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Abstract

This paper focuses on the problem of active sites in heterogeneous catalysis through a review based on three examples from the literature, namely metal nanoparticles, zeolites and transition metal oxides (redox MvK-type mechanism). Self-organizing phenomena in catalysis may reflect various complexity structures, including the self-repair and reorganization of active sites, the mutual interactions between neighbouring sites, the mass transfer limitations (i.e. shape selective control), the dynamic active networks of “sites-joined”, and so on. These phenomena may give rise to non-linear dynamics in catalytic processes. The latter typically result in a non-linear combination of distinct complexity structures and hence catalytic behaviours may appear with multicomponent systems, as zeolites and mixed oxides. Thus, the algebraic hyperstructures are introduced as a model to describe the complexity of catalysis. The solid catalyst acts as a hyperoperator computing a non-linear combination of complexity structures, namely multivalued operation (\circ). This hyperoperation is weak associative since the complexity structures (sets) contain the n -polytopes as common elements. As a result, the complexity structures in catalysis belong to Hv-structures, the largest class of hyperstructures which satisfy the weak properties.

Keywords: Catalytically active sites; self-organizing phenomena; complexity structures; hyperstructures; Hv-structures.

1 Introduction

The active sites represent the "heart" of a catalyst and hence it is not surprising that a large number of theoretical studies and experiments in the field of heterogeneous, homogeneous and enzymatic catalysis focus on the characterisation of active centres present on the catalyst surface.

In recent years, considerable progress has been made in the characterization of catalytic reactions at solid surfaces. Indeed, thanks to the development of *in-situ* spectroscopies and to advanced scanning probe techniques, it has been possible to study active sites under working conditions and to investigate the elementary processes underlying a reaction on an atomic scale [1]. As a result, many investigations have confirmed that active sites are dynamic entities that can continuously change their physico-chemical properties depending on the reaction conditions [1,2]. Dynamic STM analysis also revealed that active centers may include more than one single site to form "reactive networks" [3-5].

A "real" catalyst surface is structurally and compositionally complex and multifunctional interface, exposing various adsorption/reaction sites. Thus, the surface properties have their relevant consequences on the chemical reactivity [6,8]. Moreover, there is an important aspect contributing to the gap between surface science and catalysis, that is related to the reaction mechanism and can be denoted as "chemical complexity". Catalytic reactions may involve mixtures of several reactants and/or intricate reaction networks with multiple steps and pathways [9,10]. Typically, the more complex the reaction mechanism, the slower the turnover rate as the elementary reaction steps involve more complex molecular rearrangements [11]. The catalyst has to regenerate itself through the desorption of products and the self-repair of active sites after each catalytic cycle.

During a reaction, the catalyst surface typically receives a mix of fluctuating molecules (i.e. reactants, products, poisons, etc.) and hence many active centres (or regions) on the surface may interact with each other through mass/heat transport phenomena and surface strain [2,7]. This suggests that solid catalysts operate through sophisticated self-organizing phenomena, in which both structural parameters and kinetic effects play a role [6].

The concept of "self-organization" indicates the order formation in both thermodynamically closed and open chemical systems [2]. Closed systems tend to reach the equilibrium conditions by reducing their free energy,

although kinetic constraints may limit the attainment of equilibrium. On the contrary, open systems far from the equilibrium (i.e. reactions at steady-state flow conditions) exhibit the interaction between chemical kinetics and transport phenomena. Moreover, there is an unexpected relation between the chemical kinetics and the space-time structures of reaction systems. These systems belong to the class of irreversible processes creating entropy and may be described through kinetic equations with broken time symmetry instead of canonical equations [12].

Non-equilibrium systems were first studied by I. Prigogine [13] who denoted them as “dissipative structures” and were later incorporated in the framework of synergetics by H. Haken [14]. Specifically, Prigogine showed the complexity of time in non-equilibrium systems, through the concepts of symmetry breaking, irreversibility and time’s arrow. Consequently, catalytic reactions cannot be reduced to classical dynamics or quantum mechanics in deterministic, time-reversible descriptions [12]. However, it is impossible to know exactly the spatio-temporal self-organizing phenomena occurring in systems far from equilibrium due to fundamental limitations having their origins in the mathematical structures [8]. Noteworthy, the causality condition on a space-time appears inaccessible by strictly deterministic processes and the complexity of time is still greater than one can imagine in a linear framework.

Such effects have been experimented with CO oxidation over Pt single crystal surfaces by G. Ertl [2,8,16]. Indeed, under certain external conditions (i.e. p_{CO} and temperature) the Pt surface can alternate between two states, showing regular oscillations in reaction rates. However, at high CO pressure values ($p_{\text{CO}} > 5 \cdot 10^{-5}$ mbar) a new irregular behaviour occurs, giving rise to chaotic phenomena.

Self-organization phenomena appear in different regions of the solid surface and the interactions which determine the values of relevant kinetic constants and transport coefficients mainly depend on short-range forces [8,15].

In open systems where different entities, such as atoms, molecules, defects, and so on are able to move and interact with each other, phenomenological rate equations of the concentrations of the reactant species are usually derived from material, energy or momentum balance equations, leading to reaction-diffusion dynamics. Consequently, the resulting spatio-temporal concentration patterns are no longer governed by atomic dimensions but

through the so-called diffusion length. Thus, the temporal evolution of the resulting concentration patterns in open systems far from the equilibrium can be described through a set of non-linear partial differential equations, combining the chemical kinetics with the diffusion processes of the adsorbed species, as follows:

$$\frac{\partial x_i}{\partial t} = F_i(x_j) + \nabla^2 D_i x_i$$

where x_j are the state variables (i.e. surface concentrations) of the reacting chemicals, F_i are the non-linear operators expressing the chemical kinetics, D_i are the diffusion coefficients and p_k are a set of parameters [16].

In fair agreement with our previous studies [17,18], in the present work we investigate the complexity of active sites in heterogeneous catalysis through a review based on three examples from the literature, namely metal nanoparticles, zeolites and transition metal oxides acting via redox MvK-type mechanism. Moreover, the hyperstructures are proposed as a model to describe the complexity of catalysis. Introduced in 1990, the Hv-structures proved to have a lot of applications in several applied sciences, such as linguistics, biology, chemistry, physics, and so on [20].

Algebraic hyperstructures are a natural extension of classical algebraic structures: in an algebraic structure, the composition of two elements is an element, while in an algebraic hyperstructure, the composition of two elements (i.e. reactant molecules) is a set (i.e. the reaction products) [19,20]. Thus, it will be proved that various complexity structures in catalysis belong to the Hv-structures, the largest class of hyperstructures which satisfy the weak properties [19].

2 Metal clusters and nanoparticles

The chemical reactivity of nanostructured systems is often related to the size and shape of the metal particles (= structure-sensitive reactions), as well as to the nature of the support materials [21-24]. On the contrary, in structure-insensitive reactions all the surface sites exhibit comparable reactivity on several planes of a single crystal. For instance, hydrogenation reactions are usually structure-insensitive since they can occur in many different arrangements of surface atoms. This is mainly due to the fact that