REACTION MECHANISM AND DEACTIVATION MODES OF HETEROGENEOUS CATALYTIC SYSTEMS

Krassimira KUMBILIEVA* and Lachezar PETROV

Institute of Catalysis, Bulgarian Academy of Sciences, ul."Acad.G.Bonchev" block 11, Sofia 1113, Bulgaria

The peculiarities of catalyst deactivation effects are discussed in association with the mechanism of their origin. The harm caused by impurity poisoning can be controlled by means of feed purification, but the problems become much more complicated when the changes in the catalyst performance are provoked by interactions of species which are a constituent part of the basic process. In these cases, the kinetics of the basic reaction and the deactivation regularities, especially those concerning the generation of deactivating agents (coke) are mutually dependent. The most commonly observed modes of activity changes – sharp drop in the beginning of the process; or smooth decrease; or stepwise character of the catalyst deactivation – are associated with causal mechanistic specificities. Accordingly, the deactivation kinetics is not unique within the entire conversion interval. Deeper knowledge on the mechanism of catalyst deactivation can be helpful for finding kinetic resources for reducing the harmful consequences. Different aspects of these problems are discussed.

INTRODUCTION

One of the major problems related to the use of heterogeneous catalysts is the decrease of the catalyst productivity in the course of the process. The deactivation effects appreciably influence the entire reaction network of the majority of catalytic systems; nonetheless, the deactivation kinetics is poorly studied. The early studies described the drop of catalytic activity as a function of time on stream; but descriptions of that type are empirical. Different phenomena of chemical or physical nature provoke deactivation effects: accordingly, sintering, impurity poisoning, and site-blockage deactivation phenomena are distinguished.[1] The first two types of deactivation can be studied separately from the mechanism of the target reaction, as far as sintering depends on temperature, and impurity poisoning can be controlled by means of feed purification. The problems become much more complicated when the changes in the catalyst performance are provoked by interactions of species which are a constituent part of the entire process. In these cases, referred as self-poisoning,[2] the catalyst deactivation cannot be eliminated, but knowledge on the mechanism of the deactivating phenomena and their relation to the overall kinetics can reveal resources for reducing the harm from deactivation.

The most widespread type of deactivation is caused by coke, and Froment[3] suggested to correlate the decay of the catalyst activity with the amount of deposited coke. Following this approach, a variety of models have been derived, most of which cover the approximation of separable deactivation kinetics.[3,4] The approach of "inseparable deactivation kinetics"[5] envisages mutual correspondence between the mechanism of the main and deactivation reactions. Another essential approach was that suggested by Beeckman and Froment[6,7] rendering the fraction of active sites $\varphi(t)$ as the product of the probability $P(t)$ that a site is accessible, and the conditional probability $S(t)$ that the site is not covered at time t:

$$\varphi(t) = P(t)S(t) \qquad (1)$$

Through the suggested discussion, the authors would like to focus on the correlation of commonly observed modes of activity changes, on the one hand, and the models applicable to describe

* Corresponding author: kumbilie@ic.bas.bg; kumbilie@bas.bg; kumbilieva@yahoo.com

different cases of catalyst deactivation, on the other, with causal mechanistic specificities.

RESULTS AND DISCUSSION

The catalyst deactivation may follow different kinetics according to the mechanism of blockage of active sites. Accordingly, the changes of the reaction performance may follow different regularities, *e.g.* sharp drop in the beginning of the process; or smooth decrease; or stepwise character of the catalyst deactivation. When the deactivation is called forth by carbon depositions, the generation of coke precursors is as a rule the slow step, determining for the deactivation kinetics.

Separable deactivation kinetics

The models covering the approximation of separable deactivation kinetics[3,4] express the reaction rate as the product of the initial reaction rate r_0 and the deactivation function $\phi(u)$ where u may stand for time on stream t, or extent of conversion x, or amount of coke C, etc. Strictly speaking, this approximation does not require correspondence between the apparent rate of the process and the mechanism of deactivation.

Nonetheless, observations and models concerning the particular processes differ by the types of the relevant "deactivation function", which points to different mechanism patterns responsible. Different expressions can be derived to describe the deactivation function $\phi(u)$, depending on the mechanism. Thus, some of the most common mechanistic types of deactivation may be described in terms of the extent of conversion (x) as follows:

$\phi(x) = 1 - \beta\sqrt{x}$ deactivation through dissociative adsorption;

$\phi(x) = 1 - \beta x$ deactivation through one-center adsorption;

$\phi(x) = 1 - \beta x^2$ deactivation through two-center adsorption;

$\phi(x) = \exp(-\beta x)$ deactivation by product adsorption on exponentially inhomogeneous surfaces;

In case diffusion restrictions are governing the process, the apparent deactivation law $\phi(x)$ may be expressed as a linear function.

Considering that most often deactivation is caused by blockage of active sites, it is reasonable as well to describe the deactivation function in terms of the surface concentration of the sites put out of action (θ_c). In the most common cases,

$$\phi(\theta_c) = \exp(\varepsilon\theta_c), \tag{2}$$

$$\text{or } \phi(\theta_c) = \xi(1 - \theta_c)^n, \text{ for n = 0.5; 1; 2}, \text{ depending on the mechanism pattern} \tag{3}$$

For $n = 1$, the activity drop versus θ_c would be linear, abrupt or steep, depending on the strength of sites eliminated. For n=2 and not very high values of ξ the deactivation may manifest a stepwise character – being initially negligible, and become apparent only after attaining a critical value θ_c^* of the blocked fraction of active sites.

By way of example of a concrete model following the approach of separable deactivation kinetics, we shall quote the hydrogenation of

nitrobenzene into aniline over commercial Cu catalyst.[8] We have proved the following dependency for the intrinsic reaction rate r_k:

$$r_k = \frac{k_1 P_{nb}(t) P_H(t)}{1 + k_2 P_{nb}(t)} . \phi_k(t) \tag{4}$$

$\phi_k(t)$ is the function describing the deactivation caused by coke generated from nitrobenzene:

$$\phi_k(t) = 1 - K\left[P_{nb}(t)/P_H(t) - P_{nb}(t_0)/P_H(t_0)\right] \tag{5}$$

$P_{nb}(t_0), P_H(t_o), P_{nb}(t)$, and $P_H(t)$ stand for the initial and current concentrations of nitrobenzene and H_2, correspondingly. This dependence is in agreement with the mechanism. According to the suggested reaction scheme, hydrogen from the gas phase joins successively intermediates formed from the adsorbed nitrobenzene; parallel to it, there takes place the coke formation from the same

intermediates. The deactivation function takes into account the fact that coke formation is enhanced for higher nitrobenzene concentrations, and decreases on raising the hydrogen concentration. Such a kinetic model, although not directly arising from the reaction mechanism, is nevertheless coincident with its main assumptions. In view of the above-stated, one can see that separable

deactivation kinetic models can also reflect in one way or another the mechanism peculiarities.

Non-separable deactivation kinetics

The non-separable deactivation approach is more strict, as far as it takes into account the correlation of deactivation with the kinetics and mechanism of the basic process, and the origin of sources of deactivation. Shown in Table 1 are the kinetic models derived[9] for some typical mechanisms of coke formation accompanying a simple reaction occurring on single catalyst sites after the general scheme:

$$A + Z \longrightarrow [AZ] \longrightarrow [BZ] \longrightarrow M + Z \quad (6)$$
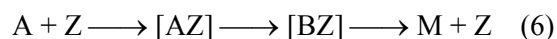
The models developed[9-11] assume that intermediates may further evolve into coke precursors, which is often coupled with interactions with gas phase molecules. Accordingly, the deactivation kinetics would be a function of the partial pressures P_j of the responsible reactants, the surface concentrations of intermediates (θ_i) and the coke precursors (θ_c):

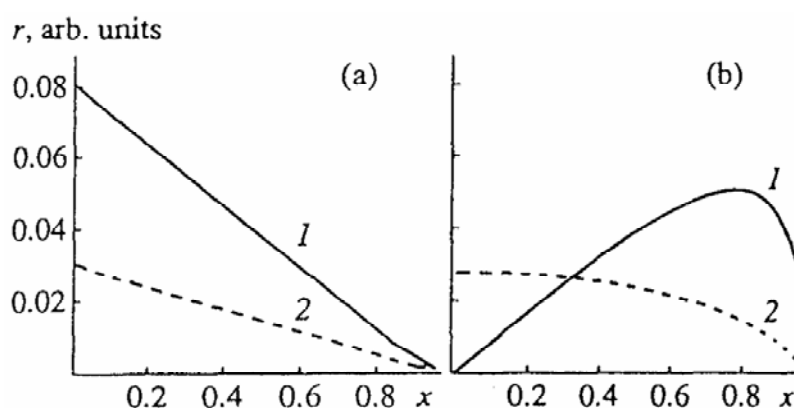$$\Phi = \Phi(P_j(x)\,\theta_i, \theta_c(t)). \quad (7)$$

Fig. 1 – Reaction rate conversion curves under kinetic (1) and diffusion (2) control prognosed for model reactions proceeding via parallel-parallel (a) and parallel-series (b) mechanism patterns.

Assuming various feasible interactions of different surface intermediates with initial reactants or products from the gas phase responsible for the generation of coke precursors, different types of deactivation are distinguished, leading to different evolution of the process. Thus the deactivation kinetics can be related to the mechanism of generation of the deactivating agents. The analysis performed showed that even for such a simple reaction the variety of deactivation regularities can be appreciable. In addition, the mode of drop of the catalyst performance may be different in the presence and absence of diffusion limitations. The plots in Figure 1 show the simulated dependence of deactivation on conversion calculated for model reactions proceeding under kinetic and diffusion control via parallel-parallel and parallel-series deactivation schemes (Table 1).

The scheme referred as "series-consecutive" approximates the mechanism of isoamylene dehydrogenation to isoprene accompanied by coke

formation over a commercial calcium-nickel phosphate catalyst.[12] According to the kinetic description derived on the basis of detailed experimental study in the kinetic region,[12] the rate of isoprene production r_{iso} and the rate of coke formation ϕ_c can be expressed in terms of the conversion x and amount of coke deposited C and $Q = C^{2/3}$ as follows:

$$r_{iso} = \frac{k_1 P_0 (1 - x)}{1 + Q + k_2 P_0 x} \quad (8)$$

$$\phi_c = P_0 \left\{ \frac{k_3 + k_4 x}{1 + Q + k_2 P_0 x} + \frac{k_5 + k_6 Q \exp(-C)}{1 + Q + k_2 P_0 x} \right\} \quad (9)$$

The denominators of the equations relevant to the rates of the main and coke formation reactions are similar, and this is a reflection of the fact that both these processes occur on common active sites.

Table 1

Schemes and simulation kinetic descriptions of the simplest mechanism patterns of coke formation accompanying reactions of the type A + Z $\longrightarrow$ M + Z

Scheme	Mechanism patterns	Simulation rate of the basic reaction	Rate of formation of coke precursors
parallel	A+Z →[AZ] ...→ [BZ]… →[MZ]→ M+Z (slow) [AZ] $\xrightarrow{slow}$ (PZ) → ... → coke	$\dfrac{k(1-x)\sigma}{1+K_s(1-x)}$	$\dfrac{k*_1 P_0(1-x)\sigma}{1+K_s(1-x)}$
series	A+Z →[AZ] ...→ [BZ]… →[MZ]→ M+Z (slow) [BZ] $\xrightarrow{slow}$ (PZ) → ... → coke	$\dfrac{k(1-x)\sigma}{1+K_s(1-x)}$	$\dfrac{k*_2 P_0(1-x)\sigma}{1+K_s(1-x)}$
parallel-parallel	A+Z →[AZ] ...→ [BZ]… →[MZ]→ M+Z (slow) [AZ] + **A** $\xrightarrow{slow}$ (PZ) → ... → coke	$\dfrac{k(1-x)\sigma}{1+K_s(1-x)}$	$\dfrac{k*_1 P_0(1-x)(1-x)\sigma}{1+K_s(1-x)}$
parallel-consecutive	A+Z →[AZ] ...→ [BZ]… →[MZ]→ M+Z (slow) [AZ] + **B** $\xrightarrow{slow}$ (PZ) → ... → coke	$\dfrac{k(1-x)(1-C_1 P_0)\sigma}{1+K_s(1-x)}$	$\dfrac{k*_1 P_0 x(1-x)\sigma}{1+K_s(1-x)}$
series-parallel	A+Z →[AZ] ...→ [BZ]… →[MZ]→ M+Z (slow) [BZ] + **A** $\xrightarrow{slow}$ (PZ) → ... → coke	$\dfrac{k(1-x)\sigma}{1+K_s(1-x)}$	$\dfrac{k*_2 P_0(1-x)(1-x)\sigma}{1+K_s(1-x)}$
series-consecutive	A+Z →[AZ] ...→ [BZ]… →[MZ]→ M+Z (slow) [BZ] + **B** $\xrightarrow{slow}$ (PZ) → ... → coke	$\dfrac{k(1-x)(1-C_2 P_0)\sigma}{1+K_s(1-x)}$	$\dfrac{k*_2 P_0 x(1-x)\sigma}{1+K_s(1-x)}$

The non-uniformity in the rate of coking is not an exception. In some cases, this phenomenon can be linked to the non-uniformity of the adsorption strength of active sites. Indications are that the formation of coke is favored by tight bonds between the catalyst surface and the intermediates. Lability of bonds reduces the probability for coke precursors to come into existence.

Multiplicity of active sites

A special class of catalysts are those in which more than one type of active sites participate in the catalytic performance. Detailed study of these catalysts gains in importance in view of the properties of bimetallic catalysts efficient for reforming, dehydrogenation, HDS, HDN, and many other industrial processes. Distinct types of sites may differ by configuration, adsorption ability, contribution to different reaction routes, vulnerability. Specifically for the particular systems, the types of sites may be independent (sovereign); transform into each other depending on the operation conditions (*e.g.,* the CUS and Brønsted acid sites of HDS and HDN catalysts[13-15]),

or follow other relations. Numerous examples are reported in literature that the bi-metallic catalysts manifest higher resistance to the action of coke.[16] This may be associated with ligand and/or geometric effects. Coke precursors originate predominantly from intermediates tightly bound to the catalyst surface.[10] The additives may modify the adsorption properties of the catalyst.[16-19] On the other hand, evidence is presented in literature that coking is structure-sensitive, requiring large ensembles or catalytic clusters.[20] The introduction of a second metal may result in increased dispersion, and hence decreased area of the active phase islands, thus reducing their capacity for large ensembles facilitating the coke formation. At the same time, the main reaction may be either structure insensitive (*e.g.* dehydrogenation requiring 1 Pt atom), or require ensembles of different configuration or size, and therefore, exert different structure sensitivity. Following this logics, on applying the model of Froment (1), the features of each site type should be considered. For the case of *n* types of sites, assuming as a first approximation that all types of sites are of similar accessibility, the approach may be specified as:

$$\varphi(u) = \sum \varphi_j(u) = P(u)\{S_1(u) + S_2(u) + ... + S_n(u)\} \qquad (10)$$

The $\varphi_j(u)$ functions denote the contribution of each type of sites; $S_j(u)$ standing for the individual probability of the *j*-th type site to be working. These functions may evolve in different way for types of sites requiring different surface ensembles; and accordingly, some of the reaction routes may be affected more appreciably than the others.

By way of example, we shall refer a process studied in detail in:[21,22] butane dehydrogenation over In or Sn promoted Pt/alumina catalysts. Initially, the accompanying coke formation proceeded by a constant rate, but the coke formed did not affect the catalyst activity. When the coke deposited attained a critical amount (c*), the coke formation rate abruptly dropped, while the basic reaction kept its quasi-stationary regime. This would last for 7 hrs on the unpromoted Pt catalyst, 15 hrs on the In-promoted, and 20 hrs on the Sn-promoted samples. When the coke deposits attained a second critical value- C** (respectively, 1.8 wt%, 2.3 wt% and 6.8 wt% for the different samples), a decrease of the basic reaction rate was observed, depending linearly on the amount of coke exceeding C**. Detailed studies of these catalysts performed elsewher[23] by use of IR-spectroscopy, DTA, EPR, XPS and other methods have shown that the presence of promoters brings to smaller sizes of the active-phase islands. The data has supplied evidences that the additives make for weaker strength of the centers of tight adsorption, on the one hand, and facilitate the migration of coke precursors formed inside the metal-phase islands towards the interface with the support. The observed peculiarities of the process[21, 22] can be adequately described within the frames of a model assuming participation of three types of active sites: (i) single Pt centers of strong adsorption affinity facilitating dehydrogenation; (ii) catalytic clusters (ensembles) involving a number of Pt (and possibly Sn or In) surface atoms in proper configuration facilitating cracking; (iii) centers on the interfaces Pt/carrier or Pt/promoter facilitating dehydrogenation, of weaker adsorption ability. The intermediates adsorbed on interfaces are less tightly bound, and this raises the chances of the dehydrogenation products arising on them rather to desorb than become involved in condensation processes. Two types of precursors responsible for the coke formation are postulated: precursors arising from intermediates tightly adsorbed onto the catalytic clusters inside the active phase islands; and precursors located onto the interfacial sites in consequence of the migration of the first type of precursors. According to the reaction scheme postulated,[24] the coke patterns located on different types of sites influence in different way the evolution of the reaction system. The relations following from the suggested model qualitatively explain the experimentally observed stepwise character of the deactivation kinetics, as well as other promoter-provoked effects.

CONCLUSIONS

The unstationary effects accompanying many heterogeneous catalytic reactions are to be examined in close relation with the reaction mechanism. Following the understanding that the reaction mechanism plays a guiding role in the processes evolution, research into the laws of catalyst deactivation can be conductive to elucidating the specificities in the mechanism of the deactivation phenomena as an integral part of the basic process. 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 mechanism. The deactivation kinetics is linked to the peculiarities of generation of the deactivating agents. The different modes of catalyst deactivation exhibited under different conditions reflect specific features of the variety of phenomena involved in the reaction system. In case the limiting step is the formation of coke precursors, 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 for the formation of the precursors.

Deeper knowledge on the relation between the process mechanism and catalyst deactivation makes for adequate predicting the behavior of the reaction system under different operation conditions, and for finding resources for reducing the harmful effect of deactivation on the yield of the target products.

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