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Nanostructure effects on the kinetics and deactivation at reactions over multifunctional catalysts

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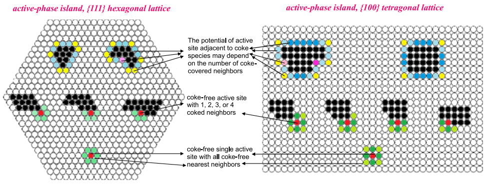
HIGHLIGHTS

- Catalyst deactivation rate depends on the size of supported metal particles.
- Nanosized metal particles are highly sensitive for poisoning and deactivation.
- Multi-centered and single active sites differ in vulnerability level on coking.
- Coking lowers probability for site ensembles catalyzing structure-sensitive routes.
- Active sites edging coke have reduced potential to favor structure-sensitive steps.

GRAPHICAL ABSTRACT



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ABSTRACT

This study brings into focus some nanostructure-size effects on the deactivation kinetics at reactions over supported multifunctional catalysts. The active phase dispersion as nano-sized islands on the support predetermines diversities in the action of active sites depending on their location and structure. In view of this, the applied approach assumes participation of active site types differing by coordination, configuration and contribution to various reaction routes. The suggested model concerns regularities associated with the availability of active surface atoms in proper arrangements which facilitate structure-sensitive reactions. Problems linking the vulnerability of active sites with their geometry and structure are put to discussion. Furthermore, the model relates the probabilities for action of different site types to the size of active-phase islands. The effect of site blockage on the probabilities for existence of multi-site active centers (catalytic clusters) facilitating structure-sensitive reactions is explored. The performed analysis points out that, when matter concerns reactions facilitated by multi-centered active sites, two distinct reasons can be specified, by virtue of which coke species may affect the activity of catalytic clusters: (i) canceling the action of partially or totally coke-covered cluster configurations and (ii) reducing the capability of the adjacent active atoms to construct multi-centered active configurations.

1. Introduction

Detailed study of bi- and multifunctional supported catalysts gains in importance in view of their wide application in industrial processes. Most of these processes are accompanied by coke formation. The presence of active sites of different properties and nature, facilitating networks of mutually dependent reaction

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routes, provokes essential challenges to forecasting the overall effects. For that matter, it is of importance the development of kinetic models reflecting how the contribution of distinct types of sites to the catalytic action is influenced by the diversities in their activities. At the same time, when facing the problems concerning the deactivation of multifunctional catalysts, it should be accounted that active sites differing by nature, configuration, adsorption ability, contribution to different reaction routes (see, e.g. Yang and Satterfield, 1983; Topsøe et al., 1989, 1996; Ozkan et al., 1994; Furimsky and Massoth, 1999), may be vulnerable in different way by the actual deactivation-responsible factors. To this end, thorough examination is required to gain better understanding on various aspects of the phenomena. Adequate models considering the constituent effects are needed for finding resources to reduce the harmful consequences from the deterioration of the catalyst properties. Notwithstanding this necessity, such models are still in deficiency.

The well-known classification of Boudart (1969) specifies two major classes of heterogeneous catalytic processes, specifically structure-insensitive and structure-sensitive reactions. The rate of structure-insensitive reactions depends on the surface concentration of the active-metal atoms, and is not significantly influenced by the sizes of the moiety containing the active component. As shown in a series of works (e.g., Biloen et al., 1977, 1979; Broekhoven et al., 1985; Cortright and Dumesic, 1994; Ribeiro et al., 1994), one or two adjacent surface atoms can facilitate structure-insensitive reactions. Conversely, the rate of structure-sensitive reactions can be markedly changed when changes of metal dispersion, crystal planes or defect structures take place. Typical examples are hydrogenolysis, isomerization, polymerization, cracking, coke formation. These reactions are facilitated by the so-called catalytic clusters (Sinfelt, 1973, 1977, Slinkin, 1981) – principally, ensembles involving several (M) atoms of the active metal in proper configuration for multiple-site adsorption (Sinfelt, 1973, 1977; Anderson, 1973; Biloen et al., 1977, 1979; Slinkin, 1981; Laine, 1983; Broekhoven et al., 1985, Ho, 1988; Meitzner et al., 1988; Perot, 1991; Cortright and Dumesic, 1994; Ribeiro et al., 1994; Jablonski et al., 1999; Bendarova et al., 2002).

Bond (1985) advanced observation and theoretical arguments that certain peculiarities in the behavior of supported catalysts can be interpreted as evidence for the availability of more than one type of active sites, each being characterized by individual configurations of the constituent surface atoms and specificity of the kinetic parameters. He points in his working hypothesis that catalysts may change from favoring structure-sensitive reactions (e.g. hydrogenolysis) to favoring structure-insensitive reactions (e.g. dehydrogenation) in result of alterations (including poisoning or coke formation) which reduce the average size of the entities of the active metal.

Furthermore, the dispersion of the active phase of catalysts as nano-structures on the support gives rise to diversities in the properties of active sites depending on their geometry and location.

The differences in the coordination of sites arising from their location (internal or interfacial) within the island structures, may call forth differences in catalytic properties and stability of action. The active sites located on the interface of the active phase with the support are coordinately unsaturated, and may be hence classified as similar to the pattern of the crystalline edges and corners. The analysis performed in Yang and DePristo (1994) points out that the free energy of the internal atoms depends on the size of the island, contrary to the energy values characterizing edge and corner sites. The internal and the interfacial sites may facilitate different reaction routes. In general, the routes catalyzed by various types of sites should follow different kinetic regularities. The geometric factors may result in ligand effects. Problems associated with the ratio of internal and interfacial active sites gain in actuality in view of the growing interest for elucidating the action of supported Au catalysts (e.g., Haruta et al., 1993; Bond and Tompson, 1999; Cortie and Lingen, 2002). Following the understanding that interfacial sites may exhibit unique activity (Somorjai, 1992), various models have been advanced, aimed to explain the catalyst behavior with due regard for the properties of internal and interfacial active sites.

Recently, Parmon (2007, 2010) adduced thermodynamic considerations that if the number of active centers contained in a given nanostructure is smaller than a certain critical value $N_{cr} \approx 100$, this can modify the adsorption and catalytic properties of the comprised active metal atoms. On applying the thermodynamic analysis derived (Parmon, 2010) and the Temkin theory (Temkin, 1979) for reaction kinetics exhibited on nonuniform catalyst surfaces, Murzin put to discussion the impact of size effects on the kinetics of several catalytic processes (Murzin, 2009, 2010a, 2010b). Qualitative analysis and numerical calculations evidenced that the kinetic regularities can vary depending on the size of the nanostructures on which the reactions are proceeding.

Kinetic analysis of processes realized with participation of different types of active sites, are still scarce. The considerations corresponding to the theory of real adsorbed layer (Roginsky, 1960; Kiperman, 1979; Rutkin and Petersen, 1979; Temkin, 1986; Boudart, 1986) require sophisticated mathematical processing, especially in concern of medium surface coverage. The models frequently considered are developed within the frames of the conventional Langmuir–Hinshelwood kinetics, by tacit consent ignoring the effects reasoned by surface non-uniformity. Yet, under conditions of medium coverage, effects conditioned by non-uniformities of the catalyst surface may outgrow some of the postulates for the ideal adsorbed layer. The uncertainty whether it is convenient to apply the related approximations imposes an essential theoretical barrier for deriving kinetic models considering the participation of sites with different properties.

The problem gains in complicity when the effects of catalyst deactivation have to be considered. The reaction networks of many complex processes involve routes resulting in formation of species deteriorating the catalyst activity. Coke formation may be considered as the most common reason for catalyst deactivation. The generation of coke precursors is a structure-sensitive reaction, requiring multi-centered catalytic clusters.

Deeper insight on these phenomena requires linking the problems of nonstationary or quasi-stationary reaction proceeding and problems associated with diversities in the properties and vulnerability of the different types of active sites.

Murzin (2002) suggested an approach for the kinetic description of processes occurring through a surface collision of species adsorbed on two distinct sites of different nature. The model proposed in Liberkova et al. (2002) describes the activity and selectivity of a Pt/SnO_2 catalyst in terms of apolar and polarized types of sites, characterized by different deactivation profiles.

Facing the necessity to account for effects called forth by non-uniformity of the catalyst surface, special models have to be derived for processes involving active sites of different action, properties, structure and vulnerability. Given the fact that coke formation is a structure sensitive reaction, it is both of academic and practical interest the development of models focused on the participation of various active site types in processes accompanied by catalyst deactivation.

2. Approach

In this study, we shall try to model the geometric factors determinative for the availability of active sites facilitating structure-sensitive and structure-insensitive reactions, and for the related coke-caused variations of the catalyst action. Accordingly, it is desirable to distinguish the contribution of active site types characterized by different structure and properties.

In view of avoiding discrepancy with the Hinshelwood–Langmuir kinetics, we developed an original approach (Kumbilieva and Petrov,