RESEARCH

MATHEMATICAL MODELING OF PLATFORMING

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Catalytic reforming of low-octane naphtha cuts into a high-octane component of commercial gasoline is conducted in a three- or four-reactor block with a stationary bed of solid (pelleted) $Pt,Re/\gamma-Al_2O_3$ catalyst. This catalyst is sensitive to moisture and sulfur and nitrogen compounds. For this reason, the naphtha cut that distills within 85-180°C undergoes hydrotreating at high temperature and a cut containing hydrocarbons from the three basic classes is obtained: paraffins, naphthenes, and aromatics without contaminants of sulfur and nitrogen compounds. The naphthene hydrocarbons consist of cyclohexane and cyclopentane fractions.

Aluminum oxides can exist in the form of eight modifications: $\lambda-Al_2O_3$, $\ddot{a}-Al_2O_3$, $\div Al_2O_3$, $\grave{e}- Al_2O_3$, $\eta-Al_2O_3$, $\beta-Al_2O_3$, $\gamma-Al_2O_3$, $\alpha- Al_2O_3$. In industry, only $\gamma-Al_2O_3$ is used as a support for platforming catalysts. This oxide is most stable at temperatures of 500-600°C and it turns into $a- Al_2O_3$ at 700°C and higher.

Ensembles of polyhedrons in $\{AlO_4 \cdot AlO_6\}$ containing $[AlO_4]$-tetrahedrons and $[AlO_6]$-octahedrons bound at the apices in its crystal lattice are an important property of $g- Al_2O_3$. According to the theory of catalysis by polyhedrons, the $[AlO_4]$-tetrahedron exhibits high catalytic activity in cracking and isomerization of hydrocarbons due to the elevated acceptor capacity, acidity, and chemisorption capacity.

The $\alpha-Al_2O_3$ modification is a closely packed lattice of combinations of ensembles of $\{AlO_6 \cdot AlO_6\}$-octahedrons bound at the apices, edges, or faces. These ensembles exhibit insignificant catalytic activity in the reactions indicated above. For this reason, $\alpha- Al_2O_3$ is not used as a reforming catalyst support.

The acid or acceptor properties of $\gamma- Al_2O_3$ improve when it is combined with zeolites in the H form. The lattice of the zeolites is constructed of ensembles of $\{AlO_4 \cdot SiO_4\}$-tetrahedrons. In these ensembles, the silicon oxygen tetrahedron plays the role of a promoter, increasing the acceptor strength of the aluminum oxygen tetrahedron.

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Reforming catalysts must exhibit activity not only in reactions of the "acid" type (cracking, isomerization, dismutation, etc.), but also in dehydrogenation, hydrogenating, and dehydrocyclization reactions. The metal phase on the surface of the support – aluminum oxide, zeolite, or a mixture of both – give the catalyst these properties.

The metal phase is applied on the surface of the support from aqueous solutions of the corresponding salts. After drying, heat treatment, and reduction, it consists of discrete particles 1-10 nm in size. It also contains metal particles such as $[PtPt_4]^0$, $[PtPt_4]^{2+}$, or $[MeMe_4]^0$, $[MeMe_4]^{2+}$, where Me is rhenium, palladium, tin, etc.

As a consequence, the atoms and ions in the metal phase are packed in tetrahedrons bearing a different charge. These tetrahedrons have elevated donor properties and catalyze dehydrogenation of naphthenes and dehydrocyclization of n- and isoparaffins, as well as hydrogenation of coke deposits on the surface of the catalyst.

Catalysts prepared by the impregnation method exhibit multifunctional properties after sulfuring. They induce so-called fast reactions – dehydrogenation and hydrocracking – as well as slow reactions – dehydrocyclization and dehydroisomerization of alkylpentanes.

After halogenation, the catalysts undergo sulfiding in a stream of hydrogen sulfide or sulfur-containing compounds to regulate the rate of hydrocracking and dehydrocyclization of paraffins, i.e., to decrease the rate of the first reaction and increase the rate of the second reaction.

It follows from the above that platforming of low-octane naphtha cuts in the presence of multifunctional catalysts is a multiparametric process, and the degree of freedom of variation of the parameters is significant with respect to their number and the limits of variation. Creating a mathematical model for such a complex process is more an art than a rigorously defined problem. In operation of reforming units, the laws of random interactions of the parameters, which have been determined in the simplest case, play an important role.

Statistical and determined sets of parameters thus interact in conditions of reforming of naphtha cuts on multifunctional catalysts. The number and degree of variation of the parameters are a function of the design and operating conditions of the unit – ideal displacement, ideal mixing, or intermediate regime of flow of the reagents through the reactor.

An important number of mathematical models of the platforming process is described in the literature; they usually reflect the level of knowledge of the investigator concerning the given problem and his predilection for a particular method of creating such models – empirical or theoretical. For this reason, there are no mathematical models that are invariant with respect to the content and set of equations.
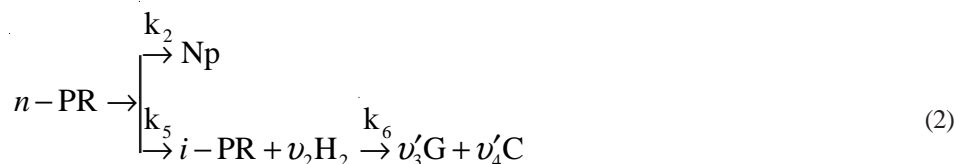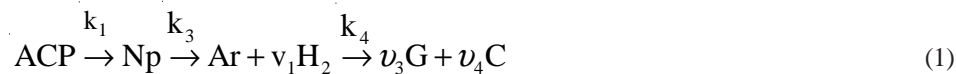
Creation of a mathematical model of the platforming process in our case included the following stages:

● accumulating a significant mass of experimental data from an industrial unit concerning the effect of different parameters on the quality and yield of reformate and hydrocarbon gas;

● processing these data to reveal certain patterns by a statistical-mathematical method (method of least squares);

● constructing tables and graphs to determine the correspond correlations between the parameters and then analyzing them;

● creating a kinetic scheme of the process;

● deriving kinetic equations for stationary and nonstationary process conditions and for a heterogeneous system with consideration of the hydrodynamic regime;

● establishing the adequacy of the kinetic equations with experimental dependences using kinetic constants determined with the experimental data.

KINETIC SCHEME OF REFORMING

In creating the kinetic scheme, it was assumed that the following reactions of transformation of hydrocarbons of the paraffin, naphthene, and aromatic classes take place on Pt,Re/γ- Al_2O_3 catalyst: dehydrogenation of naphthenes, dehydroisomerization of alkylpentanes into naphthenes followed by dehydrogenation, dehydrocyclization of paraffins and destructive isomerization of n-paraffins. These reactions can take place parallelly, parallelly-sequentially, or in one stage.

The kinetic scheme of catalytic reforming of the naphtha cut was represented as:

$$ACP \xrightarrow{k_1} Np \xrightarrow{k_3} Ar + v_1H_2 \xrightarrow{k_4} v_3G + v_4C \tag{1}$$

$$n-PR \to \begin{cases} \xrightarrow{k_2} Np \\ \xrightarrow{k_5} i-PR + v_2H_2 \xrightarrow{k_6} v_3'G + v_4'C \end{cases} \tag{2}$$

where ACP are alkylcyclopentanes; Np are naphthenes; Ar are aromatics; G is hydrocarbon gas; C is coke; n-Pr, i-Pr are n- and isoparaffins; k_1-k_6 are the rate constants of the corresponding stage of the process; v_1–v_4, v_3', v_4' are stoichiometric coefficients.

KINETIC EQUATIONS IN GENERAL FORM

Catalytic reforming of the naphtha cut in the presence of hydrogen-containing hydrocarbon gas is conducted: in the gas phase of the reaction mixture; in a stream; in conditions of ideal displacement of the reaction mixture over a stationary catalyst bed. In industrial conditions, it takes place in stationary conditions after a fixed time.

Based on these assumptions, the equations for the rate of conversion of hydrocarbons of the corresponding classes with consideration of the basic postulate of chemical kinetics for schemes (1) and (2) are:

for n-paraffins

$$\frac{dn_{n\text{-Pr}}}{Sdl} = (k_2 + k_5)\delta_{n\text{-Pr}} \tag{3}$$

for isoparaffins

$$\frac{dn_{i\text{-Pr}}}{Sdl} = k_5\delta_{n\text{-Pr}} - k_6\delta_{i\text{-Pr}} \tag{4}$$

for naphthenes

$$\frac{dn_{Np}}{Sdl} = (k_1 + k_2)\delta_{n\text{-Pr}}k_3\delta_{Np} \tag{5}$$

for aromatic hydrocarbons

$$\frac{dn_{Ar}}{Sdl} = k_3 \delta_{Np} - k_4 \delta_{Ar} \tag{6}$$

for hydrocarbon gas

$$\frac{dn_G}{Sdl} = k_6 \delta_{i\text{-}Pr} \delta_{H_2} + k_4 \delta_{Ar} \delta_{H_2} \tag{7}$$

where n is the molar feed rate for the corresponding hydrocarbons; S, l are the surface area and length of the catalyst bed; ä is the fraction of the surface of the catalyst occupied by the corresponding hydrocarbons and hydrogen.

After transformations, Eqs. (3)-(6) become:

for n-paraffins

$$n_A^0 \frac{d(x-y)}{Sdl} = k_1^* (1 - x - z) \tag{8}$$

for isoparaffins

$$n_A^0 \frac{d(z-u)}{Sdl} = k_1^* (1 - x - z) - k_6^* \left(\gamma_{n-Pr} + z - u\right) \tag{9}$$

for naphthenes

$$n_A^0 \frac{d(x-u)}{Sdl} = k_1^* (1 - x - z) - k_3^* \left(\gamma_{Np} + x - y\right) \tag{10}$$

for aromatic hydrocarbons

$$n_A^0 \frac{d(y-u)}{Sdl} = k_3^* \left(\gamma_{Np} + x - y\right) - k_4^* \left(\gamma_{Ar} + y - u\right) \tag{11}$$

where n_A^0 is the molar feed rate of the initial naphtha cut; x, y, z, u are the fractions of substances converted and obtained; k_1^* are the rate constants of the corresponding stages of the process, including the real rate constants and adsorption coefficients; γ is the ratio of the number of moles of the corresponding classes of hydrocarbons to the number of moles of the initial naphtha.

The following simplified kinetic equations for transformation of hydrocarbons of each class are obtained by integration of Eqs. (8)-(11):

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for paraffins

$$n_A^0(1 - x - y) = k_1^*$$ (12)

for isoparaffins

$$n_A^0(\gamma_{i-Pr} + z - u) = \frac{k_1^*}{k_1^* - k_6^*}\left(n_A^0 e^{-k_1^*/n_A^0} - k_6^*\right)$$ (13)

for naphthenes

$$n_A^0(\gamma_{Np} + x - u) = \frac{k_1^*}{k_1^* - k_6^*}\left(n_A^0 e^{-k_1^*/n_A^0} - k_3^*\right)$$ (14)

for aromatic hydrocarbons

$$n_A^0(\gamma_{Ar} + x - u) = k_4^*$$ (15)

The rate constants k_1^*, preexponential factors in the Arrhenius equation, and activation energies were calculated with the experimental kinetic dependences using the Arrhenius equation.

The dependences of the rate constants on the temperature in Arrhenius form have the following concrete form:

$$k_1^* = 17700\, e^{-26000/RT}$$
$$k_3^* = 2.34 \cdot 10^7\, e^{-62300/RT}$$
$$k_4^* = 21000\, e^{-28000/RT}$$
$$k_6^* = 56\, e^{-2500/RT}$$

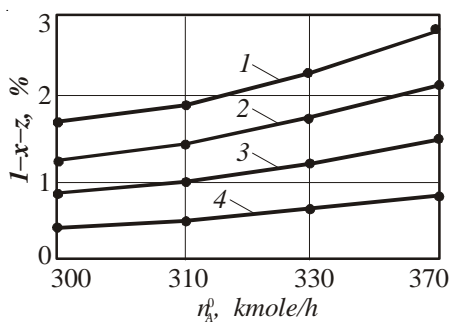where R is the universal gas constant; T is the temperature.

Fig. 1. Residual content 1–x–z of n-paraffins in reformate as a function of the molar feed rate n_A^0 of naphtha cut into the reactor at the temperature of: 1) 480°C; 2) 490°C; 3) 500°C; 4) 510°C.

The fit of these equations to the experimental data can be judged on the example of the graphic dependence of the residual content of n-paraffins in the reformate on the molar feedstock feed rate n^0_A into the reactor (see Fig. 1). As we see, the experimental data – points – coincide with the curves calculated with Eq. (12).

According to this mathematical-kinetic model, hydrocarbons of different classes are transformed at different rates in the reforming conditions.

The experimental values of the rate constants and activation energies are in the order:

$$k^*_{Np} > k^*_{n-Pr} > k^*_{Ar} > k^*_{i-Pr}$$

$$E_{Np} > E_{Ar} > E_{n-Pr} > E_{i-Pr}$$

According to these data, dehydrogenation of naphthenes and transformation of aromatic hydrocarbons are fast processes and dehydrocyclization and destructive isomerization of n-paraffins are slow processes.

As a consequence, the kinetic model can be used to not only refine the kinetic scheme of a very complex process but also to determine the distribution of the reagents by kinetic rates with identification of fast and slow reactions.