

SOME PROBLEMS OF REACTION KINETICS AND MECHANISMS OVER DECAYING CATALYSTS

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Received July 1, 1992

Accepted July 28, 1992

Dedicated to Dr Miloš Kraus on the occasion of his 65th birthday.

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In this review, recent investigations by the authors of certain aspects of the kinetics of processes accompanied by catalyst deactivation are summarized. Correlation of the data with reaction mechanism is discussed.

1. INTRODUCTION

The development of the theory of catalysis is to a great extent connected with the solution of kinetic problems. Of great interest is the kinetics of processes accompanied by catalyst deactivation, in correlation with the reaction mechanisms. These aspects are discussed in the present paper, based on our recent investigations concerning this problem.

2. CORRELATION BETWEEN DEACTIVATION KINETICS AND REACTION MECHANISMS

As is generally known, the changes of catalyst activity in the course of the process may be caused, on the main, by the following types of interactions:

1) Strong and irreversible adsorption of some reactants, removing thus from the reaction the occupied active sites of the catalyst surface.

2) Interaction of either the reactants or impurities with some catalyst centres, resulting in the formation of undesired chemical compounds, changes of valency state, etc.

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

4) Formation of coke precursors blocking the catalyst surface.

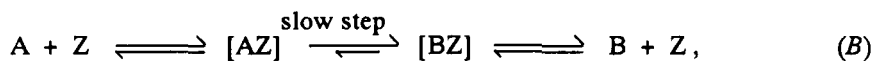
Interactions of types 1 and 2 are not directly associated with the mechanism of the catalytic process, although they may exert indirect influence upon it. Thus, the catalytic action may be diverted into another trend resulting in the formation of different chemical compounds such as oxides, carbides, sulfides, halogenides, etc. Interactions of types 3 and 4 are directly connected with the reaction mechanisms, and the nature of deactivation should be considered as a constituent part of the process scheme. By way of example of type 3 we shall refer to the "deep" oxygen adsorption over silver catalyst¹ or to the diffusion of the lattice oxygen in chromia catalyst towards the catalyst surface^{2,3}.

Coke formation may be considered as the most common reason for catalyst deactivation. We shall not consider here the cases when the coke precursors arise from mixture impurities, since then coke formation is not connected with the reaction mechanisms. From the standpoint of elucidating the correlation between the reaction mechanisms and catalysts deactivation⁴, it is much more of interest to draw attention to those cases where the formation of coke precursors appears to be an integral part of the catalyst process as a whole. Such types of deactivation are defined by some authors as the self-poisoning.

For the sake of simplicity, let us denote the catalytic reaction as

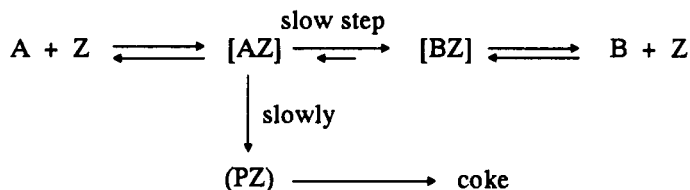


where Z stands for an active catalyst site. Froment and Bischoff⁶ proposed to classify the accompanying deactivation reaction as parallel, when the coke deposits are formed from the reactant A, or as consecutive, when the coke deposits are formed from the product B. Furthermore, Wolf and Petersen^{9,10} related the model to a more detailed mechanism considering a certain sequence of elementary steps:



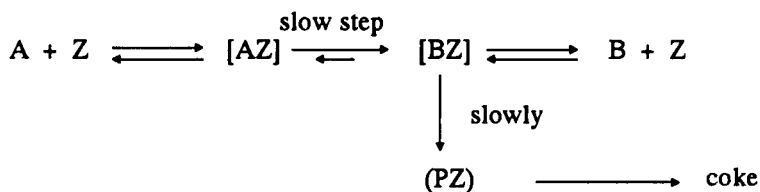
where [AZ] denotes the adsorbed reactant, [BZ] the adsorbed product. When the process is accompanied by formation of deactivating agents, the parallel and consecutive poisoning may be represented after Wolf and Petersen⁹ by the following schemes:

Parallel poisoning



SCHEME 1

Consecutive poisoning



SCHEME 2

(PZ) denotes the poison precursor.

After these models, parallel poisoning takes place in case the coke precursors arise from the intermediates formed before the slow step. In case the coke precursors arise from intermediates formed after the rate determining step, the deactivation mechanisms is considered as consecutive poisoning.

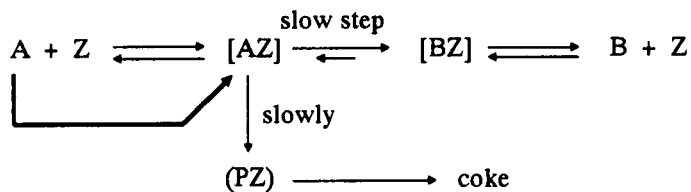
In the processes following Schemes 1 and 2, coke formation depends on the reaction ability of the intermediates and the strength of their bonds with the catalyst surface. In this connection, the following general rule may be defined:

The introduction of additives which weaken the bonds of the catalyst surface with the intermediates, thus increasing their reactivity, results in decreased coke formation.

The above statement is supported by experimental findings given in several works⁵⁻⁷.

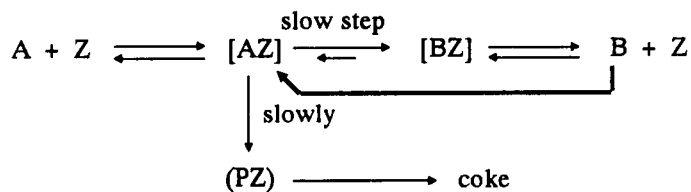
In general, it is necessary to consider the fact that coke precursors often come to existence as a result of the interaction between reactants from the gas phase and reaction intermediates. Therefore, it is reasonable to extend⁴ the latter classification, including as a first approximation the following schemes:

Parallel-parallel



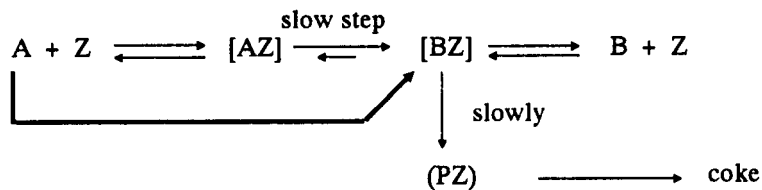
SCHEME 3

Parallel-consecutive



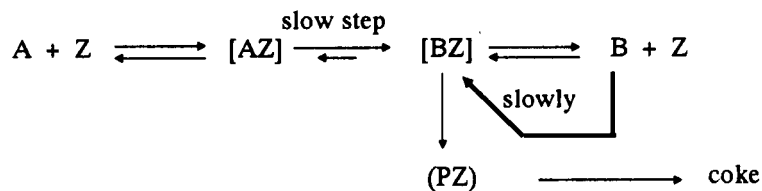
SCHEME 4

Consecutive-parallel



SCHEME 5

Consecutive-consecutive



SCHEME 6

The bold lines in Schemes 3 – 6 indicate that the marked species react from the gas phase with the pointed intermediates to form coke precursors. In the lack of such interactions Schemes 3 and 4 come to Scheme 1, and Schemes 5 and 6 to Scheme 2.

The analysis of Schemes 1 – 6 leads to the following obvious conclusion: Coke formation is closely connected with the power of the bonds of the responsible intermediates with the catalyst surface, on the one hand, and the reaction mechanism, on the other. Lability of bonds reduces the probability for coke precursors to come into existence. Tight bonds between the catalyst surface and the intermediates favour the formation of carbon deposits.

In the main, the assertion started remains effective on substituting more complicated reaction models for Eq. (A).

The introduction of Schemes 3 – 6 provides a good service in understanding the influence of diffusion on deactivation kinetics. We shall go into more details about it a little later.

3. KINETIC DESCRIPTIONS

Two common approaches are usually to consider the influence of catalyst deactivation on the reaction kinetics, namely, the "separable deactivation kinetics"^{11,12} and the "unseparable deactivation kinetics"¹³. The "unseparable deactivation" approach is more strict, as far as it takes into account the correlation of deactivation with the kinetics and mechanisms of the basic reaction. On the other side, the "separable deactivation" approximation often appears much more convenient for kinetic simulations. In this connection, we shall discuss some of our works, where these approaches have been applied.

The kinetics and mechanism of the dehydrogenation of low paraffins over modified platina–alumina catalyst were studied^{5 - 7} both under stationary and nonstationary conditions. In particular, the rates (r) of dehydrogenation of both isobutane and propane can be described by kinetic equations of the type:

$$r = \frac{k P_1 \gamma}{P_1 + k' P_2 + K(C - C_0)}, \quad (1)$$

where P_1 and P_2 stand for the partial pressures of the initial paraffin and the product, γ is a coefficient considering the reaction reversibility, C is the surface concentration of coke, C_0 is its threshold value, for which drop of conversion is observed. The coefficient k' considers the strength of adsorption of the olefin, k is the rate constant. The rate determining step is the dissociative adsorption of the paraffin, characterized by the coefficient k . The experimental data, obtained for catalysts with different modifying additives, can be described by the same equation, using different values of the coefficients, correspondingly. Coke arises mainly from olefin products. It is important to

note, that the optimal modifying additives (Sn and In) produce the lowest deposits of coke. Besides, the coefficient k' exhibits lowest values for the equations describing the processes over catalysts with these additives, which indicates that they weaken the olefin intermediate bonds with the catalyst surface. The introduction of additives which are less effective results in lower reaction rates, and thus higher k' values as well as in increase of coke formation rate.

Therefore, Eq. (1) may be considered as a typical example of a correlation arising from the concepts of unseparable deactivation kinetics. The kinetic description of coke formation proposed⁵⁻⁷ is coincident with the basic reaction mechanism as well.

By way of example of kinetic description following the approach of separable deactivation kinetics, we shall analyze the hydrogenation of nitrobenzene to aniline over commercial copper catalyst¹⁴. The catalyst undergoes deactivation due to coke formation. After the quasistationary approximation, the reaction rate r_k in the kinetic region may be described by the equation:

$$r_k = \frac{k_1 P_{nb} P_H}{1 + k_2 P_{nb}} \Phi_k(t) , \quad (2)$$

where P_{nb} and P_H are the current partial pressures of nitrobenzene and hydrogen, Φ_k is the function describing the catalyst deactivation:

$$\Phi_k(t) = 1 - K [P_{nb}/P_H - (P_{nb}/P_H)_0] . \quad (3)$$

The "0" denotes the initial values.

The form of the deactivation function takes into account the fact that the coke formation is enhanced for higher partial pressures of nitrobenzene, and decreases on raising the hydrogen concentration*. Such a dependence may be explained in agreement with the process mechanism. According to the supposed reaction scheme, hydrogen from the gas phase joins successively the intermediates formed from the adsorbed nitrobenzene. Parallel to it, there takes place formation of coke precursors from the same intermediates. In the absence of deactivation in an open system, $(P_{nb}/P_H)^t = (P_{nb}/P_H)_0$, $\Phi = 1$, and the kinetic description comes to the equation for the reaction rate on the fresh catalyst. In that way, such a kinetic model, although not directly arising from the

* Unfortunately, a misprint has appeared in Eqs (6) - (12) of our work¹⁴ in which the ratios (P_H/P_{nb}) should be read as (P_{nb}/P_H) .

reaction mechanism, is nevertheless to a great extent coincident with its main assumptions.

On specifying the requirements for choosing the right approach, some authors^{15,16} suppose that the "separable deactivation kinetics" is applicable to the assumption of ideal adsorbed layer (coincident to catalyst surface uniformity), while the "unseparable deactivation kinetics" is more proper for the cases considering real adsorbed layer (what answers to the catalyst surface with either intrinsic or induced nonuniformity). We find no reasonable grounds for such a delimitation, the more so that energetically nonuniform catalyst surfaces may react as quasiuniform^{17,18}. When the widespread linear relation is realized for different parts of a nonuniform catalyst surface, the reaction rate characterizing different parts may keep the same, due to compensation effects from changes in the energies of activation and adsorption. The choice between "separable" or "unseparable" deactivation kinetics should be determined by the ability of the selected method to correlate the deactivation process with the reaction mechanism.

4. DIFFUSION EFFECTS IN PROCESSES ACCOMPANIED BY CATALYST DEACTIVATION

A valuable contribution to the insight into those problems is introduced by a series of works^{19 - 26}. The latest review by Krishna²⁷ is specially devoted to diffusion influence on catalyst deactivation. Here, we shall focus on some of our investigations concerning aspects of the problem to which little attention has been paid by the other authors.

It is generally accepted that intraparticle diffusion is disadvantageous for catalytic processes realized on industrial pellets, so far as the diffusion resistance lowers the reaction rate. Nevertheless, the situation may differ when the process is subject to catalyst deactivation. When modelling the processes accompanied by catalyst deactivation under industrial conditions, three interconnected factors should be considered:

- 1) Changes of the main reaction rate caused by mass transfer into pores of the catalyst grains.
- 2) Modifications of the rate of deactivation caused by diffusion restrictions.
- 3) The diffusion-modified deactivation influence on the basic process.

When analyzing the relations between the above effects, we showed^{29,30} that their superposition may bring to mutual compensation. Moreover, there exists a domain of operation conditions where the effective rate of the process under diffusion control may even exceed the rate of the process in the kinetic region. Calculations confirming this conclusion were carried out first²⁹ for a model reaction of the type $A \leftrightarrow B$, and thereupon^{30 - 32} for reactions of industrial importance.

Besides the rate of coke formation, particular attention should be paid to the formation of coke deposits along the pellet radius. In this connection, we should like to correlate the peculiarities of coke disposals with the schemes of coke precursors formation mentioned above.

For Schemes 1 and 3, the most logical conclusion seems to be that the concentration of coke precursors is directly related to the concentration of the initial reactant A. As

far as a concentration gradient of A is available, it is expected that depending on the adsorption affinity of A for the catalyst, coke will deposit either near the pore opening, or uniformly throughout the pore length.

Deposition of coke precursors near the pore opening is especially disadvantageous for a long-term catalyst use in case the coke molecules grow in the form of dendrites hampering mass transfer to the fresh catalyst inside the pore. In this connection, Beeckman and Froment^{33,34} defined the probability $\varphi(t)$ that a given catalyst site remains active at moment t as:

$$\varphi(t) = P(t) \psi(t), \quad (4)$$

where $P(t)$ is the probability that the site is accesible, and $\psi(t)$ is the conditional probability that the site is not poisoned.

However, some authors (e.g. Zhorov²⁸) claim that coke is mainly friably structured, which allows the access of reactants to the inside of the catalyst pellet.

On the other hand, it may be expected that coke depositions near the pore opening besides deteriorations in the main reaction rate may modify the deactivation kinetics as well.

Further, we shall consider the reaction of nitrobenzene hydrogenation on copper catalyst. As mentioned above, the kinetics of the process on small catalyst grains is described by Eqs (2) and (3), in accordance with Schemes 1 and 3. When the process is carried out on large industrial grains, it is affected by intraparticle resistance, and the kinetic description takes the form:

$$r_{\text{dif}} = \frac{k_1 \sqrt{D}}{R_{\text{eff}}} \sqrt{P_{\text{H}} [P_{\text{nb}} - k_3 \ln(1 + k_2 P_{\text{nb}})]} \Phi_{\text{dif}}(t), \quad (5)$$

where D is the diffusion coefficient, R_{eff} is the effective pellet radius, and the function

$$\Phi_{\text{dif}}(t) = 1 - K [1 - P_{\text{nb}}/(P_{\text{nb}})_0] \quad (6)$$

describes the changes in the catalyst activity.

Comparing the deactivation model in the kinetic region (3) with that for the diffusion region (6), one can see the essential difference. The deactivation in the kinetic region is a function of the partial pressures of nitrobenzene and hydrogen, whereas in the diffusion region, it is formally a function only of the nitrobenzene partial pressure. A possible explanation of this fact is associated with the reaction scheme supposing parallel-parallel mechanism of catalyst blockage. After this model, it is expected in the

kinetic region that the concentration of the surface intermediates responsible for formation of coke precursors, will be dependent on partial pressures of both nitrobenzene and hydrogen. The situation is different in the presence of moderate diffusion limitations. Because of their small sizes, hydrogen molecules are capable to penetrate into pores of the catalyst grain more easily than nitrobenzene molecules. That is why the concentration gradient of hydrogen along the pellet radius is negligible against that of nitrobenzene. In view of this, the concentration of the coke precursors inside the pellet will be dependent mainly on the rate of nitrobenzene diffusion which is proportional to its gasphase 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.

As regards the deactivations following Schemes 2, 4, 5, and 6, the surface concentration of coke precursors is proportional to partial pressures of the gas products and to the surface concentrations of their intermediates. So far as the gradient of product concentration falls towards the pellet external surface it is quite probable that coke precursors will arise mostly inside the pellet, and the coke front will move in the course of the process towards the pellet surface. The experimental confirmation of such dynamics of coke deposition has been adduced by Japanese authors³⁵. It may be expected that moderate diffusion resistance may reduce deteriorative influence of coke on the apparent catalytic activity, thanks to the fact that the areas near the pellet surface will remain longer unpoisoned.

The notion exposed proved effective to explain the results following from the analysis of the kinetics of the hydrogenation of isoamylenes to isoprene over a commercial nickel-calcium-phosphate catalyst. Using the kinetic data obtained^{36,37}, we simulated³⁰ the process both under kinetic and diffusion control. The factor governing the region was supposed to be the size of catalyst pellets, the other operating conditions being kept the same. The calculations indicate that the decrease of the reaction rate with time is smoother in the diffusion region. As a result, regardless of the initial diffusion-caused retardation of the reaction rate, after a certain period of time, the effective rate of the process under diffusion control will exceed the rate in the kinetic region. On the other hand, the lower rate of the catalyst deactivation in the diffusion region could prolong the operation time of the catalyst. Experimental verification of these results is given elsewhere^{31,32}.

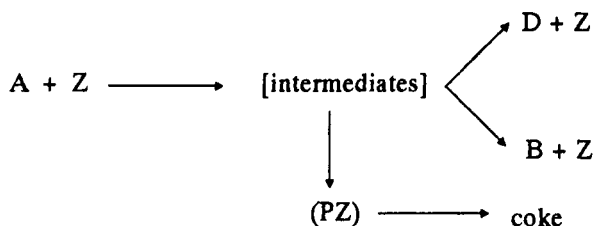
Similar results were obtained for the isoprene production by catalytic decomposition of dimethyldioxane over a calcium phosphate catalyst. The process is also exposed to catalyst deactivation due to coke formation. The concentration of coke precursors is related to the product concentration, in agreement with the mechanism of consecutive deactivation. Experimental observations supported the theoretical prediction that the

effective rate of the process affected by diffusion resistance becomes at a given moment higher than the rate in the kinetic region.

5. JOINT EFFECTS IN SELECTIVITY

Selectivity is closely associated with the characteristics of the reaction system and process mechanism. The influence of diffusion on selectivity, as well as selectivity changes caused by deactivation have been separately studied in detail. 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 focus on their combined action in relation to the process mechanism. Some of our considerations on this point were briefly reported³⁹.

As a first approximation, one can take the simple scheme:



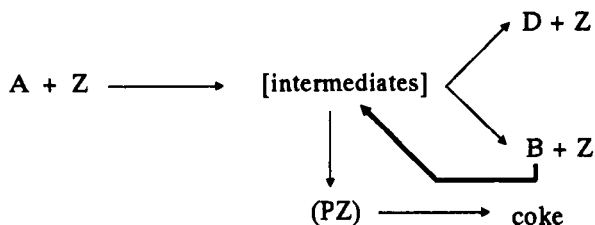
SCHEME 7

where B denotes the desired product, D the side product and (PZ) the coke precursors. Different mechanisms for the formation of each of the products may be realized. The different mechanisms are characterized by different kinetic descriptions and relations of the basic and the side reactions.

In accordance with the concept considered earlier³⁸, we interpret selectivity as the ratio between the rate of the desired reaction and the total rate of conversion of the initial reactants.

Kinetic expressions relating selectivity to conversion were derived³⁹ for various types of reaction schemes. The analysis of such functions can provide useful information about the variation of selectivity in the course of deactivation, under kinetic or diffusion control. The simulation results indicate that selectivities connected with different mechanisms may either decrease or increase with the drop of total conversion. In view of this, calculations were carried out for the various reaction schemes to elucidate how the conversion into the desired product is to change in the course of deactivation in the absence and presence of diffusion limitations. As far as for certain mechanisms the selectivity increases with the decreasing total conversion, the combined influence of diffusion resistance and deactivation may bring the process to a point where the conversion into desired product attained under diffusion control will exceed the corresponding "desired" conversion in the kinetic region.

As an example, we shall consider a model reaction following Scheme 8:



SCHEME 8

According to the Scheme 8, coke precursors arise on interaction between the desired product from the gas phase and the intermediates. Such a scheme is quite feasible and may model, say, the process of dehydrogenation of isoamylenes to isoprene on a commercial phosphate catalyst accompanied by both cracking and coke formation⁴⁰. It follows from the analysis of the selectivity function that the selectivity increases with the drop of conversion both in the absence and presence of diffusion restrictions, keeping, however, the higher values in the diffusion region. On the other hand, moderate diffusion may reduce the harmful effect of deactivation, on the account of the higher selectivity. This gives ground for conclusion that the intraparticle resistance may appear advantageous for some types of complicated reactions over decaying catalysts, from the standpoint of increasing the extent of conversion into desired products.

6. CONCLUSIONS

Knowing the relation between the process mechanism and catalyst deactivation, one can model more successfully the behaviour of the reaction system under kinetic or diffusion control. The considerations stated show the importance of examining the joint effects of catalyst poisoning and resistance to mass transfer into the pores of the catalyst with regard to both the changes in the process rate and selectivity. In addition, peculiarities of the changes predicted are closely connected with the mechanism of the main and side reactions. It emerges from the analysis performed that in certain cases the diffusion resistance may prove advantageous in view of reducing the harmful influence of deactivation, on the one hand, and enhancing the selectivity, on the other. Some of these conclusions were supported by experimental results. It can be expected that extending the approach on other reaction systems may contribute to the optimal process design. In particular, the more careful study of the possibilities of practical application which make use of the favourable effect of diffusion resistance on the selectivity of the process seems promising. Further analysis of these problems is closely connected both with the theory of catalysis and the optimisation of process design.

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