 4. A view of program “Activity” (a window of plant choosing).

catalytic surface occupied by coke; α is kinetic constant; k_r , k_c are rate constants of reactions of hydrogenation and coke formation; P_{H_2} is pressure of hydrogen; Y_n is concentration of naphthenes in raw stock.

Rate of decreasing of optimal activity is given by

$$da_{opt} / dG = -\beta$$

where β is deactivation rate. The calculations were carried out with our program "Activity" (Fig. 4).

The level of the catalytic activity is an integral index of the equilibrium between formation and hydrogenation reactions of coke structure, and it depends on the catalyst elemental composition (ratio Pt/Re), its activity and durability. This parameter changes during service cycle and its value can be used for forecasting a term of working contact regeneration.

The computer express-estimation of a level of acidic and metal activity allows prediction of the current activity of the catalyst basing on daily analysis of gases, the structure of initial raw materials and technological parameters. The technique is introduced at Omsk, Achinsk and Angarsk ORFs.

Appendix

THE ALGORITHM OF ACTIVITY REGULATION

1. The estimation of a level of activity with program "Activity".
2. Calculation a_{opt} with program "Prognoz":
 - a) if $a \leq a_{opt}$, $O.N. \leq O.N_{req}$ (where O.N. is octane number, $O.N_{req}$ is regulated octane number, a is catalytic activity, a_{opt} is optimum level of catalytic activity) then an octane number is regulated by temperature;
 - b) if $a = a_{opt}$ then an operating regime is regulated by temperature;
 - c) if $a > a_{opt}$ then temperature regime is changed till $O.N_{req}$.