KINETIC STUDIES OF CATALYST DEACTIVATION IN HETEROGENEOUS CATALYSIS (REVIEW)

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ABSTRACT

The solution of different problems concerning the catalyst deactivation is very essential for the optimal process design. In view of this, various aspects of the kinetics of processes accompanied by catalyst deactivation, in relation with different mechanism patterns are discussed in this paper. The deactivation functions derived are related to the surface concentrations of the intermediates and to the partial pressures of the gas reactants responsible. Different types of deactivation schemes are distinguished, leading to different evolution of the processes. The joint effects of catalyst deactivation and intraparticle resistance limitations are thoroughly analysed. Special attention is devoted to kinetic problems connected with the joint effects of catalyst deactivation and mass transfer on the selectivity of complex reactions proceeding via different mechanism patterns.

Keywords: catalyst deactivation, kinetics, mechanism, selectivity, diffusion resistance.

INTRODUCTION

One of the major problems related to the use of heterogeneous catalysts is the loss of catalyst activity and/or selectivity with time on stream. The changes provoked by the catalyst deactivation play a significant, although disadvantageous role for a large number of important industrial processes. Presently, there are no scientific approaches allowing catalyst deactivation to be entirely eliminated. The effort of researchers are directed at finding resources for reducing the harmful consequences from the deterioration of the catalyst activity and selectivity. In this connection, it is both of academic and manufacture interest more detailed knowledge on the kinetics of processes accompanied by catalyst deactivation, in correlation with the reaction mechanism.

It is widely recognised the classification suggested by Hughes [1] provisionally dividing the deactivation phenomena according to the reasons causing the loss of catalyst activity: (1) poisoning of catalysts by impurities present in the reaction mixture; (2) sintering of the catalyst; (3) changes in the catalyst activity provoked by formations which are a constituent part of the reaction mechanism. The consequences of impurity poisoning can be reduced by means of purification of the reaction mixture, which makes the problem rather technological than kinetic. The sintering (or thermal deactivation) generally takes place at high reaction temperatures (above 500°C), and results from loss of either catalytic surface area due to crystalline growth, or of support area due to support collapse. As far as temperature is the most important factor responsible for the class of thermal deactivation, the basic efforts for its prevention lie in establishing the reasonable optimal temperature regime of the process which would ensure satisfactory reaction rate, and avert drastic deterioration of the catalyst structure.
From kinetic point of view, it is of greatest interest examining the peculiarities of processes in which the deactivation effects are originating from interactions or species participating in the reaction mechanism. Generally, these effects can be specified as follows:

- Strong (sometimes irreversible) adsorption of initial reactants, or final products, or intermediate species that arise in the succession of elementary steps involved in the reaction mechanism. Some authors define these effects as “self-poisoning”. It is worth noting the essential difference of this type of deactivation effects from the effects originating from impurity poisoning. The point is that purification can make a good service for protecting from impurity poisoning, but hardly stave off self-poisoning, as far as the species responsible for the latter are integral participants of the process.

- Interactions of the reactants with some catalyst centers, resulting in changes of valency state, formation of undesired chemical formations, etc.

- Penetration through the surface layer or induced diffusion of the catalyst lattice components towards the catalyst surface.

- Blockage of the active catalyst sites, on the main by coke deposits.

Coke formation may be considered as the most common reason for catalyst deactivation. It is a widely recognised assumption that the generation of coke precursors is determining for the process of coke formation. From the standpoints of elucidating the correlation between the reaction mechanism and catalyst deactivation, it is of interest to focus on those cases where the formation of coke precursors is called forth by the interactions involved in the reaction mechanism. In view of this, the scheme suggested by Wolf and Petersen [2,3] is of key importance for understanding the principles of the applied approximations. According to this scheme, the mechanism of coking is specified as parallel in case the coke precursors originate from species or surface intermediates formed before the slow step of the basic reaction: while the series (consecutive) mechanism of coke formation is implemented when surface intermediates generated after the slow step give rise to coke precursors. There may also be interactions of intermediates of different type, which corresponds to a combined scheme of coking.

As regards the kinetic description of the influence of catalyst deactivation on the reaction performance, two common approaches are usually applied, namely, the “separable deactivation kinetics” [4, 5], and the “unseparable deactivation kinetics” [6]. In the model of “separable deactivation kinetics”, the rate of the entire process is expressed in the form of the product of the function of the initial rate on the fresh catalyst, and the function characterising the deactivation-caused change of the catalyst activity. The “unseparable deactivation” approach is based on the principle that there should be a correspondence between the kinetics of the basic reaction, the kinetics of generation of blocking agents (coke in particular), and the kinetics of deactivation. Such an approach is more strict, as far as it takes into account the correlation of deactivation with the mechanism of the overall process. On the other side, the “separable deactivation” approximation often appears more convenient for kinetic simulations. In this connection, we shall discuss below some of our works, based on applying of both these approaches.

**MECHANISTIC CONSIDERATIONS**

The general scheme of a reaction occuring on single catalyst sites may be presented as:

\[
A + Z \rightarrow [AZ] \rightarrow [MZ] \rightarrow M + Z \quad \text{slow}
\]

where A and M denote respectively the key initial reactant and the product, Z is an active site on the catalyst surface, [AZ] and [MZ] stand for surface intermediates formed before and after the slow step, correspondingly. In these terms, and denoting by (PZ) the coke precursor, the schemes of parallel and series coke formation specified by Wolf and Petersen may be presented as follows:

\[
[AZ] \rightarrow [PZ] \rightarrow coke \quad \text{(parallel)}
\]

\[
[MZ] \rightarrow [PZ] \rightarrow coke \quad \text{(series)}
\]

Usually coke formation is initialized by adsorption of gas feed species or product molecules on catalyst sites. The intermediates formed may further evolve
into coke precursors, which is often coupled with interactions with molecules from the gas phase. In view of this, the deactivation function should be linked to the surface concentrations of the intermediates as well as to the partial pressures of the gas reactants responsible. Following these considerations, we have extended [6, 7] the classification proposed by Wolf and Petersen, with the following typical mechanisms of generation of coke precursors:

\[ nA + [AZ] \rightarrow [PZ] \rightarrow coke \text{ (parallel-parallel)} \quad (4) \]

\[ nM + [AZ] \rightarrow [PZ] \rightarrow coke \text{ (parallel-consecutive)} \quad (5) \]

\[ nA + [MZ] \rightarrow [PZ] \rightarrow coke \text{ (series-parallel)} \quad (6) \]

\[ nM + [MZ] \rightarrow [PZ] \rightarrow coke \text{ (series-consecutive)} \quad (7) \]

Postulating that the limiting step is the formation of coke precursors, the various mechanisms distinguished for the formation of coke precursors assume feasible interactions of different surface intermediates with either initial reactants or products from the gas phase. When the coke precursors are generated after schemes (2) or (3), the kinetics of coke formation is related to the surface concentrations of the intermediate. In case schemes of the type (4)-(7) are realised, the kinetic description of deactivation is function of both the surface concentrations and the partial pressures of the involved participants. Following this approach, different types of deactivation schemes are distinguished, leading to different evolution of the processes. The deactivation kinetics is considered as a function of the surface concentrations of the intermediates and the partial pressures of the gas phase reactants responsible:

\[ \Phi = \Phi(P_j(x), \theta_i, \theta_i(t)) \]

x – extent of conversion (0 < x < 1);

\( P_j(x) \) – partial pressure of the j-th reactant, expressed as a function of conversion;

\( \theta_i \) – surface concentration of the i-th intermediate;

\( \theta_i(t) \) – surface concentration of the coke precursors.

Various deactivation models were derived on the basis of the mechanism specificity. The deactivation kinetics was related to the peculiarities of generation of the deactivating agents. Shown in Table 1 are the kinetic models corresponding to these simplest mechanisms of coke formation. The symbol \( \sigma \) stands for the fraction of unoccupied active sites. The expressions given in Table 1 for the rates of the basic reaction and for those of coke formation proceeding via different mechanisms correspond to the model of unseparable deactivation kinetics. The rates of coke formation obey different functional dependencies on the conversion for each particular case, in accordance with the mechanistic schemes. It follows from the formulae derived that the coke formation rate should be higher at higher conversions for the cases of parallel-consecutive and series-consecutive mechanism (e.g., when product from the gas phase participate in the generation of coke precursors), and lower at high conversion values if the coke formation follows some of the other schemes. Hence, the trend in the change of coke formation rate on increasing the conversion can indicate a type of coke formation mechanism.

**DEACTIVATION KINETICS AND INTRAPARTICLE DIFFUSION EFFECTS**

In case the process is occurring on catalyst grains of industrial size, one of the important problems is the influence of intraparticle diffusion resistance. Different aspects of the problem are highlighted in a series of interesting works, among which we would mention [1, 9-17]. As a rule, precautions are taken to avoid the diffusion restrictions, so far as the latter lower the reaction rate and the target yield. However, the situation is not so evident in regard of processes subject to catalyst deactivation. Actually, in the start of the process, the basic reaction rate is lower under diffusion control, but the intraparticle diffusion effects may substantially modify the catalyst deactivation dependencies. Depending on the mechanism peculiarities, the influence of diffusion may either increase, or decrease the effect of deactivation, evoking different after-effects. In a series of works [18-20], we have developed the concept that when modeling the deactivation kinetics of processes affected by intraparticle diffusion, it is reasonable to take into account not only the changes of the main reaction rate caused by mass transfer into the catalyst pores, but also the modifications of the rate of deactivation caused by diffusion resistance.
In view of clarifying the influence of diffusion restrictions, it is of use to derive the kinetic description in terms of conversion, as far as the intraparticle resistance predetermines lower conversion attained in the beginning of the process. Using as a first approximation the formula proposed by Pshezhtesky and Rubinstein, we express the reaction rates of the main and the deactivating reactions by a set of equations of the following form:

\[ r_d = \frac{\sqrt{2D_0 p_0}}{R} \int_{x_i}^{x_e} r_k(x)dx \]

**basic reaction under diffusion control**

\[ \Phi_d = \frac{\sqrt{2D_0 p_0}}{R} \int_{x_i}^{x_e} \Phi_k(x)dx \]

**deactivating reaction under diffusion control**

\( r_e \) – intrinsic rate of the basic reaction;

\( \Phi_k \) – rate of the deactivating reaction under kinetic control;

\( p_0 \) – initial partial pressure of the key reactant;

\( x_i \) – conversion at the surface of the catalyst grain;

\( x_{eq} \) – equilibrium conversion;

\( R \) – efficient grain radius.

On substituting for \( r_e \) and \( \Phi_k \) the rate expressions relevant to particular processes, the performance of these processes under conditions of diffusion control can be simulated.

The analysis of the deactivation-vs-conversion curves can be indicative whether the influence of deactivation on the rate and selectivity would be more sensitive at high or low conversions. Shown in Fig. 1 are curves for the dependence of deactivation functions on conversion calculated for model reactions proceeding under kinetic and diffusion control via parallel-parallel and parallel-consecutive deactivation schemes (Table 1), for reasonable values of the rate coefficients corresponding to the assumption that the rate of the slow step of the basic reaction is an order of magnitude lower than the rates of the fast steps; and an order of magnitude exceeding the rate of formation of coke precursors. As it is seen for the case of parallel-parallel scheme of coking, the deactivation function increases in the region of high conversions, the increase being more explicit under kinetic control. In the case of parallel-consecutive mechanism of coke formation, the curves of the deactivation rate would pass through an extremum in the kinetic region. Accordingly, the character of the deactivation-versus-conversion dependencies predetermines the evolution of the basic processes under kinetic or diffusion control. The plots on Fig. 2 show the simulated evolution of the total reaction rates in the absence and presence of diffusion restrictions. On performing the simulations, the size of the catalyst grains was considered to be the only factor determining the diffusion limitations.

As an example, we would refer to the analysis performed in regard of two important industrial processes, namely, hydrogenation of nitrobenzene to aniline over commercial Cu catalyst, and dehydrogenation of isoamylens into isoprene over a commercial calcium-nickel-phosphate catalyst.

![Fig. 1. Conversion curves of the rates in the kinetic (1) and diffusion (2) regions for model reactions proceeding via (a) parallel-parallel; (b) parallel-consecutive mechanism patterns.](image)

**Hydrogenation of nitrobenzene to aniline over commercial Cu catalyst:**

According to experimental data obtained [21] on small catalyst grains, the kinetic description of the process follows the approach of separable deactivation kinetics:

\[ r_e = \frac{k_e p_{nh} p_H}{1 + \alpha_e p_{nh}} \Phi_k(t) \]

**basic reaction rate under kinetic control:**

\[ \Phi_k(t) = 1 - K \left\{ \frac{p_{nh}}{P_H(t)} - \frac{p_{nh}}{P_H(t=0)} \right\} \]

**deactivation function under kinetic control.**
The deactivation function takes into account the observations that coke formation is enhanced for higher nitrobenzene concentrations, and slows down on raising the $H_2$ concentration. According to the supposed reaction scheme, $H_2$ from the gas phase joins successively the intermediates generated from adsorbed nitrobenzene. Parallel to this, the same intermediates may give rise to coke precursors.

On applying the modified formula of Pshiezhetsky and Rubinstein, the following relations were obtained in regard of the basic and deactivation rates under diffusion control:

$$r_{df} = \frac{kDP_\alpha}{R} \sqrt{\frac{P_{nb} - \beta \ln(1 + \alpha P_{nb})}{\alpha}} \Phi_{df}(t)$$

reaction rate under diffusion control;

$$\Phi_{df}(t) = 1 - \kappa \left\{ \frac{1 - (P_{nb})_t}{(P_{nb})_{t=0}} \right\}$$

deactivation function under diffusion control.

The experimental data obtained on catalyst grains of industrial size confirmed these relations with accuracy 11.8%.

In the kinetic region the deactivation is function of the partial pressures of both nitrobenzene and hydrogen, whereas in the region of diffusion control, it formally appears a function only of the nitrobenzene concentration. Because of their small sizes, hydrogen molecules are capable to penetrate into the catalyst pores more easily than the nitrobenzene molecules, and for this reason, the concentration gradient of hydrogen along the grain radius may be considered negligible against that of nitrobenzene. Correspondingly, the probability for formation of coke precursors along the catalyst grain radius will be dependent mainly on the rate of nitrobenzene diffusion, which on turn is proportional to its gas phase concentration.

This example shows how the diffusion resistance may modify the function of deactivation. As for duration of the catalyst exploitation, both simulation results and experimental observations indicate that the catalyst deterioration will be more appreciable under diffusion control.

**Dehydrogenation of isoamylenes into isoprene**

The situation is different when product molecules participate in the generation of coke precursors. It follows from the kinetic analysis that reduced rate of coke formation is to be expected at low conversions. Therefore, opposing effects may be expected under conditions of diffusion limitations: decrease in the basic reaction rate, lower conversion, and reduced rate of the deteriorating coking reaction. These counter effects can compensate each other. Moreover, under certain conditions, in the course of deactivation the process may come to a point when the current rate in the presence of diffusion restrictions even exceeds the rate in their presence. Such a conclusion has been experimentally confirmed for isoprene production processes commented below.

According to published experimental data [22] obtained on small catalyst grains:

$$r_k = \frac{kP_\alpha (1 - x)}{1 + Q + \alpha P_\alpha x}$$

basic reaction rate under kinetic control.
\[ \Phi_i = P_0 \left[ \frac{k_2 + k_1 x}{1 + Q + \alpha P_x} + \frac{k_4 + k_1 x}{1 + Q + \alpha P_x} \right] Q \exp(-\mu Q) \]

**Deactivation function**

\[ Q = C^{2/3} \]

\( C \) – coke deposited per gram-catalyst.

The coke formed in the course of this process is from the product (isoprene) and its adsorbed forms (series-consecutive mechanism). The concentration of coke precursors is related to the product concentration, which would be lower under diffusion control. The analysis performed brought to the conclusion that the deactivation process will be less pronounced under conditions of moderate diffusion limitations. Conditions could be found under which the slowed-down fouling countereffects the adverse effect of diffusion on the target reaction. In such a case, the process may come to a point when the rate of the catalytic reaction affected by diffusion resistance will be higher than the rate in the kinetic region.

To verify this suggestion, we applied the modified formula of Pshezhetsky and Rubinstein, to obtain the specific dependencies of the basic and deactivation reaction rates under diffusion control as explicit functions of conversion:

\[ r_{dif} = \frac{\sqrt{2D_1 P_0}}{R} \sqrt{\int_{x_i}^{x_{eq}} r_k(x)dx} \]

\[ \Phi_{dif} = \frac{\sqrt{2D_2 P_0}}{R} \sqrt{\int_{x_i}^{x_{eq}} \Phi_k(x)dx} \]

Applying these equations, we have simulated the process performance in a plug flow reactor packed with small or large catalyst pellets, for operating conditions close to those in industry (atmospheric pressure, \( T=953K \), initial partial pressure of isooamylene 0.248 atm, space velocity 500 h\(^{-1}\)). The results obtained show how the superposition of two opposite effects influences the process. Initially, the isoprene formation rate in the kinetic region considerably exceeds the rate of the reaction under diffusion control. However, the decrease of the reaction rate with time is smoother in the region of intraparticle resistance due to the diffusion-induced retardation of deactivation. As a result, at a given mo-

Some of the results calculated for values of the parameters \( D_1 = 0.004 \text{ cm}^2/\text{s} \), \( D_2 = 0.0001 \text{ cm}^2/\text{s} \), and sizes of the pellets 0.05 cm in the kinetic region against 1.5 cm in the region of diffusion resistance, are plotted in Fig. 3a. It can be seen from the calculated curves of conversion vs. time on stream shown that the drop of conversion is steeper in the kinetic region, and after some time, the conversion attained under diffusion control would exceed the conversion in the kinetic region. Such a prediction was confirmed by experimental results. The experimental curves obtained in a laboratory flow reactor are plotted in Fig. 3b.

**Some kinetic resources for optimization of the process design**

As is generally known, the deactivation problems impose that a considerable number of industrial processes affected by deterioration of the catalyst properties would be realised in cycles, each cycle consisting of a work period, \( \tau \), and a rest period, \( \tau_y \). It is obvious that the duration of \( \tau \) should be determined by the permissible range of activity decrease caused by coke formation. The plots in Fig. 4 show the increase of isoprene

![Fig. 3. Evolution of the extent of conversion (x) for the dehydrogenation of isooamylene in a flow reactor at 953 K under conditions of kinetic (——) and intraparticle diffusion (-----) control: (a) calculated curves for space velocity 250 h\(^{-1}\) and initial partial pressures 0.04 atm; (b) experimental curves of space velocity 500 h\(^{-1}\) and initial partial pressures 0.284 atm.](Image)
yield with time on stream for equal work periods of the catalyst under kinetic and diffusion control, i.e., \( \tau_k = \tau_d = 20 \text{ min} \); \( \tau_0 = 10 \text{ min} \). The calculated amount of coke deposited by the end of the work cycle was about 20 mg per gram catalyst in the kinetic region, and 12 mg per gram catalyst in the diffusion region. These results show a possibility of prolonging the useful working time of the catalyst, in case the work period is determined as the time of drop of the conversion below a certain value. Thus if the value of 20% is assumed to be the lower boundary of conversion, it would be reached for time \( \tau_k = 20 \text{ min} \) in the kinetic region, and in 60 min. time \( (\tau_d = 60 \text{ min}) \) under conditions of moderate diffusion resistance. The plots in Fig. 5 show the predicted increase with time of the isoprene yield in the kinetic and in the diffusion resistance regions under the suggested assumptions.

Evidently, for processes in which the product molecules from the gas phase are responsible participants in coke formation, it may turn out advantageous to lead the process on larger catalyst grains, in view of reducing the deterioration of catalyst activity. In cases when intraparticle diffusion resistance proves to be advantageous, this should be taken into account in the process design.

COKING PROFILES INSIDE THE CATALYST PORES

In addition, the analysis of the combined effects of catalyst deactivation and mass transfer should pay primary importance to the distribution of the coke deposits along the radius of the catalyst pellet. In view of the key contribution of surface intermediates to coke formation, when modeling the deactivation kinetics of processes occurring on large catalyst grains, it is correct to take into account not only the diffusion factors, but also the inherent distribution of surface intermediates along the radius of the catalyst pellet. Considering a single-ended pore, the kinetic description of the process includes a set of coupled non-linear differential equations relating the mass transfer and the deactivation kinetics with the particular position inside the catalyst grain [23].

Each of the mechanisms defined by (2)-(7), may bring to certain specificities in the profile of coke coverage inside the grain pores. In case the coke precursors arise through surface transformations of the intermediates of type [AZ], or by contribution of the feed species, the blocked fraction of the pores is most appreciable in the areas adjacent to the pellet surface. Deposition of coke at the entrance of the pores has an especially harmful influence on the catalyst activity, as long as the most efficient areas of the active surface come the first to be out of action. For these cases, it would be preferable to realise the process on small catalyst grains, in view of providing kinetic regime, thus avoiding the harm caused by the pore blockage. In case the coke precursors originate through surface transformations of intermediates of the type [MZ], the maximum of coke deposits is prognosed to lay near the core of the grain. In case interactions of surface intermediates with desorbed product molecules play a key role for the generation of coke precursors, the indications are that the deactivation function may be hump-shaped along the grain radius. In the

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Fig. 4. Calculated increase of isoprene yield with time under conditions of kinetic (-----) and intraparticle diffusion (-----) control for \( \tau_k = \tau_d = 20 \text{ min} \), \( \tau_0 = 10 \text{ min} \).

Fig. 5. Calculated increase of isoprene yield with time under conditions of kinetic (-----) and intraparticle diffusion (-----) control for \( \tau_k = 20 \text{ min} \), \( \tau_d = 60 \text{ min} \), \( \tau_0 = 10 \text{ min} \).
early, most productive stages of the process, the inner surface area adjacent to the pore mouth would be less affected by the coke formation process. Thus, the most efficient for the main reaction zone of the catalyst surface is expected to keep its activity in higher extent under diffusion control. In view of the optimal process design, it may be concluded that sizes of the catalyst pellets providing moderate diffusion limitations will hinder the deteriorative action of coking.

PROBLEMS OF SELECTIVITY

The problem appears still more complicated when the selectivity effects are to be considered. The influence of diffusion on selectivity, as well as selectivity changes caused by deactivation have been separately examined in numerous studies. Yet, little attention has been paid to the joint effects of mass transfer and coke formation on the selectivity of complex reactions. Here, we shall briefly touch their combined action in relation to the process mechanism.

From the standpoints of kinetics, the problem may be associated with the functional dependence of selectivity on conversion. The analysis performed [24] indicates that, depending on the reaction mechanism, the selectivity may either decrease or increase with the drop of conversion. In this respect, it is of use to examine the calculated curves of selectivity versus conversion, which we call “selectivity-conversion curves”. These curves have their specificity for different reaction schemes. In view of this, we distinguish three types of selectivity associated with the intimate mechanism:

**Fork selectivity type**: the primary intermediates undergo a succession of surface transformations, in the course of which two branching routes arise:

\[ A + Z \rightarrow [AZ] \rightarrow [\ldots] \rightarrow \overset{k_1}{\rightarrow} M + Z \quad \text{main reaction} \]

\[ A + [IZ] \rightarrow D + Z \quad \text{side reaction} \]

Generally, processes following this type of mechanism are characterised as isokinetic [25] both in the absence of deactivation and in case the coke precursors are formed as a result of the interaction of the side product with surface intermediates or free catalyst sites. In case the coke precursors arise from the interaction of the initial species with surface intermediates, it follows from the analysis performed in [24] that the selectivity would slightly decrease with the drop of conversion. As regards the case when coke precursors come into existence after the interaction of the desired product with either free catalyst sites or sites occupied by intermediates, the indications are that the selectivity should increase in the course of deactivation.

**Competitive-parallel selectivity type**: the formation of the desired and the side products is realised as if through competing interactions of the initial species with free catalyst sites or some of the intermediates, respectively:

\[ A + Z \rightarrow [AZ] \rightarrow [IZ] \rightarrow [MZ] \rightarrow M + Z \quad \text{main reaction} \]

\[ A + [IZ] \rightarrow D + Z \quad \text{side reaction} \]

The kinetic calculations performed for values of \( k_1 \) comparable to \( k_1 \) predict that the selectivity should exert lower values at low conversion. The harm caused by the catalyst deactivation on the total yield is supposed to gain in strength because of the decrease of selectivity. This effect is more pronounced when the molecules of the main product are engaged in the formation of coke precursors. The analysis of the theoretical selectivity-conversion curves indicates that the decrease of selectivity with conversion should be more appreciable in the kinetic region, and less considerable under diffusion control. Thus, on leading the process on small catalyst grains, the total conversion is initially high, but drops more abruptly with time; on the other hand, the selectivity is expected to be lower and to fall appreciably in the course of deactivation. In the presence of moderate intraparticle resistance, by contrast, initially the total conversion is lower, but exerts smoother decrease. The selectivity is higher and remains hardly changed with the drop of conversion. In consequence, depending on the operation parameters, it may turn out advantageous to carry out processes of this type on pellets of size providing moderate diffusion limitations.

**Consecutive selectivity type**: the side product comes into existence through interactions of surface intermediates with desorbed molecules of the target product.
A+Z $\rightarrow$ [AZ] $\rightarrow$ [IZ] $\rightarrow$ [MZ] $\rightarrow$ M+Z  

main reaction

$k_i$

$M + [IZ] \rightarrow D + Z$  

side reaction

The selectivity is to be lower for higher extents of conversion, as far as high concentrations of the product will enhance the side reaction. The analysis of the selectivity-conversion curves calculated for $k_i$ comparable to $k_i$ indicates that the increase of selectivity with the fall of conversion is more strongly expressed in the absence of intraparticle resistance. Thus, the selectivity is expected to increase in the course of deactivation, and this tendency is more appreciable in the kinetic region. Conformably, the target yield will be influenced by two opposing factors: the delay of the reaction rate, and the increase of selectivity. The effects are more noticeable under kinetic control. The more intense raise of selectivity in the course of the reaction is to overcompensate the effect of more intense fall of the total conversion. Hence, it seems more advantageous to realize processes of such type on catalyst grains of smaller size, preventing the diffusion effects.

**CONCLUSIONS**

On deriving the kinetic models of processes accompanied by catalyst deactivation, particular attention should be paid to correlating the kinetics and selectivity with the intimate reaction mechanism. Knowing the relation between the process mechanism and catalyst deactivation, one can prognose more successfully the behaviour of the reaction system under different operation conditions. The catalyst deactivation may follow different kinetics according to the mechanism of blockage of active sites. It should be not skipped from consideration that in many processes the formation of the blocking agents is a constituent part of the reaction mechanism. The deactivation kinetics is linked to the peculiarities of generation of the deactivating agents. Assuming that the limiting step is the formation of coke precursors, various mechanisms are distinguished for the formation of coke precursors assuming feasible interactions of different surface intermediates with either initial reactants or products from the gas phase. The deactivation kinetics is considered as a function of the surface concentrations of the intermediates and the partial pressures of the gas phase reactants responsible. When modeling the deactivation kinetics of processes affected by intraparticle diffusion, it is reasonable to take into account not only the changes of the main reaction rate caused by mass transfer into the catalyst pores, but also the modifications of the rate of deactivation caused by diffusion resistance. The analysis performed indicates that for a number of processes, the deactivation-caused drop of the basic reaction rate will be less appreciable under diffusion control. The superposition of the op-
posing effects may bring to their mutual compensation. Moreover, for certain reaction mechanisms, there exists a domain of operation conditions where the effective rate of the process under diffusion control may even exceed the rate in the kinetic region. A particular approach is devoted to modelling the distribution of coke deposits along the radius of the catalyst grain, depending on the mechanism of their generation. Calculations considering the changes in selectivity of processes accompanied by catalyst deactivation indicate that under the action of deactivation, the selectivity may either decrease or increase, depending on the reaction mechanism. The changes are expected to be more appreciable in the absence of intraparticle diffusion.

The kinetic predictions may serve practical use with respect to elucidating the resources for reducing the harmful effect of deactivation on the yield of the target products.

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