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Kinetic Models of Catalyst Deactivation in Paraffin Dehydrogenation

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Abstract—The results of studying the deactivation of both unpromoted platinum–alumina catalysts and those promoted with K, Li, In, Sn, and W in the dehydrogenation of lower and higher paraffins are discussed. The main reason for catalyst deactivation is found to be coke formation. The rate laws of coke formation and paraffin dehydrogenation in the non-steady-state regime of the reaction are derived. The catalyst sulfuring is found to enhance its stability. The effects of oxygen and water impurities on the reactions and coke formation are studied.

INTRODUCTION

The dehydrogenation of paraffins fills an important place in the synthesis of monomers for synthetic rubber and other products of organic synthesis. Platinum catalysts that are usually supported on aluminum oxide [1–3] exhibit a high efficiency in the dehydrogenation of paraffins to olefins. Promoters improve the activity, selectivity, and stability of platinum–alumina catalysts. The most frequent side reaction that leads to catalyst deactivation is the formation of coke. The preliminary sulfuring of catalysts is used to reduce coke formation [4, 5]. Sulfuring somewhat decreases the catalyst activity but significantly increases their stability [6–8].

In this paper, we generalized the results of our investigations on the regularities of platinum–alumina catalyst deactivation in the dehydrogenation of lower (propane, isobutane, *n*-butane, and isopentane) and higher (*n*-decane, *n*-dodecane, and C_{10}–C_{12} mixtures) paraffins, on the kinetics of their dehydrogenation in the non-steady-state regime, and on the effect of impurities (sulfur, hydrogen sulfide, oxygen, and water vapors) on the catalytic activity.

Two types of catalyst deactivation kinetics (“separable” and “nonseparable”) were considered in [9–12]. In the case of separable kinetics, individual factors are introduced into rate laws to describe a decrease in the catalyst activity. In the second case, a decrease in the catalyst activity results in a change in the form of kinetic relations or, at least, in the numerical values of some constants. Describing the regularities of deactivation, we proceeded from the concepts of nonseparable kinetics and considered that the description of a process in steady-state and non-steady-state regimes should be interrelated and based on the general reaction mechanism [13–15].

EXPERIMENTAL

The experiments were performed in a seamless soldered flow-circulation setup that involved a quartz reactor with a spring-controlled McBain balance [16] at an atmospheric pressure in the presence of hydrogen. A catalyst was placed in a stainless-steel netted pan mounted on a calibrated tungsten spring with a quartz filament. A 2-mm gap between the pan and the reactor wall provided good conditions for mass transfer at a circulation rate of up to 1000 l/h and allowed obtaining the complete kinetic curve of coke formation during a single experiment. The experiments with different samples of catalyst showed that, at a constant space velocity of the reaction mixture, the same amount of coke per 1 g of catalyst was always formed. The sensitivity of the spring was 34 mg/mm, its extension was measured with a KM-6 cathetometer (the accuracy of measuring was 0.01 mm). The gas mixture was analyzed with a chromatograph. To determine the composition of coke, the amounts of CO_2 and H_2O formed from it during regeneration were measured. The amount of coke measured by the extension of the spring of the McBain balance and that determined from the weight of burnt products were virtually equal.

The compositions of test platinum catalysts supported on γ-Al_2O_3 are presented in Table 1.

The surface area of platinum was determined by the solubility method [17].

RESULTS AND DISCUSSION

The Initial partial pressures of lower paraffins and hydrogen varied from 125 to 670 hPa and that of especially introduced olefin varied from 0 to 75 hPa. The space velocity of paraffins (V^0) ranged from 1500 to 36000 h^{-1}, the temperature varied from 500 to 600°C. The amount of coke formed (C) was in the range from 1.4 to 70.6 mg/g Cat.

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† Deceased.

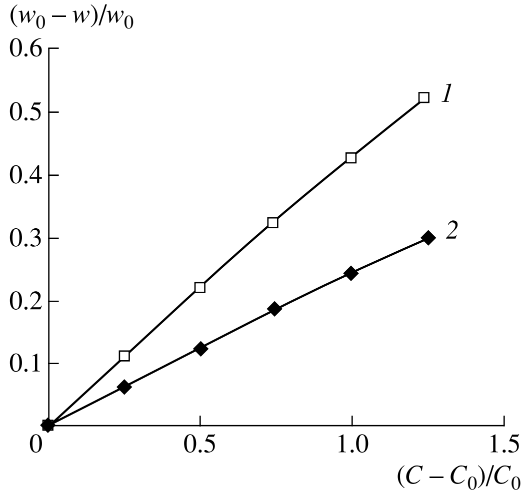

Fig. 1. Relative activity of catalyst II as a function of the relative amount of coke deposited during the dehydrogenation of isobutane at $P_1^0 = P_{H_2}^0$ = 500 hPa, $V_{C_4H_{10}}^0$ = 4500 h^{-1}, and (*1*) 500°C and (*2*) 570°C (w_0 is the steady rate of dehydrogenation before a decrease in the catalyst activity).

Higher paraffins were dehydrogenated at 430–500°C, space velocities of *n*-decane, *n*-dodecane, and especially added α-decene and α-dodecene ranging from 210 to 5140 h^{-1}, partial pressures of hydrocarbons ranging from 0.25 to 81 hPa and that of hydrogen ranging from 310 to 980 hPa. Under these conditions, the amount of coke varied from 1.3 to 77.0 mg/(g Cat).

The rates of coke formation were calculated from the curves of coke accumulation by approximating them with regression equations and finding the corresponding derivatives. It was shown in special experiments that the reactions under study were controlled by kinetics.

Table 1. Composition of catalysts

Catalyst sample	Composition, wt %					
	Pt	promoters				
		Sn	In	K	Li	W
I	0.35					
II	0.35		2.0			
III	0.35	2.0				
IV	0.60			1.0		
V	0.60	2.0		1.0		
VI	0.60		2.0	1.0		
VII	0.25				0.80	0.75
VIII	1.75	2.0				

Catalyst Deactivation in the Dehydrogenation of Lower Paraffins

The dehydrogenation of lower paraffins over the test catalysts occurred at a steady rate up to a certain moment, after which a slow deactivation of catalysts began. The length of the period of a steady activity depended on the nature and concentration of promoters and reaction conditions. The linear shape of the curve of the catalyst relative activity versus the relative amount of coke formed may point to the fact that the main reason for a drop in the catalyst activity was the deposition of coke (Fig. 1). The activity began to decrease after the coke concentration reached some threshold value (C_0). The threshold coke concentrations in the dehydrogenation of isobutane over catalysts I, II, and III (Table 1) were 1.8, 2.3, and 6.8%, respectively. The rate of paraffin dehydrogenation at a coke concentration higher than C_0 was described by the following rate law:

$$w = \frac{kP_1\gamma}{P_2 + k_1P_3 + k_2P_{H_2}^{0.5} + k_3(C - C_0)}. \qquad (1)$$

Here, k, k_1, k_2, and k_3 are the constants; P_1, P_2, P_3, and P_{H_2} are the partial pressures of paraffins, olefins, dienes, and hydrogen, respectively; and γ is the coefficient that takes into account the effect of the reverse reaction [18].

To restore the initial activity of catalysts, they were regenerated by keeping in a helium flow for 1 h and then in flow of air while increasing the temperature to 500°C. The catalysts were heated until carbon dioxide and water vapor formation completely ceased. The process lasted 1.5–2.0 h. The catalysts completely regained their initial activity after regeneration. Considering that a drop in the activity was due to coke deposition, we comprehensively studied the kinetics of coke formation.

Figure 2 presents the amounts of coke formed and the rate of coke deposition (w_C) as functions of the time of isobutane dehydrogenation. Two regimes of coke accumulation can be distinguished: regime A in which the amount of coke increased rapidly and at a steady rate and regime B in which the rate of coke deposition drastically decreased. The rate of coke deposition was independent of the partial pressure of the paraffin. In regime A, w_C linearly increased with an increase in the partial pressure of olefin at a constant concentration of hydrogen and weakly depended on the hydrogen concentration at a constant concentration of olefin. In regime B, the concentrations of hydrogen, olefin, and coke affected the rate of coke deposition. Under the examined conditions, the rate of isobutane dehydrogenation began to decrease after the accumulation of 18, 23, and 68 mg of coke per 1 g of catalysts I, II, and III that operated at 540°C in a steady-state mode for 7, 15, and 20 h, respectively. Thus, promoters increased the threshold concentration of coke (C_0), after which the rate of isobutene formation began to decrease.

The rates of coke formation in regimes A and B are described by the following equations:

$$w_{\mathrm{C}}^{A} = \frac{k_{\mathrm{C}} P_2}{1 + k_4 P_{\mathrm{H}_2}^{0.5}} \quad \text{(regime A);} \qquad (2)$$

$$w_{\mathrm{C}}^{Б} = \frac{k'_{\mathrm{C}} P_2 - k''_{\mathrm{C}} P_{\mathrm{H}_2}^{2} C}{P_2 + k_4 P_{\mathrm{H}_2}^{0.5} + k_5 \Delta C} \quad \text{(regime B).} \qquad (3)$$

Here, k_{C}, k_4, k'_{C}, k''_{C}, and k_5 are the constants, $\Delta C = C - C_{\mathrm{lim}}$ is the increment of the coke amount upon the completion of coke formation in regime A. Limiting amounts of coke (C_{lim}) that were formed on the examined catalysts depended on the nature of a promoter and were maximal on catalyst III and minimal on catalyst I. The values of C_{lim} were much smaller than those of C_0. The second term in the numerator of Eq. (3) corresponded to coke removal from the catalyst surface by its conversion to methane.

Table 2 presents the composition of coke that was formed in the dehydrogenation of isobutane over different catalysts.

The total amount of coke formed over catalysts I–III was almost equal, but the initial rate of coke formation that is characterized by constant k_{C} was much higher on unpromoted catalyst I than on promoted catalysts II and III. Promoters favored hydrogen concentrating in coke; the more efficient the promoter, the higher the concentration of hydrogen [19].

The analysis of the ratio of terms in the numerator of Eq. (3) showed that the fraction of coke removed from catalyst III during dehydrogenation was the largest and the fraction of coke removed from catalyst I was the smallest. Coke that contained more hydrogen was easier to remove by hydrogen.

When 1.6% of coke was deposited, the dispersion of catalysts I, II, and III decreased by a factor of 3, 1.3, and 1.2, respectively. Thus, promotion prevented a decrease in the platinum dispersion, probably because of the migration of coke to the surface of a support and a promoter. This may be associated with the existence of two regimes of coke formation. It can be assumed that the formation of coke began on the platinum sites that had the highest adsorption strength and continued at the interface between platinum, promoter, and support, where the intermediates of coke precursors migrated to. While the boundary sites are vacant, the rate of coke deposition is constant; this corresponded to regime A. In regime B, w_{C} significantly decreased, because the sites to which the intermediates of coke precursors might migrate, turned out to be occupied by that time. Then, coke was predominantly accumulated on the support and promoter. It is not improbable that coke migration involved the multilayer coverage of the surface.

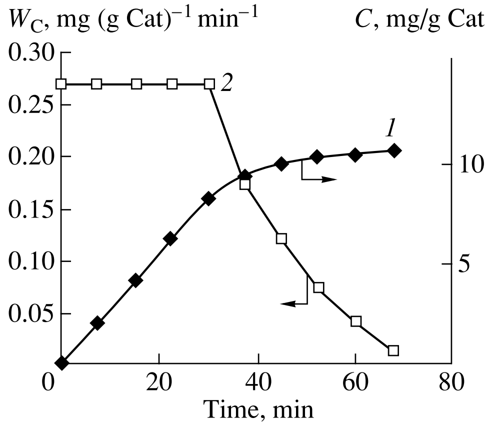

Fig. 2. (*1*) Amount of coke formed and (*2*) the rate of coke deposition as functions of the time of reaction over catalyst III (540°C, $P_1^0 = P_{\mathrm{H}_2}^0$ = 500 hPa, $V_{\mathrm{C}_4\mathrm{H}_{10}}^0$ = 4500 h^{-1}).

Thus, the promotion of platinum–alumina catalysts resulted in the enhancement of their stability in the dehydrogenation of lower paraffins and in a change in the coke structure.

Studying the effect of hydrogen sulfide additives on the kinetics of the dehydrogenation of lower paraffins and the properties of catalysts IV–VI, we showed that the introduction of H_2S at its partial pressure of up to 0.12 hPa (~0.05% of paraffin concentration) had almost no effect on the dehydrogenation rate. At a partial H_2S pressure of 1.05 hPa (0.42% of paraffin concentration), the dehydrogenation rate decreased by 16–19% of its initial level. This deactivation was reversible: the catalyst activity gained its initial level once the admission of hydrogen sulfide was discontinued. The introduction of hydrogen sulfide at an initial pressure of 0.12 hPa

Table 2. Coke formation over different catalysts ($P_1^0 = P_{\mathrm{H}_2}^0$ = 500 hPa, $V_{\mathrm{C}_4\mathrm{H}_{10}}^0$ = 4500 h^{-1}, 540°C)

Sample	Amount of coke formed for 50 min, mg/(g Cat)	Composition of coke formed for the time of reaction	
		50 min	200 min
I	13	$CH_{0.32}$	$CH_{0.24}$
II	12	$CH_{0.99}$	$CH_{0.37}$
III	12	$CH_{1.30}$	$CH_{0.69}$

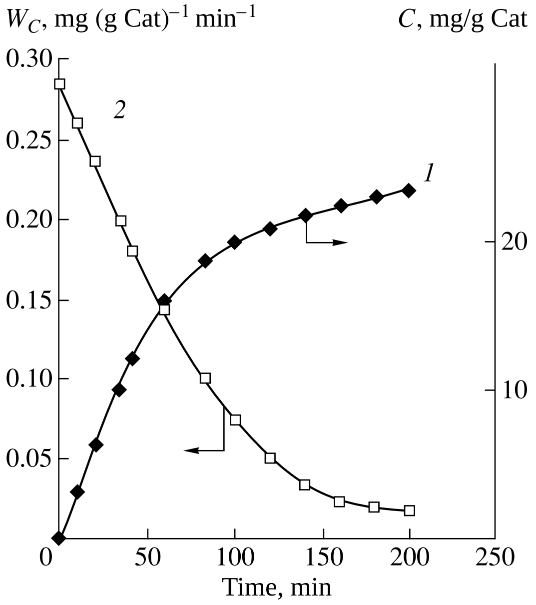

Fig. 3. (*1*) Amount of coke formed and (*2*) the rate of coke deposition as functions of the time of reaction over catalyst VII (470°C, $V^0_{C_{10}H_{22}}$ = 2000 h^{-1}).

enhanced the stability of catalysts by a factor of 1.5–2.2. The stability of catalyst VI increased to a greatest degree. In the presence of H_2S, coke was enriched with hydrogen; this made the catalyst more stable, because this hydrogen-enriched coke was more easily removed by hydrogen to free the sites on which dehydrogenation occurred.

The rate of the dehydrogenation of lower paraffins in the presence of hydrogen sulfide was described by the following rate law:

$$w = \frac{k' P_1 \gamma}{P_2 + k'_1 P_3 + k'_2 P_{H_2}^{0.5} + k'_3 P_{H_2S}}. \qquad (4)$$

The constants k', k'_1, and k'_2 numerically coincided with those obtained in the absence of hydrogen sulfide; that is, the mechanism of a simple mutual effect of catalytic reactions worked in this case [20]. This means that the numerators of the rate laws that describe the dehydrogenation of paraffins in the presence and in the absence of H_2S are the same, only the denominator of Eq. (4) contains an additional term that characterizes the retardation of the process with hydrogen sulfide.

At the same time, the principle of a simple mutual effect of catalytic reactions failed when paraffins were dehydrogenated in the presence of water vapor at an initial pressure in the range from 23 to 700 hPa. The dehydrogenation of paraffins in the presence of water vapor was described by the following rate law:

$$w = \frac{k'' P_1 \gamma}{P_2 + k''_1 P_3 + k''_2 P_{H_2}^{0.5} + k''_3 P_{H_2O}^2}. \qquad (5)$$

The fact that the partial pressure of water entered the denominator of Eq. (5) to the second power may point to the adsorption of water vapor on Pt^{4+} sites. Such an adsorption was proven by the chemical analysis of the catalyst surface [21, 22].

The dehydrogenation of isobutane over catalyst V for 10 h showed that 14 and 6 mg of coke/g of the catalyst was formed in the absence and presence of water vapor, respectively. Therefore, water vapor decreased coke formation and enhanced the stability of the catalyst by a factor of 1.5 to 2.

In the presence of water vapor, the rate of paraffin isomerization over catalysts V and VI decreased and the activity, selectivity, and stability of the catalysts in the formation of olefins enhanced.

Catalyst Deactivation in the Dehydrogenation of Higher Paraffins and Their Mixtures

The dehydrogenation of higher paraffins occurred at a constant rate up to the moment when a certain threshold concentration of coke (C_0) was reached. The values of C_0 for catalysts VII and VIII were 20–30 and 150–160 mg/(g Cat), respectively. Although these amounts were much larger than those that corresponded to a monolayer coverage of platinum, unoccupied sites on which the dehydrogenation of hydrocarbons may occur still remained on the metal surface. This means that coke deposited in multilayers not only on platinum, but on a support as well. Such a behavior of coke deposition was confirmed by the electron-microscopic studies of fresh and coked catalyst and support samples with a Tesla BS-513 electron microscope [23]. As in the dehydrogenation of lower paraffins, the relation between a relative change in the activity of catalysts and the relative amount of deposited coke pointed to the fact that the main reason for a decrease in the catalyst activity was coke formation. At $C > C_0$, the rate of the dehydrogenation of paraffins to olefins was described by the rate law similar to that proposed in [24, 25] with the difference that the more complex denominator contained a term that accounted for the coke concentration:

$$w = \frac{k P_1 - k' P_2 P_{H_2}}{P_{H_2}^{1.5} + k_1 P_2 + k_2 P_3 + k_3 (C - C_0)}. \qquad (6)$$

Catalyst VIII lost its activity in the dehydrogenation of higher paraffins at a much lower rate than catalyst VII.

Figure 3 presents the amounts of coke formed during *n*-decane dehydrogenation and the rates of coke deposition as functions of the reaction time. Comparison of Figs. 2 and 3 showed that, in the latter case, coke was formed more smoothly and two clearly defined regimes of coke formation were absent.

Based on available experimental data on the mechanism of coke formation and the regularities of the dehydrogenation of higher paraffins [24–27], we described the rate of coke formation by the following equation:

$$w_{\mathrm{C}} = \frac{k_4P_2 + k_5P_3}{D} + \frac{k_6P_2 + k_7P_3}{(D_1)^{0.5}}C^{2/3}\mathrm{e}^{-\alpha C}, \qquad (7)$$

where

$$D = P_{\mathrm{H}_2}^{1.5} + k_1P_2 + k_2P_3 + k_3C^{2/3}, \qquad (8)$$

$$D_1 = P_{\mathrm{H}_2}^{1.5} + k'_1P_2 + k'_2P_3. \qquad (9)$$

Two terms in Eq. (7) corresponded to coke formation on the coke-free surface and on the deposited coke. The factor $C^{2/3}\mathrm{e}^{-\alpha C}$ appeared in Eq. (7) in accordance with the exponential law of nucleation in topochemical reactions [28]. Coefficient α reflected the nature of condensation product formation.

The analysis of numerical values of constants of Eq. (7) showed that coke was mainly formed from dienes. In the case of catalyst VIII, the contribution of the second term was insignificant at any concentrations of coke, this supported the coke deposition mainly on platinum.

The constants in the denominators of Eqs. (6) and (7) coincided numerically. Thus, the regularities of coke formation and the dehydrogenation of higher paraffins are described by a unified kinetic model.

The rate of coke formation during the dehydrogenation of the mixtures of *n*-decane and *n*-dodecane equaled the sum of the rates of coke formation from individual hydrocarbons:

$$\begin{aligned} w_{\mathrm{C}} &= \frac{k_4P_2 + k_5P_3 + k'_4P_2 + k'_5P_3}{D} \\ &+ \frac{k_6P_2 + k_7P_3 + k'_6P_2 + k'_7P_3}{(D_1)^{0.5}}C^{2/3}\mathrm{e}^{-\alpha C}, \end{aligned} \qquad (10)$$

where

$$D = P_{\mathrm{H}_2}^{1.5} + k_1P_2 + k_2P_3 + k''_1P_2 + k''_2P_3 + k'_3C^{2/3}, \qquad (11)$$

$$D_1 = P_{\mathrm{H}_2}^{1.5} + k'_1P_2 + k'_2P_3 + k'''_1P_2 + k'''_2P_3. \qquad (12)$$

Thus, knowing the kinetics of coke formation during the dehydrogenation of individual hydrocarbons, one can calculate the rate of coke formation in the dehydrogenation of their mixtures. This is possible only in the case when the principle of a simple mutual effect of catalytic reactions is effective [20].

Interactions between the fragments that were formed during the adsorption of olefins and dienes on the pure surface of catalysts and interactions between coke and these fragments on the coked surface were assumed to be slow in the above-mentioned equations.

To estimate the effect of sulfur on coke formation in the dehydrogenation of higher paraffins, the catalysts were treated with the mixture of benzene and thiophene (14 : 1) for 1 h at 500°C [29]. The rate of coke formation on sulfured catalysts was also described by Eq. (7). However, both the rate of coke formation and the total amount of coke were much lower than those in the absence of sulfur. As a result, the stability of sulfured catalyst was 1.5–1.7 times higher than that of nonsulfured catalyst.

Impurities in the initial products and oxygen and water present in the reaction zone had a detrimental effect on the dehydrogenation of higher paraffins.

Analysis of experimental data demonstrated that the presence of up to 40 ppm of water and up to 815 ppm of oxygen had no effect on the dehydrogenation of higher paraffins and the formation of coke. An increase in the concentration of oxygen up to 4100 ppm resulted in an increase in the rate of coke formation and in a decrease in the rate of dehydrogenation. Assuming that the interaction of fragments formed during the adsorption of olefins and dienes with adsorbed oxygen was a slow stage in coke formation, we obtained the following equation:

$$\begin{aligned} w_{\mathrm{C}} &= \frac{(k_4 + k_1^0P_{\mathrm{O}_2})P_2 + (k_5 + k_2^0P_{\mathrm{O}_2})P_3}{D} \\ &+ \frac{(k_6 + k_3^0P_{\mathrm{O}_2})P_2 + (k_7 + k_4^0P_{\mathrm{O}_2})P_3}{(D_1)^{0.5}}C^{2/3}\mathrm{e}^{-\alpha C}, \end{aligned} \qquad (13)$$

where

$$D = P_{\mathrm{H}_2}^{1.5} + k_1P_2 + k_2P_3 + k_3C^{2/3} + k_8P_{\mathrm{O}_2}^{0.5}, \qquad (14)$$

$$D_1 = P_{\mathrm{H}_2}^{1.5} + k'_1P_2 + k'_2P_3 + k_9P_{\mathrm{O}_2}^{0.5}. \qquad (15)$$

Numerical values of constants k_1–k_7 and coefficient α were the same as in Eq. (7).

Analysis showed that, in the presence of oxygen, dienes weakly affected coke formation and that oxygen was strongly adsorbed on the coked catalyst surface and thus participated in chemical conversions of hydrocarbons, which occurred mainly on the formed condensation products.

With an increase in the concentration of oxygen, the rate of olefin and diene formation from higher paraffins decreased, and the rate of paraffin consumption was expressed by the following equation:

$$w = \frac{kP_1 - k'P_2P_{\mathrm{H}_2}}{P_{\mathrm{H}_2}^{1.5} + k_1P_2 + k_2P_3 + k_3(C - C_0) + k'_9P_{\mathrm{O}_2}^{0.5}}. \qquad (16)$$

Thus, the study of the deactivation of platinum–alumina catalysts in the dehydrogenation of lower and higher paraffins showed that the main reason for a decrease in their activity was coke formation. However, the regularities of coke formation depended on the size of molecules. In the dehydrogenation of lower paraffins, the main mass of coke was formed at the beginning of the reaction, whereas in the dehydrogenation of higher paraffins, coke formed more smoothly.

Excess hydrogen was necessary in the dehydrogenation of lower and higher paraffins to remove coke and stabilize platinum catalysts. The eightfold excess of hydrogen with respect to hydrocarbon was required in the dehydrogenation of higher paraffins, and the equimolar amounts of hydrogen and hydrocarbon were sufficient for the hydrogenation of lower paraffins. Here, the dual nature of hydrogen manifested itself: the wholesome effect of decreasing coke formation was to a greater or lesser extent surpassed by the detrimental kinetic factor.

The preliminary sulfuring of catalysts or the performance of dehydrogenation in the presence of small amounts of hydrogen sulfide favored the enhancement of catalyst activity.

The regularities of catalyst deactivation are an integral part of the general kinetic model that simulated the process and involved all possible conversions in steady-state and non-steady-state regimes. These regularities should be considered within the scope of the general mechanism of the given catalytic process.

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