

## AROMATIZATION OF LIGHT NAPHTHA FRACTIONS ON ZEOLITES 2. MODEL OF CATALYST DEACTIVATION

A model of catalyst deactivation in the "Zeoforining" process was developed. The deactivation rate constants and activation energies were estimated. The role of adsorbed oligomers in the reaction and the deactivation kinetics were examined. The model is intended for further modeling and optimization of the process.

In a previous paper [1], we reported the reaction kinetic model for the Zeoforining process, which is intended for gasoline production by the catalytic conversion of low-octane crude naphtha under hydrogen-free conditions. It is typical that significant coking of the catalysts occurs under such conditions, [2-4], and catalyst activity is decreased. Generally, this is caused by two different types of mechanisms: either coke precursors directly cover the active sites, or the coke blocks the entrance to the pores [5,6]. The main active sites of the Zeoforining reactions are located on zeolite particles that are finely dispersed in catalyst matrix. The catalyst used in the Zeoforining process is similar to the catalysts of MTG (methanol to gasoline) and MOGD (Mobil olefins to gasoline and distillate) processes. Therefore, most investigations of pentasil type catalyst deactivation presented in the literature were performed using methanol conversion.

Echevski et al. [2-4] established that two types of coke are formed under the conditions of the Zeoforining process. The first (low temperature, uncondensed coke) is deposited in the intracrystalline volume of zeolite, and the second (high temperature, condensed coke) is formed on the outer crystalline surface. Different temperature dependencies were observed [4] for the rate of catalyst deactivation caused by these two types of coke (Fig. 1).

A region with a relatively low rate of deactivation exists in the interval of 380-420°C (region III). At higher temperatures (>420°C) a "normal" temperature dependence is observed with the activation energy of deactivation  $E_H = (78-80)$  kJ/mol. At lower temperatures (<380°C) the rate of deactivation is characterized by a negative apparent activation energy  $E_L = -(37-40)$  kJ/mol. These two regions of the deactivation rate

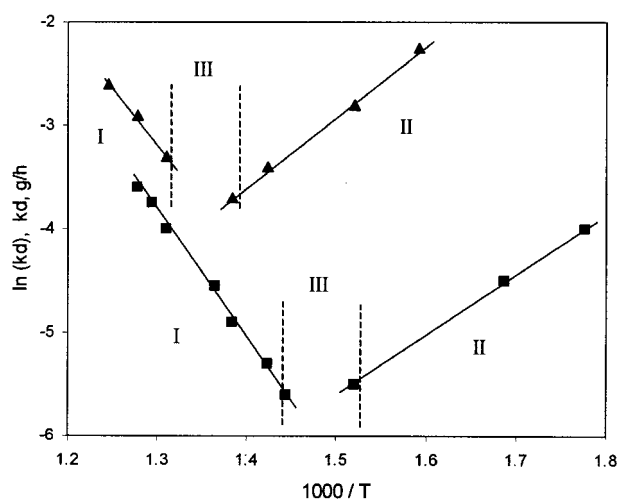


Figure 1. Temperature dependence of the deactivation rate of a pentasil type zeolite [4]. Conversion of methanol (■) and ethylene (▲).

correspond to condensed and uncondensed types of coke [4].

The available deactivation kinetics also refer to the MTG process. Comelli et al. [7] considered catalyst deactivation as  $k_i$  variations with time ( $t$ ):

$$k_1 = k_1^0 \exp(-b_1 t^{1/2}), \quad k_2 = k_2^0 \exp(-b_2 t), \quad (1)$$

where  $k_1$ ,  $k_2$  are the reaction rate constants for the formation of non-aromatic and aromatic products.

Ortega et al. [8] presented the deactivation kinetics in the form:

$$r_i = r_i^0 a, \quad \frac{da}{dt} = -(k_{dA} X_A + k_{dC} X_C + k_{dD} X_D) a, \quad (2)$$

where  $a$  is The relative activity;  $k_{di}$  the deactivation rate constants; A, C, D the oxygenates, light olefins and heaviest products respectively.

Deactivation kinetics are the subject of this paper, based on experiments with two Zeoforining catalysts and commercial feedstock, and based on the reaction kinetics presented in ref. [1].

Table 1. Experimental data on catalyst deactivation [9].  $P = 0.1 \text{ MPa}$ ,  $V_0 = 2.0 \text{ h}^{-1}$ .  
Conversion of straight-run gasoline of the Astrakhan gas-processing plant.

Time on stream, hour	1		120		240		300	
Temperature, °C	420		450		480		500	
Composition, % wt.:	Init.*	Mod.*	Init.	Mod.	Init.	Mod.	Init.	Mod.
n-Paraffins	9.6	8.1	10.8	8.5	18.5	9.3	28.5	12.2
i-Paraffins+Naphthenes	45.4	52.1	45.3	53.0	42.3	56.7	36.5	57.0
Olefins	1.5	1.7	2.8	2.7	4.1	3.7	5.1	4.2
Aromatics	20.7	24.8	21.1	25.2	17.6	22.6	14.5	19.8
Yield of gasoline, % wt.	75.7	84.9	77.2	86.6	78.4	88.6	79.5	89.0

\*Init. – "Initial Catalyst", Mod. – "Modified Catalyst"

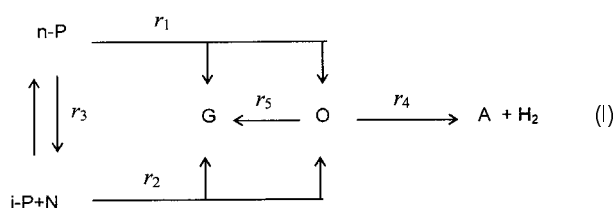
### ANALYSIS OF THE EXPERIMENTAL DATA

The experimental data, which were used for catalyst deactivation modeling, were obtained by Ahmetov and Karatun [9] in an isothermal reactor with a fixed catalyst bed (Table 1).

It may be seen from Table 1, that stepwise increase of the temperature was applied in the experiments (like in industry). The yield of liquid product increased with time, indicating that the active centers of the primary cracking reaction were deactivated first. At the same time, the aromatic content and gasoline octane number decreased due to the deactivation of active centers of hydrogen disproportionation in the unsaturated intermediates. It may be assumed that "deactivation reactions" are connected closely with these two types of conversion and are related to olefins and oligomers as coke precursors.

### MODEL OF DEACTIVATION

In ref. [1] we proposed the following conversion scheme of lumped components:



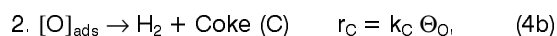
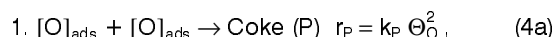
where A, O, G, n-P, i-P+N – are lumped components of aromatics, olefins, gases, n – paraffins, i – paraffins and naphthenes;  $r_j$  – are the reaction rates.

Assuming two active centers, and in accordance with the reaction kinetics of ref. [1], the reaction rate equations on the deactivating catalyst take the form:

$$\begin{aligned}
 r_1 &= k_1 (1-\Theta_o) Y_{n-P} a_C, \\
 r_2 &= k_2 (1-\Theta_o) Y_{i-P+N} a_C, \\
 r_3 &= k_3 (1-\Theta_o) Y_{n-P} [1 - Y_{i-P+N} / (K_P Y_{n-P})] a_C, \\
 r_4 &= k_4 \Theta_o^2 a_P, \\
 r_5 &= k_5 \Theta_o Y_H a_P,
 \end{aligned} \quad (2)$$

where  $Y_i$  is the molar fraction of the  $i$ -th component;  $Y_H$  – the molar fraction of hydrogen;  $k_j$  – the reaction rate constant;  $K_P$  – the equilibrium constant;  $a_C$ ,  $a_P$  – the relative activities of centers covered by condensed and uncondensed (polymeric) coke;  $\Theta_o$  is the fraction of active centers occupied by adsorbed olefins.

Coke formation can be presented as surface oligomerization and hydrogen disproportionation reactions:



Because olefins (light olefins and especially oligomers) are strongly adsorbed on the active sites of the catalyst,  $\Theta_o$  is proportional (at low temperatures 300–440°C) to the molar fraction of olefins in the reaction mixture  $\Theta_o \sim b_o Y_o$  [1]. At higher temperatures (420–500°C, see Table 1) a Langmuir type equilibrium should be used:

$$\Theta_o = b_o Y_o / (1 + b_o Y_o) \quad (3)$$

where  $b_o = b_o^0 \exp(Q_o/RT)$  is the adsorption equilibrium constant;  $Q_o$  is the heat of adsorption.

In order to derive the deactivation model, the equations of the coke formation rates (4) must be used. Under catalyst deactivation any coverage  $\Theta_j$  (surface concentration of the intermediate) is related to the fraction of deactivated centers  $\Theta_D$  as follows [10,11]:

$$\Theta_j = \Theta_j^0 (1 - \Theta_D) \quad (6)$$

This relationship is valid for any reaction (under the quasi-steady state assumption [10]) including the reaction of coke formation. So, for  $r_P$  and  $r_C$  one may write:

$$\begin{aligned}
 r_P &= k_P \left( \frac{b_o Y_o}{1 + b_o Y_o} \right)^2 (1 - \Theta_P)^2, \\
 r_C &= k_C \frac{b_o Y_o}{1 + b_o Y_o} (1 - \Theta_C),
 \end{aligned} \quad (7)$$

where  $\Theta_P$ ,  $\Theta_C$  are the surface coverages by "polymeric" and "condensed" coke.

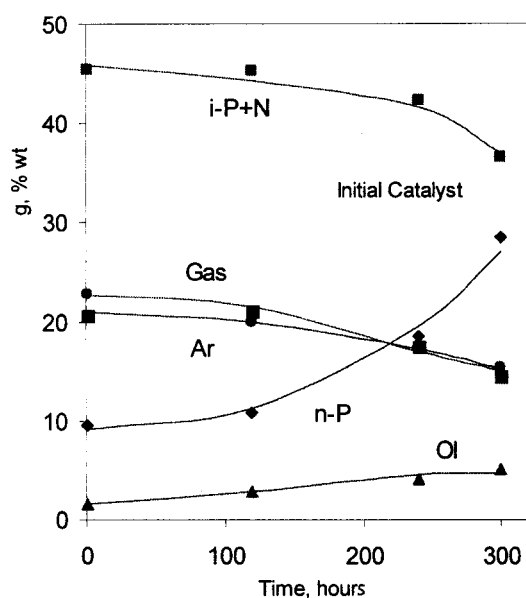
From the definition of the relative activity  $a_i = r_i/r_i^0$  [10], it is clear that  $a_P = 1 - \Theta_P$  and  $a_C = 1 - \Theta_C$ . The deactivation kinetic equations may then be written as:

$$\frac{da_P}{dt} = -k_P \left( \frac{b_o Y_o}{1 + b_o Y_o} \right)^2 a_P^2,$$

$$\frac{da_C}{dt} = -k_C \frac{b_o Y_o}{1 + b_o Y_o} a_C, \quad (8)$$

These equations together with the mass balance equation (9) for an isothermal integral reactor [1] were used to analyse the experiments on catalyst deactivation.

$$\sigma \frac{dY_i}{d\tau} + Y_i \frac{d\sigma}{d\tau} = \sum_{j=1}^R v_{ij} r_j, \quad r_j = r_j^0 a_j, \quad (9)$$



when  $\sigma = \Sigma n_i/\Sigma n_i^0$  is the coefficient of total mole number;  $v_{ij}$  – the stoichiometric coefficient of the  $i$ -th component in the  $j$ -th reaction;  $\tau$  – the contact time;  $t$  – the time on stream.

## RESULTS AND DISCUSSION

The results are presented in Fig. 2 and indicate good model prediction of the product composition dynamics. The values of the deactivation rate constants are presented in Table 2.

Note that the deactivation kinetics of two types of catalyst were analyzed. The first was the "Initial catalyst" (3-Zn-HZSM-F, 35% Al<sub>2</sub>O<sub>3</sub>), and the second was the "modified catalyst" with improved stability [9]. The "modified catalyst" provides a higher yield of aromatics and gasoline (lower yield of gas) and better stability (Table 1, Fig. 2). Analysis of the model (equations 8, 9)

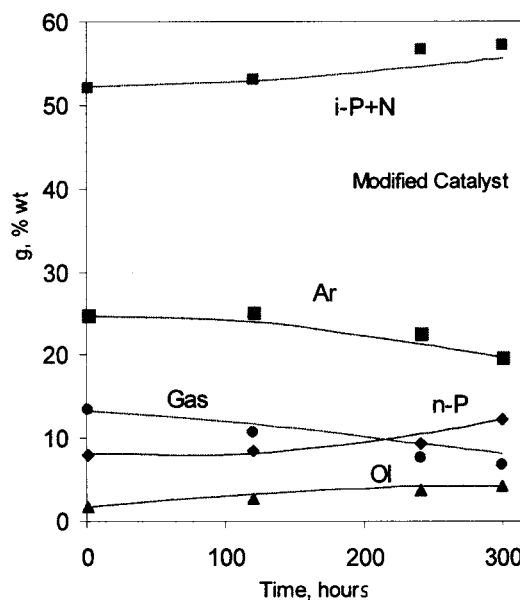


Figure 2. Product composition dynamics under catalyst deactivation. Points—experiment [9]; lines – model prediction

Table 2. Values of the kinetic parameters

No.	Reaction	Reaction and deactivation rate constant (at T = 420°C), h <sup>-1</sup>			Activation energy, kJ/mol		
		k <sub>j</sub>	Initial Cat.	Modified Cat.	E <sub>j</sub>	Initial Cat.	Modified Cat.
1	n-P → O + G	k <sub>1</sub>	20	18	E <sub>1</sub>	70	70
2	i-P+N → O + G	k <sub>2</sub>	1.5	1.45	E <sub>2</sub>	80	70
3	n-P ↔ i-P+N	k <sub>3</sub>	2.0	0.6	E <sub>3</sub>	10	-0
4	2O → A + 3H <sub>2</sub>	k <sub>4</sub>	0.45	0.6	E <sub>4</sub>	60	60
5	O + H <sub>2</sub> → G	k <sub>5</sub>	3.1	1.0	E <sub>5</sub>	80	-0
6	[O] <sub>ads</sub> → Coke (C)	k <sub>C</sub>	0.005	0.005	E <sub>C</sub>	60	60
7	2 [O] <sub>ads</sub> → Coke (P)	k <sub>P</sub>	0.015	0.01	E <sub>P</sub>	40	40
8	O ↔ [O] <sub>ads</sub>	b <sub>o</sub> *	100	100	Q <sub>o</sub>	45	60
Mean error, %			4.5	6.0			

\*b<sub>o</sub> – dimensionless

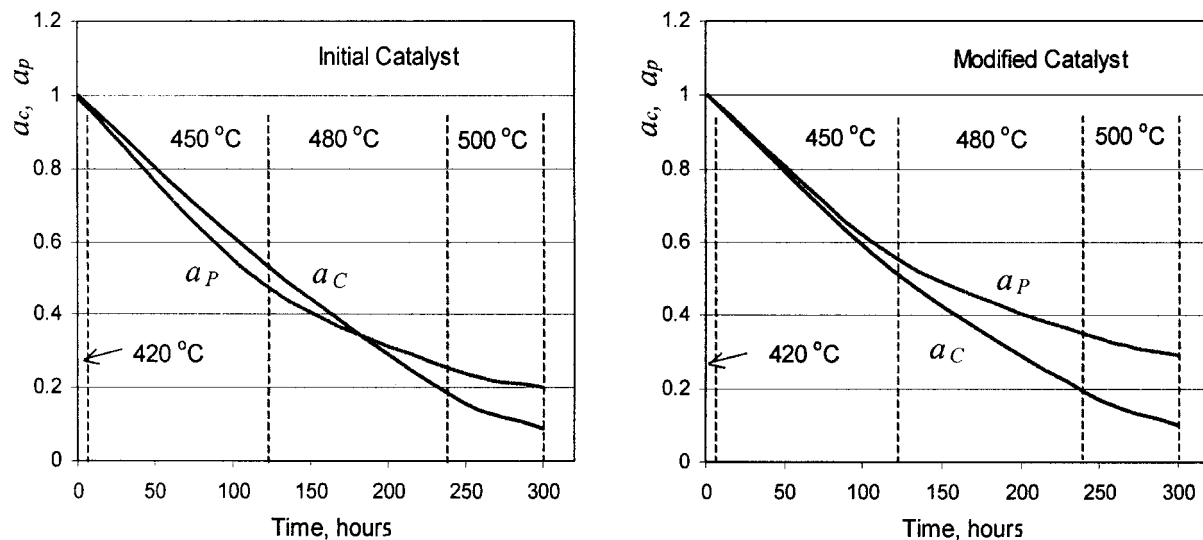


Figure 3. Activity vs. time curves during catalyst deactivation (initial and modified catalyst)

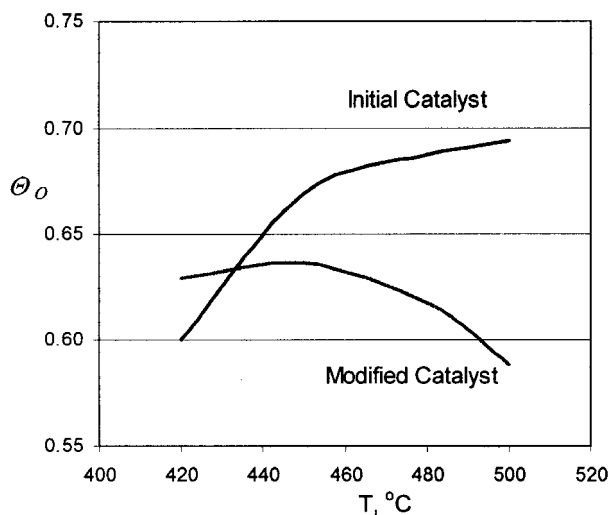


Figure 4. Dependence of olefin coverage on temperature

and the values of the kinetic parameters enable the elucidation of the character of catalyst modification. It should be mentioned that the rate constants of the main reactions ( $k_1, k_2, k_4$ ) did not change significantly after modification. That probably means that the total number of active sites did not change. On the other hand, the rate constants of isomerization ( $k_3$ ) and hydrogenation ( $k_5$ ) decreased three times and their activation energies approached zero. Since the isomerization equilibrium is shifted to *n*-paraffins, that leads to an increase in the *i*-paraffin concentration and in the octane number of gasoline. The lower rate of hydrogenation provides a lower concentration of gas and, therefore, a higher yield of gasoline.

Regarding the deactivation kinetics, similar rate deactivation constants were observed on both catalysts. Nevertheless, some differences in the activity dynamics

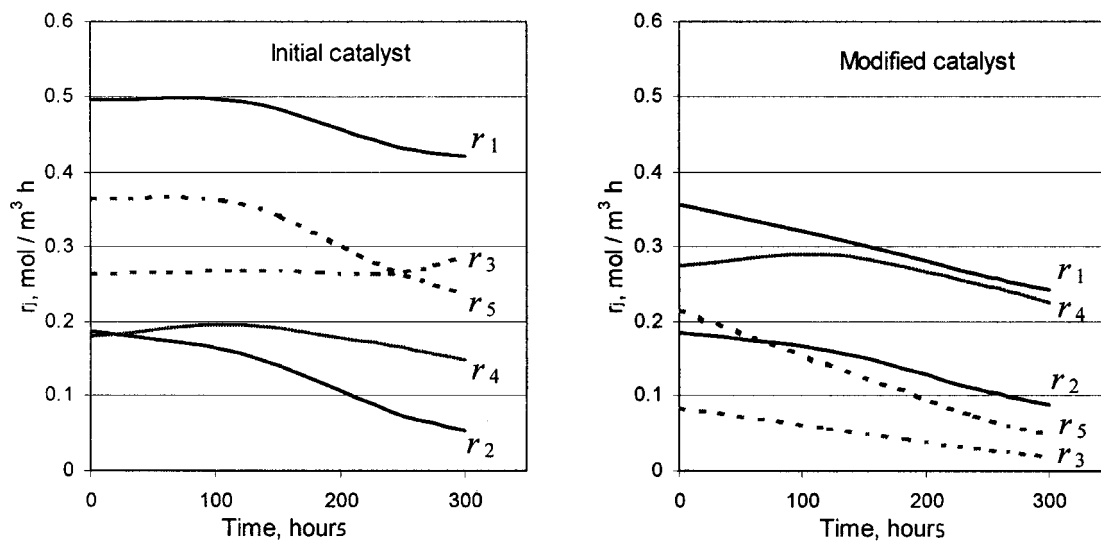


Figure 5. Reaction rate vs. time curves during catalyst deactivation (initial and modified catalyst)

were noticed (Fig. 3). They are due to the differences in olefin coverages ( $\Theta_o$ ) on the "initial" and "modified" catalysts (Fig. 4), which originate from different heats of adsorption ( $\Theta_o$ ). The cooperative effect of olefin adsorption and hydrogenation, paraffin isomerization, and catalyst deactivation results in different relations of reaction rates on these catalysts (Fig. 5).

It may be seen, that the reaction rates of n-paraffin cracking ( $r_1$ ), i-paraffin isomerization ( $r_3$ ) and olefin hydrogenation ( $r_5$ ) are decreased on the "modified catalyst", while the reaction rate of aromatization ( $r_4$ ) is increased. These reaction rate combinations lead to an increase in the gasoline yield and octane number of gasoline.

It should be noted, that we used several models to analyse the of experimental data:

1.  $r_P = k_P Y_o^2 a_P^2$ ,  $r_C = k_C Y_o a_C$ ,
2.  $r_P = k_P Y_o^2 a_P^2$ ,  $r_C = k_C Y_o a_C (1 - a_P)$ ,
3.  $r_P = k_P Y_o^2 a_P^2$ ,  $r_C = k_C a_C$ ,
4.  $r_P = k_P a_P^2$ ,  $r_C = k_C a_C$ ,
5.  $r_P = r_C = k_P a_P$ .

Nevertheless, only the model (Eq. 7) with olefin adsorption (and inhibition) provides an acceptable description of the experiments on both the "initial" and "modified" catalysts. Moreover, only this model has

kinetic parameters that are similar for two types of catalyst (Table 2).

The next report will be devoted to the mathematical modeling and optimization of the Zeoforming process in a tubular reactor such as the one used at the Nizhnevartovsk gas-processing plant.

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## IZVOD

### AROMATIZACIJA LAKIH BENZINSKIH FRAKCIJA NA ZEOLITIMA 2. MODEL DEAKTIVACIJE KALIZATORA

(Naučni rad)

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Proces Zeoforming je razvijen za proizvodnju visokooktanskog benzina iz lakih benzinskih frakcija na zeolitnim katalizatorima bez korišćenja vodonika. Na bazi analize eksperimentalnih podataka koje su urađene u laboratorijskim integralnim reaktorima, razrađen je kinetički model ukupno sa deaktivacijom katalizatora.

Objašnjena je ključna uloga olefina i oligomera u deaktivaciji katalizatora koksom.

Određeni su kinetički parametri reakcija i deaktivacije (konstante brzina reakcija, energije aktivacije). Model je namenjen za optimizaciju procesa.

Ključne reči: Proces Zeoforming • Deaktivacija katalizatora • Model deaktivacije •  
Key words: Zeoforming process • Catalyst deactivation • Deactivation model •