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## Selectivity effects related to the diversity of active sites operating on nanostructured multifunctional catalysts

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### ABSTRACT

The goal of the present study was to gain a better understanding of the selectivity of processes over multifunctional catalysts exhibiting diversity of operating active sites. The concept is that the concurrent performance of different types of active sites may provoke effects on the process selectivity comparable to the effects resulting from the kinetic regularities and activation energies of the occurring reactions. Accordingly, in the kinetic model the authors introduce specific parameters reflecting the contribution of distinct types of active sites, facilitating different reaction routes. Reasons are adduced how suchlike parameters serve to account the impact of various reaction routes occurring on different types of sites. The suggested approach links the deactivation-caused selectivity changes to dissimilarities in the vulnerability of different types of active sites. This work relates the probabilities for action of different types of sites to the size of active-phase islands. Various reaction mechanism patterns are modeled to examine relevant selectivity effects.

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## 1. Introduction

The authors dedicate this study to the series of pioneer works of Gault and colleagues concerning the correlation between the diversity of the active sites operating and the varieties of reaction mechanisms observed on some catalyst surfaces (see, e.g., Refs. [1–9]). The concepts developed by Gault and colleagues with account of the Ledoux classification [10] maintain the idea that specific groups of reaction mechanisms are associated with distinct types of active sites. These concepts have withstood for more than three decades the test of time and new findings and are relevant to the present state of knowledge.

It is well recognized nowadays by lots of distinguished researchers (see, e.g., Refs. [11–16]) that active sites differing in coordination, nature, configuration, location, and physicochemical and adsorption properties may participate in the operation of multifunctional catalysts. The differences may influence the catalytic properties and thus selectivity to various reaction routes. At the same time, usually the regularities describing the reaction rates along the different routes are by tacit consent derived by applying the concept of ideal adsorbed layer. Practically, it is acknowledged that such essential simplifications of this concept as homogeneity of the adsorption properties of the catalyst surface, equivalence of active sites, negligibility of electronic effects, absence of lateral interactions are not precise in many cases of heterogeneous catalytic processes. Nonetheless, the model is routinely applied, because the kinetic problems to be solved become much more difficult if any of its simplifications is removed. On the other hand,

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in certain circumstances it is of importance both theoretically and for practical purposes some of the effects, which are neglected by its limitations, are to be taken into account in the process description. The approaches addressed to move beyond the ideal adsorbed layer frames are scarce and seek for the possibility of removing only one or two of its simplifications, for the sake of solubility of the resulting set of equations and lucidity in the result interpretation. The choice of the simplifications to be removed naturally depends on the concrete catalytic system and the problems brought into focus.

The problems linked to the participation of active sites differing in coordination, configuration, adsorption, and catalytic properties in the performance of multifunctional catalysts gain in actuality in view of the wide application of such catalysts in reforming, dehydrogenation, hydrodesulfurization, hydrodenitrogenation (HDN), and other industrial processes. Adsorption nonuniformity of the catalyst surface may provoke effects, which can hardly be explained within the frames of ideal adsorbed layer. Actually, various experimental data are in good agreement with kinetic models assuming the contribution of active sites of unequal adsorption activity. Such an approach applied for modeling the catalytic combustion of *p*-xylene over Pd catalysts gave us the opportunity of elucidating the regularities following from the experimental data and of better understanding the peculiarities of the catalyst deactivation including its reversibility under the influence of the reactant atmosphere [17]. Another essential point of concern is the mode of adsorption, which can be realized on active sites of different configuration. Thus, it is believed for the case of hydrotreating processes that depending on the configuration of the adsorbed form (e.g., vertical or planar, via heteroatom or via benzoic ring, etc.), various routes of the reaction network may be facilitated [13,18–26]. Pertinently the mode of adsorption may condition specific selectivity effects.

The dispersion of the active phase of supported catalysts in the form of nanosized islands conditions diversity in the properties of active sites depending on their location, coordination, and structure. Consequently, the populations of internal and interfacial active sites, appreciably differing in coordination, become comparable. It is reasonable to consider the diversities in the coordination and behavior of internal, edge, corner [3–5,8,9], and valley anion vacancies [18]. This is particularly significant for processes the reaction network of which involves structure-insensitive reactions (facilitated by a single active metal atom [27–31]) and structure-sensitive routes facilitated by catalytic clusters—ensembles of adjacent active atoms constructing multicentered adsorption sites [18–23,27–40]. The finite number of active metal surface atoms comprised within the active-phase islands may restrain the population of such active sites. Occurrence of structure-sensitive reactions may thus be predetermined by the sizes of the structures containing the active component. The consequences following from the structure sensitivity or insensitivity of the concurrent routes exercise reciprocal effects on the process selectivity, but these effects are hardly reflected in the functions applied to predict the selectivity. On this account, appropriate models are necessary to reflect the

specificity of complex reaction systems. Various models have been suggested to relate the catalyst action with the properties of internal and interfacial active sites with due understanding that edge active sites exhibit unique activity and free energy characteristics [3,5,8,9,41,42]. The models developed by Gault and colleagues take their rightful place in this field. Exploring the behavior of several processes on nonuniform catalysts, Murzin [43–45] adduced factual arguments about the influence of the active-phase nanostructures on the reaction kinetics. Until now, however, kinetic analysis of processes realized with the participation of different types of active sites is far from sufficient.

The aim of this study was to gain a better understanding of some linked aspects of the selectivity of complex processes occurring on supported multifunctional catalysts. The approach suggested is associated with the necessity to consider (1) the nanostructure character of the active phase and (2) the participation of active sites differing in coordination, configuration, adsorption, and catalytic properties in the performance of multifunctional heterogeneous catalysts. To avoid additional complexity of the mathematic solutions at the present level of the approach, we skip from consideration of the electronic effects and lateral interactions.

## 2. Approach

In Refs. [17,47–51], we suggested an approach providing a way to consider the participation of several types of active sites in the operation of heterogeneous catalysts. For avoiding contradiction with the Langmuir–Hinshelwood kinetics, this approach assumes that in case  $n$  types of active sites participate in the catalytic performance, the catalyst surface can be modeled as consisting of  $n$  coexisting ideal adsorbed layers, each of which can be specified by own intrinsic characteristics. The function of current overall catalyst activity  $a(t)$  can be presented as a vector sum of the individual activity functions ( $a_j$ ) associated with the action of the particular active site types:

$$a(t) = \sum_{j=1}^n a_j(t) \quad (1)$$

Furthermore, we consider the fact that the active phase dispersed on the carrier often constitutes nanosized fragmentations comprising a finite number of active metal surface atoms. To avoid misunderstanding in the further, so far as these fragmentations are called by different authors “particles”, “clusters”, “islands”, and so forth, it is worth itemizing some of the notions and terms used in this study. We shall designate the aforementioned fragmentations as “active-phase islands”. The term of “catalytic cluster” specifies an ensemble of several (viz.  $M$  in number) proximal active surface atoms properly located to facilitate a structure-sensitive reaction [32–34].

In Ref. [46], we developed an approach accounting the population of catalytic clusters within the active-phase nanostructures and explored the relation of the size of active-phase islands with the probabilities for action of multisite active centers facilitating structure-sensitive reactions. The goal of this study was to extend the approach

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