Deactivation Modes of Solid Catalysts with Different Active Sites

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Abstract: An approach is suggested to distinguish different types of active sites responsible for different reactions on bifunctional catalysts. The model assumes a non-uniform vulnerability of active sites that depends on their location. Problems on the relationship between the dispersion of the active phase and selectivity are discussed. The effect of coke formation on the activity change of different sites is analyzed.

Key words: solid catalyst; deactivation mode; bifunctional catalyst; active site

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It is widely recognized that more than one type of active sites can be distinguished on bi- and poly-functional catalysts. The detailed study of these catalysts is very important because of their wide application in industrial processes, such as reforming, dehydrogenation, hydrodesulfurization, and hydrodenitrogenation. For this, it is necessary to develop kinetic models that reflect the contribution of distinct types of sites that are influenced by their diverse nature and properties. Such published models are still scarce. The presence of active sites of different nature and properties, while facilitating networks of mutually dependent reaction routes, is a challenge to forecasting the overall effects. It is both of academic and practical interest to obtain more detailed knowledge on the kinetic effects arising from the specific features of distinct site types, and their correlation with the reaction mechanism.

Distinct types of sites may differ by nature, configuration, adsorption ability, contribution to different reactions, vulnerability, etc. (e.g., [1–5]). Each type is affected in its own way by various deactivation factors. Hence, the complexity of such catalytic systems is not only with the variety of interactions and species involved in the reaction network but also with the deactivation functions relevant to the different types of active sites.

1　Approach

It is of significance to distinguish the function of catalyst activity (denoted as $\varphi(u)$) from the deactivation function (denoted by $\Phi(u)$) that describes the rate of activity decrease. The activity is due to the contributions of groups of active sites. So far, the decrease in activity is most frequently described using a function characterizing the catalyst activity $\varphi(t)$ at time t defined as the ratio of the rate $r(t)$

to the initial rate on the fresh catalyst (r^0):

$$\varphi(t) = \frac{r(t)}{r^0} \tag{1}$$

In the simplest case, when the functions are considered time dependent ($u \equiv t$), the analysis of the behavior of the reaction system is performed by the analysis of the functions $\varphi(t)$ and $\Phi(t)$:

$$\Phi(t) = \frac{\mathrm{d}}{\mathrm{d}t}\varphi(t) = \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{r(t)}{r^0}\right) = \frac{1}{r^0}\frac{\mathrm{d}r}{\mathrm{d}t} \tag{2}$$

Different approaches have been developed to describe deactivation kinetics by use of the deactivation function $\Phi(u)$. Depending on the mechanistic model considered, the function argument (u) may be the time on stream (t), degree of conversion (x), fraction of blocked sites, concentration of poisoning agent, amount of deposited coke (C), or some other factor that play a key role in the deactivation phenomena.

$$\Phi(u) = -\frac{\mathrm{d}}{\mathrm{d}u}\varphi(u) = -\frac{\mathrm{d}}{\mathrm{d}u}\left(\frac{r(u)}{r^0}\right) = -\frac{1}{r^0}\frac{\mathrm{d}r}{\mathrm{d}u} \tag{3}$$

For catalytic systems with a single type of sites, the deactivation function coincides with the change of the fraction of unblocked sites $\sigma(u)$:

$$\Phi(u) = \mathrm{d}\sigma/\mathrm{d}u \tag{4}$$

The approach suggested by Beeckman and Froment [6,7] uses the current fraction of active sites $\sigma(t)$ as the product of the probability $H(t)$ that a site is accessible and the conditional probability $S(t)$ that the site is not out of action at time t:

$$\sigma(t) = S(t) \cdot H(t) \tag{5}$$

In this study, we extend this approach to the more complex case of multifunctional catalysts. The point is that the surface of many supported catalysts is often nonhomogeneous with respect to chemical content, structure, distribution

of active phase, adsorption strength, acidity, and pore sizes. Nonetheless, for many processes, these non-uniformities can be neglected and the approximation of ideal adsorbed layers can be made.

At the same time, for a large number of processes, it is more important to include the effects due to non-uniformities of the catalyst surface than to assume the postulate of an ideal adsorbed layer. The uncertainty as to which approximation to use imposes an essential theoretical barrier for the development of kinetic models for active sites with different properties.

To be consistent with Hinshelwood-Langmuir kinetics, we developed an approach with the following approximation: with **n** types of active sites contributing to the catalytic action, the catalyst surface is considered to contain **n** co-existing ideal adsorbed layers, each of which is characterized by its intrinsic parameters.

Extending the approach of Beeckman and Froment, the activity function of such a system is defined as the sum of the "individual activity" functions ascribed to the particular types of active sites. For **n** types of sites, assuming that all types of sites have similar accessibility, this is specified as

$$\varphi(u) = \sum \varphi_j(u) = \sum_{j=1}^{n} S_j(u) H_j(u) \qquad (6)$$

The $\varphi_j(u)$ functions denote the contribution of the various types of sites. $S_j(u)$ and $H_j(u)$ are the individual probability for the jth site type to be active and accessible. Since in most multifunctional catalytic systems, two or three types of active sites contribute to the catalytic performance, we shall limit the present analysis to three types of sites. Assuming that they are equally accessible, by substituting the $S_j(u)$ functions with the unblocked fractions $\sigma_j(u)$ relevant to the particular site types, the overall activity can be defined as

$$\varphi(u) = \sum \varphi_j(u) = H(u)\{\sigma_1(u) + \sigma_2(u) + \sigma_3(u)\} \quad (7)$$

Depending on their adsorption ability, nature, configuration, location, the particular kinds of sites may facilitate different reaction routes. When modeling such processes, it is important to consider the peculiarities and vulnerability of each type of sites. The deactivation function $\Phi(u)$ is defined as the change of the overall contribution of active sites. For three site types of similar accessibility, we get:

$$\Phi(u) = \partial\varphi(u)/\partial u = H(u)\{\partial\sigma_1/\partial u + \partial\sigma_2/\partial u + \partial\sigma_3/\partial u\}$$
$$+ \{\sigma_1(u) + \sigma_2(u) + \sigma_3(u)\}(\partial H/\partial u) \qquad (8)$$

By analyzing this relationship, various trends in the evolution of the catalytic system can be predicted that depend on the quantitative changes to the intrinsic functions: $\partial\sigma_1/\partial u$, $\partial\sigma_2/\partial u$, $\partial\sigma_3/\partial u$, and $\partial H/\partial u$. The functions that describe the changes in the contribution of the jth site type are specified as:

$$\phi_1 = \frac{\partial\sigma_1}{\partial u} \cdot H ; \quad \phi_2 = \frac{\partial\sigma_2}{\partial u} \cdot H ; \quad \phi_3 = \frac{\partial\sigma_3}{\partial u} \cdot H ; \qquad (9)$$

$$\phi_4 = \frac{\partial H}{\partial u} \cdot \sigma_1 ; \quad \phi_5 = \frac{\partial H}{\partial u} \cdot \sigma_2 ; \quad \phi_6 = \frac{\partial H}{\partial u} \cdot \sigma_3 \qquad (10)$$

$$\Phi(u) = \phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6 \qquad (11)$$

Several terms of individual contributions to the overall deactivation function can thus be distinguished. Accordingly, some reaction routes may be more affected by deactivation than others. As the deactivation function is generally defined as the change of the activity function $\varphi(u)$, this gives better insight into the key factors (u_j) responsible for the catalyst activity.

Another essential point is that some factors may influence the activity in opposite direction due to the different types of sites (e.g., $\partial\sigma_1/\partial u > 0$, but $\partial\sigma_2/\partial u < 0$). The dominant effect in such a situation would be a change in selectivity. As these changes may vary in the course of the process, the effect on selectivity can be rather complicated.

By way of example, consider a mechanistic pattern in which the ith site type is deteriorated by feed reacting species, while some product species inhibit the jth site type. If we use for **u** the degree of conversion ($u \equiv x$), it turns out that

$$\partial\sigma_i/\partial x \neq \partial\sigma_j/\partial x ; \qquad (12)$$

with

$$\partial\sigma_i/\partial x \leqslant 0 \quad \text{simultaneously with} \quad \partial\sigma_j/\partial x \geqslant 0 \qquad (13)$$

Eq. (13) may be interpreted physically as follows. If the process is carried out at high conversion, the low concentration of the feed reactant harmful for the activity of the ith type of sites will cause the latter to be less affected by deactivation, in contrast to the sites of jth type that are more vulnerable at high conversion (high concentration of the deactivating product). The fall of conversion, which is frequently the trivial result of catalyst deactivation, will lead to the inverse effect due to the changing composition of the reaction mixture, namely, the increase in the concentration of unconverted feed species will lead to more deactivation of the ith type of sites, and the decrease in the product content will lower the deactivation of the jth type sites.

In case the ϕ_j terms are affected to different extents by changes in the reaction medium, the function $\phi_m(u)$ for the apparent evolution of the catalytic system can be specified as

$$\phi_m(u) \equiv \max\{\phi_1(u), \phi_2(u), \phi_3(u), \phi_4(u), \phi_5(u), \phi_6(u)\} \quad (14)$$

Under conditions for which the magnitude of the $\phi_m(u)$ function substantially exceeds the other terms of $\Phi(u)$, its contribution to the deactivation behavior of the catalytic system will be dominant, and the deactivation kinetics can be approximated to coincide with $\phi_m(u)$. The evolution of the catalytic system will follow the corresponding behavior

$$\Phi(u) \cong \phi_m(u) \text{ as long as } \phi_m(u) \geqslant \sum \phi_{i \neq m} + \Delta \qquad (15)$$

It should be noted, however, that although effects resulting

from the $\phi_{i\neq m}(u)$ terms appear negligible, they can influence the catalytic system in some way. The accumulative effect of hidden changes can bring the system to a state where $\phi_n(u) > \phi_m(u)$, and a stepwise change in the deactivation law be observed. The apparent evolution of the catalytic system will follow a new behavior.

In the particular case where access to active sites is not affected, $\partial H/\partial u = 0$, and the terms ϕ_4, ϕ_5, and ϕ_6 can be eliminated. However, in the general case, especially when u is the amount of coke deposits near pore openings, this diffusion-dependent term may exceed the other terms and become dominant in the deactivation function.

For a bi-dispersed catalyst, for which the *type_2* and *type_3* sites are characterized by equal accessibility, and different from the accessibility of the *type_1* sites, we get:

$$\varphi(u) = \sigma_1(u)H_1(u) + H_2(u)\{\sigma_2(u)+\sigma_3(u)\} \quad (16)$$

Correspondingly, the deactivation function takes the form:

$$\Phi(u) = \frac{\partial\varphi}{\partial u} = \frac{\partial\sigma_1}{\partial u}H_1 + \left\{\frac{\partial\sigma_2}{\partial u}+\frac{\partial\sigma_3}{\partial u}\right\}H_2 +$$

$$\sigma_1\left(\frac{\partial H_1}{\partial u}\right) + \{\sigma_2+\sigma_3\}\frac{\partial H_2}{\partial u} \quad (17)$$

It is essential to consider such a relation in those cases where the sites of a given type are located in the smaller pores. When the process is accompanied by coke formation, the coke will first block the fine pores, and this can result in the stepwise termination of the contribution of the sites located inside them.

Another point of concern is that each distinct site type may be affected in its own way by various deactivation factors. The initial ratio $(\sigma_1^0:\sigma_2^0:\sigma_3^0)$ of the different types of sites may depend on the catalyst nature, preparation procedure, and reaction conditions. Both the initial values of σ_1, σ_2, σ_3, and their evolution can depend on the reaction conditions. Starting from different initial ratios, each type of sites can evolve in its own way that depending on its vulnerability. The complexity of such catalytic systems is not only due to the variety of interactions and species in the reaction network, but also with the deactivation functions that describe the contributions of each type of active sites and their changes in the process. The functions describing the changes in the contribution of the jth site type can be specified as $\phi_j(u) = \partial\sigma_j/\partial u$. By including these functions in the model, and estimating their relative magnitude (see Eq. (11)), certain steps of the reaction network can be lumped according to the vulnerability (reversible or irreversible) of the centers active for these steps.

2 Discussion

2.1 Deactivation of catalysts with acid-base active centers

It has been suggested (e.g. [5,8,13]) that the active sites due to coordinatively unsaturated anionic vacancies (CUS) and Brönsted acid sites of hydrodesulfurization and hydrodenitrogenation catalysts can be converted into each other by changing the H_2S concentration. Increasing the H_2S concentration over a NiMo/Al$_2$O$_3$ catalyst would convert anionic vacancies on which hydrogenation occurs into hydrogenolysis Brönsted sites, which are less vulnerable to poisoning from N-compounds. In the suggested model, we shall denote by (σ_{CUS}) the fraction of coordinatively unsaturated sites, and by (σ_{Br}) the fraction of Brönsted sites. An increase of H_2S concentration will result in a lower initial value (σ_{CUS}^0) of the anionic vacancies at the expense of a higher initial value (σ_{Br}^0) of the Brönsted acid sites.

There is evidence in the literature (e.g., [8–13]) that nitrogen-containing species exert a stronger deteriorating effect on the unsaturated anionic vacancies than on Brönsted sites. Therefore, if we consider that the key deactivation factor u is the concentration of poisoning N-compounds, we obtain the following relationship for the deactivation functions describing the loss of activity of the CUS and Brönsted types of sites:

$$\phi_{CUS}(u) \equiv \partial\sigma_{CUS}/\partial u > \partial\sigma_{Br}/\partial u \equiv \phi_{Br}(u) \quad (18)$$

It is worth noting that each effect may in turn evolve in a different way depending on the reaction conditions. Concerning coke located on the support, some authors [14–16] suggested that its poisoning action becomes perceptible when the thickness of the coke layer becomes thick enough to cover or screen the edge vacancy centers (CUS sites) prevailing at lower H_2S concentrations.

2.2 Deactivation effects associated with the non-uniform adsorption strength of active sites

As was noted above, active sites of different adsorption strength are present on the surface of many solid catalysts. In many cases, it is possible that effects due to non-uniformities in the adsorption properties are negligible. At the same time, for a large class of processes, sites of different adsorption strength are involved and cannot be ignored when the surface concentrations of intermediates play a key role in the reaction pathways generating byproducts and/or coke species. In most cases, the reactivity of surface intermediates depends on the strength of their bonds to the catalyst surface. Strong bonds of intermediate unsaturated surface species favor the generation of coke precursors. Consequently, it is reasonable to expect that when the reaction mechanism is linked to various types of active sites, the selectivity and deactivation pattern would differ with the adsorption properties of the different sites. For this reason,

the precision of the analysis requires incorporating into the kinetic model these effects and therefore the classical Langmuir-Hinshelwood approach is not always appropriate when the non-uniformity of active sites has to be accounted for.

By way of example, we refer the model suggested [32] for the deactivation mechanism of metal-supported nonporous commercial Pd catalysts for xylene combustion. According to the experimental data reported in Ref. [32], the change of the reaction rate with time on stream showed the following trends that depending on the temperature: abrupt drop at temperatures below 270 °C, steep decrease within the temperature range 290–320 °C, and no noticeable change at higher temperatures. The kinetic analysis carried out in these studies [33,34] for the fresh catalyst indicated (i) different kinetic laws are relevant in the different temperature regions, and (ii) an almost 3-fold higher apparent activation energy on carrying out the process at temperatures below 270 °C compared to that at temperatures above 320 °C. To explain the behavior of these catalytic systems, we associated the experimental influence of temperature on the deactivation phenomena with the behavior of active sites of unequal adsorption ability. According to the evidence presented in Refs. [33–35], strongly and weakly adsorbed forms of oxygen can be distinguished on Pt and Pd catalyst surfaces. The strongly adsorbed oxygen is in equilibrium with the weakly adsorbed (mobile) oxygen, which is the reactive form. The reaction scheme constructed to model the catalytic combustion of *p*-xylene over Pd [32] from the findings established in [33–35] by use of kinetic methods and transient response studies envisages the participation of active sites of different adsorption ability: sites of weaker adsorption ability (noted as Z-sites) and strong adsorption sites (noted as Y-sites). The ratio between mobile [OZ] and tightly adsorbed forms of oxygen [OY] can be defined as a temperature dependent function (noted as K_T) that increase with temperature: $[OZ] \propto K_T[OY]$.

The overall reaction rate r_{obs} is the sum of the reaction rates r_Y and r_Z, from the two site types: $r_{obs} = r_Z + r_Y$.

The intermediates formed on the weak adsorption sites are more reactive and accordingly, the surface interactions with their participation are characterized by a lower energy of activation. The strong adsorption sites generate tightly bound surface species, which may evolve into precursors of the carbide film leading to catalyst deactivation. Also, degradation of the carbide form via interactions with the mobile forms of adsorbed oxygen can take place. A higher temperature facilitates mobility of the weakly adsorbed forms, thus intensifying the degradation of the carbide film or preventing its formation. This compensation effect increases with temperature until it reaches the level at which the deactivation effect is practically eliminated.

It is reasonable to suggest that at a lower temperature, where the (fraction) surface concentration of mobile weakly adsorbed oxygen is fairly small, the major contribution to the reaction performance is due to the tightly adsorbed intermediates, and consequently, the observable rate r_{obs} practically coincides with the rate of the pathway proceeding via the Y-type sites and intermediates: $r_{obs} \approx r_Y$. According to the postulated reaction scheme, the reaction proceeding via this route is accompanied by the formation of carbide species, which deteriorates the catalyst activity.

At higher temperatures, the surface fraction occupied by the mobile forms of adsorbed oxygen increases, and the reaction route with their participation is favored. This route is characterized by a lower energy of activation. Accordingly, the weight of the r_Z term will increase. From this trend, above a certain temperature we get $r_Z > r_Y$. On attaining the condition $r_Z \gg r_Y$, the apparent activation energy will coincide with the activation energy needed for the interaction of the weakly adsorbed species. The rate of degradation of coke precursors will compensate for the rate of their formation. Thus, the catalyst system becomes insensitive to the influence of carbon formation, and proceeds under a stationary regime.

The kinetic equations derived on the grounds of the proposed reaction mechanism and the above stated conclusions are in accord with the observations established from experimental data. More detailed information on these points can be found in the original studies [32–35].

2.3 Deactivation effects associated with non-uniform coordination of active sites

The dispersion of the active phase of catalysts as nano-structures on the support results in differences in the properties of the active sites that depend on their geometry and location (internal or interfacial). The geometric factors may result in ligand effects.

The differences in the coordination of sites arising from their location (internal or interfacial) within the island structures can lead to differences in free energy, adsorption affinity, catalytic properties, and stability of activity. The properties of the surface atoms inside the islands are related to their coordination and the peculiarities of the crystallographic facets. The active sites located on the interface of the active phase with the support are coordinately unsaturated, and may be classified as similar to those of the crystalline edges and corners. The model developed by Yang et al. [17] estimates the site energy (interaction energy per atom) for nine FCC metals for the cases of 201-, 586-, 1289-atom clusters, and semi-infinite surfaces. The analysis pointed out that the free energy of the internal atoms depends on the size of the island, whereas the energy values

for the low coordination edge and corner sites were found to be independent of cluster size. The differences in the site energies cause differences in the catalytic properties of internal and interfacial active sites. Differences associated with the ratio of internal and interfacial active sites are used in elucidating the action of supported Au catalysts, in particular, the recently developed concept (e.g., [18–20]) according to which the catalyst activity is ascribed to charged Au^{2+} sites located on the boundaries with the support. Following the understanding that metal-metal or oxide-metal interfaces can lead to the formation of sites with unique activity [21], various models have been advanced in the literature to explain the catalyst behavior from the differences in the properties of internal and interfacial active sites.

It should be noted that the internal and interfacial sites may be affected in different ways by the various deactivating agents.

Within the framework of the approach suggested here, we can model the average area of an active phase island as the area of a circle with radius ρ. We shall denote as Z-type the active sites located inside the active phase islands, and as Y-type the interfacial active sites located along the island boundaries. Let ξ stand for the radius of an individual surface atom of the active phase. In the fresh catalyst, the number N_Z^0 of single sites inside the island would be proportional to the ratio $(\rho/\xi)^2$, whereas the number N_Y^0 of the interfacial sites would be proportional to the magnitude of (ρ/ξ):

$$N_Z^0 \propto \frac{\pi \cdot \rho^2}{\pi \cdot \xi^2} = \alpha_z \frac{\rho^2}{\xi^2} \qquad (19)$$

where the coefficient α_Z accounts for the crystallographic peculiarities of the facets:

$$N_Y^0 \propto \frac{2\pi \cdot \rho}{2\xi} = \pi \cdot \frac{\rho}{\xi} \qquad (20)$$

Depending on the dispersion, the number of sites contained in the active phase varies within the range 10–3 000. Consequently, the number N_Z of internal active sites is of similar magnitude to the number N_Y of interfacial sites. The initial ratio of these two site types on the fresh catalyst is

$$\frac{N_Y^0}{N_Z^0} \propto \frac{\pi}{\alpha_z} \frac{\xi}{\rho} = \alpha \cdot \xi \cdot \left(\frac{1}{\rho}\right) \qquad (21)$$

Considering that the average size of the active phase islands is inversely dependent on the dispersion, we get the relation of this ratio with the dispersion γ of the active phase:

$$\frac{N_Y^0}{N_Z^0} = \beta \cdot \xi \cdot \gamma \qquad (22)$$

It is recognized for a number of bifunctional catalysts that internal and interfacial sites facilitate different reaction routes. In general, the routes facilitated by various types of sites follow different kinetic equations, which we shall denote respectively as $f_Z(P_j,T)$ and $f_Y(P_j,T)$. Assuming parallel reaction routes over Z- and Y-type sites and separable deactivation kinetics [22], the overall reaction rate r_{ov} is

$$r_{ov} = r_Z + r_Y = k_Z \cdot f_Z(P_j,T) \cdot \varphi_Z + k_Y f_Y(P_j,T) \cdot \varphi_Y \quad (23)$$

where r_Z and r_Y are the rates on routes due to internal and interfacial sites. The φ_Z and φ_Y functions stand for the activity of the site types, and linearly depend on their amounts:
$\varphi_Z \propto N_Z/N_Z^0$ and $\varphi_Y \propto N_Y/N_Y^0$

For the fresh catalyst, we get the following dependencies of the initial selectivities on dispersion:

$$S_Z^0 = \frac{r_Z^0}{r_Z^0 + r_Y^0} = \frac{k_Z f_1(P_j,T) \cdot N_Z^0}{k_Z f_1(P_j,T) \cdot N_Z^0 + k_Y f_2(P_j,T) \cdot N_Y^0}$$
$$= \frac{1}{1 + \frac{k_Y f_2(P_j,T)}{k_Z f_1(P_j,T)} \cdot \left\{\frac{N_Y^0}{N_Z^0}\right\}} = \frac{1}{1 + k_s \xi \frac{f_2(P_j,T)}{f_1(P_j,T)} \cdot \gamma} \qquad (24)$$

and

$$S_Y^0 = \frac{r_Y^0}{r_Z^0 + r_Y^0} = \frac{k_Y f_2(P_j,T) \cdot N_Y^0}{k_Z f_1(P_j,T) \cdot N_Z^0 + k_Y f_2(P_j,T) \cdot N_Y^0}$$
$$= \frac{1}{1 + \frac{k_Z f_1(P_j,T)}{k_Y f_2(P_j,T)} \cdot \left\{\frac{N_Z^0}{N_Y^0}\right\}} = \frac{1}{1 + \frac{1}{k_s \xi} \frac{f_1(P_j,T)}{f_2(P_j,T)} \cdot (\frac{1}{\gamma})} \qquad (25)$$

for $k_s = \frac{k_Y}{k_Z} \beta \xi$.

Considering that the intrinsic kinetic laws $f_Z(P_j,T)$ and $f_Y(P_j,T)$ are functions of temperature and partial pressures, but not the dispersion, it follows from Eqs. (24) and (25) that a high dispersion of the active phase on the fresh catalyst favors the reactions facilitated by interfacial active sites.

It is reasonable to expect a different vulnerability of the internal and interfacial active sites under the action of various deactivation factors. When the process is accompanied by coke formation, the deposition of a carbide layer on the catalyst surface hinders the access of the reactants to the active sites. This can be interpreted as a decrease of the average size of the active phase islands (or the radius ρ). From Eqs. (19) and (20), we get the following equations for the variation of the activity functions (φ_Z) and (φ_Y) on the internal and interfacial sites:

$$d\varphi_Z \propto dN_Z = \kappa_Z(\frac{2}{\xi^2}\rho)d\rho = \kappa_Z(\frac{2}{\xi})(\frac{\rho}{\xi})d\rho \qquad (26)$$

$$d\varphi_Y \propto dN_Y = \kappa_Y(\frac{\pi}{\xi})d\rho \qquad (27)$$

As can be seen, the coke-induced decrease of the island sizes will affect in different ways and extents the activity of the internal and interfacial sites. The decrease of the interfacial-type activity will evenly follow the decrease of the size

of the active phase islands. The effect will be more pronounced for a larger size (ξ) active phase. The activity of the internal sites is expected to proceed in an uneven mode because of the dependence of ($d\varphi_Z$) on the (ρ/ξ) ratio. As the island size ρ is reduced by coke formation, the activity of the Z-type sites will be most affected by the earlier coke deposits, and the deterioration effect would slow down as the moieties of the active phase decrease in size.

It can be estimated on comparing (26) and (27) that

$$d\varphi_Z = \left(\frac{2}{\pi}\right)\left(\frac{\rho}{\xi}\right)d\varphi_Y \qquad (28)$$

As the size of the active phase islands (ρ) is one to three orders of magnitude larger than the sizes of the constituent metal atoms, (ρ/ξ)$\gg$1, and consequently, ($d\varphi_Z$) $\gg$($d\varphi_Y$), the deactivation effect will be much more pronounced on the internal active sites.

It is reported in the literature (e.g.,[14–20,23]) that the interfacial sites have a weaker adsorption strength for hydrocarbons, and the adsorption of hydrogen on them is often negligible. These properties give the following with regard to coke formation: (i) interface sites do not contribute to the generation of coke precursors, (ii) the coke precursors that reach these sites by migration are favored to spillover onto the acidic support sites.

The relevant equations of selectivity variation can be derived as follows. On substituting $k_s\gamma = k_\rho/\rho$ in Eqs. (24) and (25), we arrive at the dependence of selectivity on the size of the active phase nano-structures:

$$S_Z = \frac{1}{1+k_\rho\dfrac{f_Y(P_j,T)}{f_Z(P_j,T)}\dfrac{\xi}{\rho}} \qquad (29)$$

and

$$S_Y = \frac{1}{1+\dfrac{1}{k_\rho}\dfrac{f_Z(P_j,T)}{f_Y(P_j,T)}\dfrac{\rho}{\xi}} \qquad (30)$$

Differentiating these relations, one obtains the corresponding trends for the selectivity changes:

$$dS_Z = \frac{k_s\dfrac{f_Y(P_j,T)}{f_Z(P_j,T)}}{\xi\left(k_s\dfrac{f_Y(P_j,T)}{f_Z(P_j,T)}+\dfrac{\rho}{\xi}\right)^2}d\rho \qquad (31)$$

It follows from this relationship that the change of selectivity towards the reactions on internal active sites will change with the change of the size ρ of the active phase islands. As coking results in the reduction of ρ, the selectivity to such routes will decrease in the course of deactivation. The drop will be more pronounced at the start of the deactivation process.

In contrast, the selectivity for reactions on interfacial sites

will increase following the shrinking of the active phase islands in the course of coking:

$$dS_Y = -\left\{\frac{k_s\dfrac{f_Y(P_j,T)}{f_Z(P_j,T)}}{\xi\left(k_s\dfrac{f_2(P_j,T)}{f_1(P_j,T)}+\dfrac{\rho}{\xi}\right)^2}\right\}d\rho \qquad (32)$$

The above conclusions are for the case when a single active metal atom acts as a distinct active site. Most supported catalysts are characterized by sizes of the active phase islands in the domain of nano-moieties. This is a substantial reason for the structure sensitivity of their catalyzed reactions. As is widely recognized, both single sites and catalytic clusters (active sites requiring several adjacent surface atoms in a proper configuration) participate in the performance of supported catalysts for dehydrogenation, reforming, hydrotreating, and other industrial processes [24–27]. Such reactions are usually accompanied by catalyst deactivation due to coke formation, and there arises the problem of how sensitive this is to the extent of coke coverage, which would lead to differences in the mode and kinetics of catalyst deactivation. If one reaction requires catalytic clusters, while another is facilitated by single sites, the former will be more sensitive to the activity of the nano-sized islands and the number of catalytic clusters. Thus the selectivity of multi-route processes may be markedly sensitive to purely geometric factors [25]. The authors of [23] report convincing evidence that the effect of Sn on Pt electron density depends as well on the particle size of the catalytic clusters. Coke deposits may affect in different ways the activity of single sites that favor structure-insensitive dehydrogenation and the activity of larger catalytic clusters that favor isomerization, cracking, other bond-scission steps, and coke formation. This fact is of special importance for the selectivity of structure sensitive reactions.

By way of example, we refer to a process studied in detail in [28,29]: butane dehydrogenation over In or Sn promoted Pt/γ-Al$_2$O$_3$ catalysts. According to the experimental data reported in Ref. [28], initially coke formation proceeded at a constant rate, but the coke formed did not affect catalyst activity. When the coke deposits attained a critical amount (C*), the coke formation rate abruptly dropped, while the basic reaction kept its quasi-stationary regime. This lasted 7 h on an unpromoted Pt catalyst, 15 h on the In-promoted, and 20 h on the Sn-promoted samples. When the coke deposits attained a second critical value-C** (1.8 wt%, 2.3 wt%, and 6.8 wt% for the different samples, respectively), a decrease of the basic reaction rate was observed that depended linearly on the amount of coke exceeding C**. Detailed studies of these catalysts performed elsewhere [30] by infrared spectroscopy, DTA, EPR, XPS, and other methods

have shown that the presence of promoters leads to smaller sizes of the active-phase islands. The data indicated that the additives lead to a weaker strength of the centers of strong adsorption on the one hand, and facilitated the migration of coke precursors formed inside the metal-phase islands towards the interface with the support. The observations of the process [28,29] can be adequately described by a model that assume the participation of three types of active sites [31]: (i) single Pt centers of strong adsorption affinity for dehydrogenation (further denoted as Z-type); (ii) catalytic clusters (ensembles) involving a number of Pt (and possibly Sn or In) surface atoms in the proper configuration for cracking (denoted as X-type); (iii) Y-type centers on the interfaces Pt/support (Y_s) or Pt/promoter (Y_a) for dehydrogenation. The intermediates adsorbed on interfaces are less tightly bound, and increases the chances of the dehydrogenation products on them to desorb rather than become involved in condensation processes. Two types of precursors responsible for coke formation appear reasonable [31]: precursors from intermediates tightly adsorbed on the catalytic clusters inside the active phase islands and precursors located on the interfacial sites due to the migration of the first type of precursors. According to the reaction scheme postulated [31], the coke patterns on different types of sites influenced in different ways the evolution of the reaction system. A detailed reaction scheme was proposed that considered the impact of coke located on different types of sites for the evolution of the reaction system.

Because of the pronounced adsorption strength of the X-type sites, the intermediates formed on them have longer residence time than the other intermediates. This results in some of these intermediates giving rise to the creation of coke precursors (Prec1). This assumption is in accordance with data published in literature. The proximity of adsorbed hydrogen inside the active phase entities creates conditions for surface reactions of Prec1 with [HZ] intermediates, which result in breaking the chain of coke formation. As the adsorption of hydrogen on interfacial sites is negligible, the evolution of the precursors (Prec2) into coke with possible spillover onto the support is not impeded by surface interactions terminating the coking chain. It has been shown by Kogan et al. [30] that the migration of coke precursors formed in the interior of the metal-phase islands towards the interfaces with the support is facilitated in the presence of In or Sn promoters.

If we denote by r_X* the rate of coke formation inside the Pt entities, and by r_Y* the rate of coke formation originating from Prec2 precursors, the rate of coke formation on the active phase ($r*$) can be presented as:

$$r* = r_X* + r_Y* = k* \cdot \langle [\mathrm{Prec1}] + [\mathrm{Prec2}] \rangle - b \cdot [\mathrm{Prec1}] \cdot [\mathrm{HZ}]$$

$$(33)$$

Since the migration of the precursors is fast, it can be assumed that the surface concentrations of Prec1 and Prec2 are in equilibrium.

After substitution, the coke formation rate may be presented as:

$$r* = r_X* + r_Y* = k* \cdot [\mathrm{Prec1}] \cdot \langle 1 + K_m ([Y]/[X]) - K_s \cdot [\mathrm{HZ}] \rangle$$

$$(34)$$

The coefficient K_s formally considers the impact of terminating the chain of coke formation.

When the coke formation rate is constant, its variation in time:

$$\frac{\partial r*}{\partial t} = \frac{\partial [\mathrm{Prec1}]}{\partial t} k* \left\langle 1 + K_m \left\{ \frac{[Y]}{[X]} - K_s [\mathrm{HZ}] \right\} \right\rangle \approx 0 \quad (35)$$

One can get from this equation to the following condition for quasi-stationary reaction:

$$[Y] \approx \frac{[X] \cdot \{K_s [\mathrm{HZ}] - 1\}}{K_m} \quad (36)$$

The surface concentrations of [HZ], Y-type and X-type sites are in fact quasi-stationary, being affected by coking to a certain extent. Since these changes compensate each other following Eq. (36), the coke formation will proceed at constant rate. Evidently, the Y-type sites are more affected in the course of coke formation. As the Prec2 coke precursors do not participate in reaction steps breaking the chain of coke formation, the Y-type interfacial sites should be more vulnerable, and it can be expected the reaction system will come to a point at which the condition (36) is changed into:

$$[Y] < \frac{[X] \cdot \{K_s \cdot [\mathrm{HZ}] - 1\}}{K_m} \quad (37)$$

Condition Eq. (37) is equivalent to the condition of a decreasing rate of coke formation ($\partial r*/\partial t < 0$).

It should be noted that for the case of promoted catalysts, $Y = Y_s + Y_a$, while in the absence of promoters $Y_a = 0$. Consequently, in the presence of promoters, the "capacity" of Y-type sites for keeping the quasi-stationary condition (36) would be higher. Such a conclusion is in good agreement with the experimental observations [35,36] that the introduction of promoters resulted in a longer duration of the quasi-stationary regime and higher values of the threshold coke amounts for the "coke tolerance" of the catalytic system.

The relationships from the suggested model qualitatively explain the experimentally observed stepwise character of the deactivation kinetics, as well as other promoter-induced effects. More detailed information on the reaction behavior and the model can be found in the original studies [28–31].

2.4 Deactivation of nanostructured catalysts

Here, the authors discuss an approach for identifying how

site types involving different nano-structures in multifunctional catalysts are affected by catalyst deactivation.

Under the assumption that the catalytic clusters involve internal sites, one can distinguish the Z-type sites as Z_1-type – single internal sites, and Z_m – catalytic clusters requiring (***m***) adjacent atoms. Since a finite number of surface metal atoms are involved in a particular active phase nanostructure, it is reasonable when estimating the number N_{Z_m} of catalytic clusters per active phase to take into consideration the probability μ_m that ***m*** surface atoms are used to construct a catalytic cluster. In the simplest case, the number $N_{Z_m}^0$ of catalytic clusters within an active phase island on a fresh catalyst will depend on the number of single sites N_Z^0 located within the island, the number ***m*** of surface atoms in the cluster, and the probability $\mu_m(\rho)$:

$$N_{Z_m}^0 = k_m \frac{1}{m} \mu_m \rho N_Z^0 \qquad (38)$$

Correspondingly, the overall reaction rate r_{ov} may be presented as:

$$r_{ov} = r_{Z1} + r_{Zm} + r_Y = k_{Z1} \cdot f_{Z_1}(P_j, T) \cdot \varphi_{Z1} + \\ k_{Zm} f_{Zm}(P_j, T) \varphi_{Zm} + k_Y f_Y(P_j, T) \cdot \varphi_Y \qquad (39)$$

The terms r_{Z1} and r_{Zm} distinguish the rates of reactions on single internal sites and on catalytic clusters; the $f_Z(P_j, T)$ and $f_{Zm}(P_j, T)$ terms stand for the corresponding kinetic equations.

With respect to the catalyst activity attributed to the internal sites, a differentiation is needed between reactions catalyzed by single sites and by catalytic clusters. The activity function of the latter depends on the probability (μ_m), which in turn change in the course of the formation of the coke layer:

$$d\phi_{Zm} = \frac{k_m}{(m)}\{(\mu_m)dN_{Zm} + N_{Zm}(d\mu_m)\}$$

$$= \frac{\kappa_m}{m}\left\{(\mu_m)(\frac{2}{\xi})(\frac{\rho}{\xi}) + \left(\frac{\rho}{\xi}\right)^2 d\mu_m\right\} d\rho \qquad (40)$$

Eq. (40) stands for the coke-caused decrease of catalyst activity from structure sensitive reactions, which are due to multi-center intermediates. Considering Eq. (39), the selectivity for such a reaction can be presented as:

$$S_{Zm} =$$

$$\frac{k_{Zm} f_{Zm}(P_j, T)\varphi_{Zm}}{k_{Z1} f_{Z1}(P_j, T)\varphi_{Z1} + k_{Zm} f_{Zm}(P_j, T)\varphi_{Zm} + k_Y f_Y(P_j, T)\varphi_Y} \qquad (41)$$

It is an essential point that in the course of coke buildup, the probability μ_m for availability of ***m*** single sites in proper proximity and configuration may decrease in different modes depending on the value of ***m***. This can result in different effects on the selectivity for structure insensitive and structure sensitive reactions. The system may come to a

point of no catalytic action of catalytic clusters, if the number and density of single sites contained in the active phase islands dropped to a critical level at which the probability that ***m*** of them may be close enough to form a cluster approaches zero. Under such conditions, a stepwise change in the selectivity in favor of the structure insensitive reaction may be expected.

3 Conclusions

The deactivation kinetics of catalysts with more than one type of active sites is associated with the vulnerability of each type of sites. The overall catalyst activity function may be defined as a vector sum of the inherent activity functions ascribed to the particular site types. By analyzing the specific equations for the deactivation processes on different sites, various trends in the evolution of the catalytic system can be predicted, which depend on the magnitude of the deterioration of sites differing in nature, adsorption ability, position, geometry, etc. To reflect the fact that each type of sites can evolve in its own way that depend on its vulnerability under the action of various deactivating factors, it is necessary to include in the model the deactivation functions relevant to each site type, and to estimate their relative contributions.

For catalysts with the active phase dispersed as islands on the support, models distinguishing the properties and stability of the activity of interior and interfacial sites are essential for a description of the selectivity. The suggested model indicated that a high dispersion of the active phase on the fresh catalyst favored the reactions on interfacial sites. It follows from the relationships derived that the selectivity for these reactions will increase as the sizes of the active phase islands decreased in the course of coke formation.

In the course of coke formation, the probability of the availability of single active sites in a proper proximity and configuration to construct a catalytic cluster may decrease in the different modes, giving various effects on the selectivity to structure insensitive and structure sensitive reactions. If the activity of catalytic clusters was terminated, this will result in a stepwise change in the selectivity favoring structure insensitive reactions.

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