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A brief history of the science of catalysis II: from polytopes to hyperstructures

KEYWORDS: active sites, self-organizing phenomena, complexity structures, hyperstructures, polytopes

Abstract The possibility of detecting active sites and molecules in complex environments, and following their evolution, has revolutionized the field of heterogeneous catalysis over recent decades. It has been shown that active centres are not static at solid surfaces and may interact with each other through transport phenomena and structural flexibility. These interactions lead to spatio-temporal self-organization phenomena, in which both structural and kinetic effects play a role. As a consequence, catalytic reactions typically result in non-linear combinations of complexity structures of active sites. In this scenario, hyperstructures (namely Hv-structures) have recently been proposed as a model to describe the complexity of catalysts.

ACTIVE SITES AND COMPLEXITY STRUCTURES

During the last few decades, significant developments have been made in the study of reactions at solid surfaces, showing that a catalytic surface may change under experimental conditions (1-3).

Thanks to the development of in-situ spectroscopies and to advanced scanning probe techniques, it has been possible to investigate the active sites under reaction conditions and to identify the elementary steps underlying a reaction on an atomic scale (4, 5).

Nowadays, the most recent milestone in the development of these methods is represented by four-dimensional ultrafast electron microscopy (4D UEM), in which ultrafast laser techniques are combined with electron microscopy, allowing the motion of single atoms to be studied on a timescale of femtoseconds (6). The transmission electron microscope (TEM) is a powerful tool that enables the visualization of materials with length scales smaller than the Bohr radius, though a high resolution visualization of structural changes occurring on sub-millisecond time scales is not possible. In UEM, images are obtained either stroboscopically with coherent single-electron packets or with a single electron bunch. Coulomb repulsion is absent under the single-electron condition, thus allowing imaging, diffraction and spectroscopy at the atomic scale (7). Thus, it has been shown that active sites are dynamic entities that can continuously adapt their physico-chemical properties in various environmental conditions (3, 5, 8). Moreover, complementary techniques have revealed that active centres may involve more than one single site

to form "catalytic active networks" (9, 10). For instance, in the hydrogen adsorption on the Pd(111) surface, a cluster of three or more vacant sites is required to form a reactive network for efficient H₂ dissociation, as confirmed by dynamic scanning tunnelling microscopy (STM) and density functional theory (DFT) (9).

Similarly, oxidation reactions catalysed by transition metal oxides may occur via a Mars van Krevelen (MvK) mechanism (11), whereby the active sites are not isolated species, but groupings of atoms (ions) and electrons mutually interacting in an active network (Figure 1) (11-14). These dynamic systems exhibit sophisticated self-organization phenomena and the reduction-oxidation cycles occur in a fractal dimension greater than 3 (namely 3 + e, where e represents the dimension of the boundary) (14). Noteworthy, the high complexity of these systems further depends on the fact that cations may act simultaneously as Lewis acidic and redox centres, whereas oxygen ions on the solid surface perform as Lewis bases and electron donors. These results have recently been observed for the VOC total oxidation over manganese oxide catalysts (15). Synergistic effects among active sites (or among

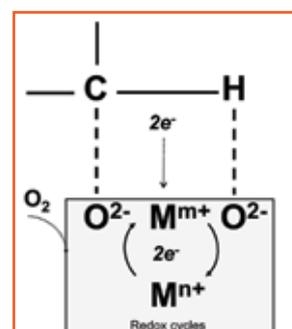


Figure 1. Schematic representation of the Mars van Krevelen mechanism.

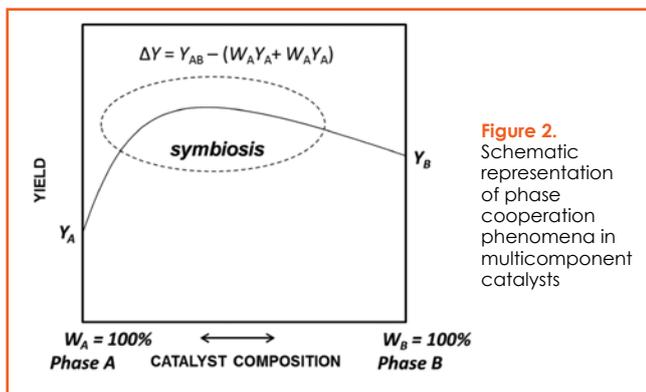


Figure 2. Schematic representation of phase cooperation phenomena in multicomponent catalysts

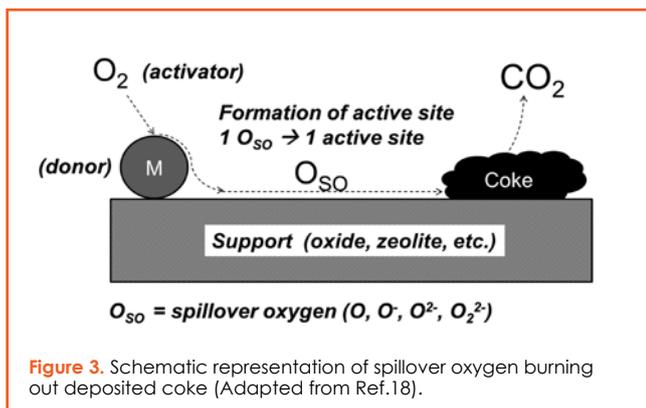


Figure 3. Schematic representation of spillover oxygen burning out deposited coke (Adapted from Ref.18).

different phases) may appear through phase cooperation and spillover effects (3). Phase cooperation (Figure 2) deals with the concept that two phases (A and B) of complimentary properties, when brought into intimate contact with each other (namely the mixture AB, in the nanoscale domain), may cooperate synergistically to give better performances (e.g. in terms of yields) than can be obtained by either of the two phases operating separately and independently from each other (16). In other words, the magnitude of the synergetic effects can be expressed as:

$$\Delta Y = Y_{AB} - (W_A Y_A + W_B Y_B)$$

where Y_{AB} , Y_A and Y_B are the yields of the mixture AB, phases A and B, respectively, measured under the same operating conditions; W_A and W_B are the weight percentages of phases A and B in the mixture AB (17, 18). On the other hand, spillover (Figure 3) involves the transport of an active species (spillover species) adsorbed or formed on one phase (donor phase) onto a second phase (acceptor) which does not form the active species under the same conditions. The first evidence for spillover originates from Khoobiar (19), who observed the formation of the hydrogen spillover from Pt, on which dihydrogen chemisorbs dissociatively onto WO_3 with the formation of the hydrogen bronze (H_xWO_3). Besides hydrogen spillover, oxygen spillover has been extensively investigated because of its key role in many oxidation processes catalysed by mixed oxides (18, 20). As a result, Delmon et al. (18) formulated the "remote-control" concept to explain the fact that many industrial catalysts used for the partial oxidation of hydrocarbons or in hydrotreatment reactions are multiphasic and that particular phase compositions give rise to synergy effects. It has been established that a "real" solid surface is structurally and compositionally complex, exposing various

adsorption/reaction sites. Moreover, as already observed by I. Langmuir "the surface atoms are not rigid but tend to arrange themselves so that the total energy will be a minimum" (21). Inward relaxation and reconstruction of solid surfaces occur via self-repair phenomena and are much more marked at low coordination sites (e.g. steps and corners) which are more "flexible" and self-repair themselves at higher rates (22). These phenomena reflect the intrinsic property of catalysts to regenerate active sites after each catalytic cycle, and represent the lowest level of self-organization at solid surfaces (23).

As a whole, small metal/metal oxide particles are more reactive than larger ones, since the electronic state and defect density change markedly at a critical size of few nanometers (ca. 2.7 nm). Moreover, the relative amounts of edge, corner and terrace sites are shape-dependent, and hence distinct geometries lead to different reactivities (24). The small particle size maximises surface active sites and modifies their electronic structure which becomes discrete. The surface energy depends on the nature of the facets. For a crystallite consisting of an ensemble of atoms, the equilibrium shape is the geometry which minimizes the surface free energy (in Wulff's sense) (24). Since the catalyst surface is multi-faceted, its catalytic properties also depend on the orientation of each crystalline plane. This dependence can be expressed in terms of the corresponding Miller indices (h, k, l) or, equivalently, the unit vector normal to the plane:

$$\mathbf{n} = (n_x, n_y, n_z) = \frac{(h, k, l)}{\sqrt{h^2 + k^2 + l^2}}$$

This anisotropy mainly concerns the activation energies, which can be expressed by cubic harmonics (25) as

$$E_x(\mathbf{n}) = E_x^{(0)} + E_x^{(4)}(n_x^4 + n_y^4 + n_z^4) + E_x^{(6)}(n_x^2 n_y^2 n_z^2) + \dots$$

for face-centered cubic crystals such as rhodium or platinum. Since the coefficients of this expansion can be fitted to data collected for a set of crystalline planes, the knowledge of the activation energies can be obtained for different planes. It has been shown that a solid catalyst acts through sophisticated self-organizing phenomena, in which both structural complexity and kinetic parameters play a role (26, 27). In fact, the catalyst surface typically receives a mix of fluctuating molecules (e.g. reactants, products, poisons, etc.) and hence active centres (or regions) on the surface may interact with each other through mass/heat transport phenomena and structural flexibility.

The resulting spatio-temporal 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:

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

where x_i are the state variables (e.g. 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 (30). In fact, the concentration patterns are no longer governed by atomic dimensions but through the so-called diffusion length.

Ertl studied the resulting spatio-temporal concentration patterns on Pt(110) surfaces during CO oxidation showing that these phenomena occur in different areas of the catalyst surface and require some forms of interaction among different sites (or regions) and self-organization in the mesoscopic domain (namely in the 10 nm – 10 µm range) (28).

It is worth recalling that rate oscillations or even irregular (chaotic) behaviour on the surface occur during catalytic reactions (29). These phenomena were first reported in 1970s by Wicke et al. for CO oxidation on Pt-based catalysts (30). Later, Ertl et al. observed that under certain operating conditions (namely pCO and temperature) a well-defined Pt(110) surface can alternate between two states, displaying regular oscillations in reaction rates (28). These remarkable results suggested that self-organizing phenomena at solid surfaces reflect different complexity structures of active sites, such as the self-repair and reorganization of active sites, the interactions among adjacent sites, the dynamic networks of "sites-joined" and so on (Figure 4) (14, 31). It has also been observed that mass/heat transfer phenomena further increase the complexity of these systems. Consequently, the catalytic behaviour of multi-component catalysts (e.g. zeolites, metal oxides, etc.) typically result in a non-linear combination of complexity structures and are therefore different from a sum of elementary behaviours (31). This means that we need an other approach, in fact an holistic one. One possibility is the use of the Theory of Hyperstructures.

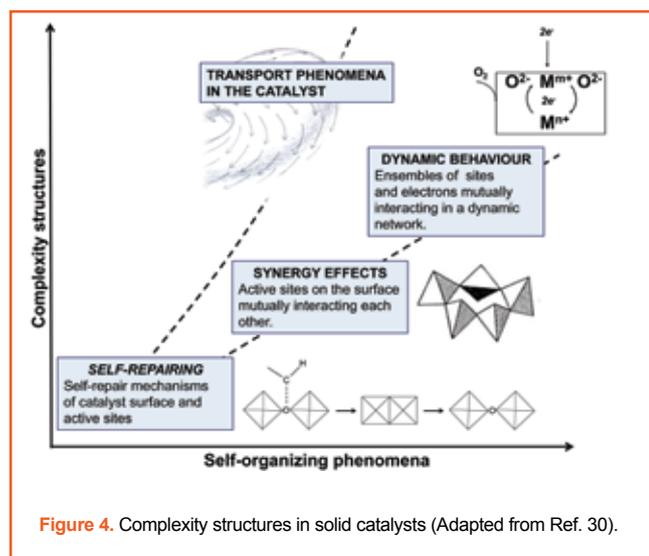


Figure 4. Complexity structures in solid catalysts (Adapted from Ref. 30).

TOWARD THE THEORY OF HYPERSTRUCTURES

First introduced in 1934 with hypergroups, by the French mathematician F. Marty (32), the algebraic hyperstructures represent an extension of the classical algebraic structures. In fact, in an algebraic structure the composition of elements is still an element, while in an algebraic hyperstructure the composition of elements is a set (32).

According to Marty's theory, a hyperstructure is every algebraic structure in which at least one hyperoperation is defined. The hyperoperation (\circ), or multivalued operation, in a set H is any operation which maps to two elements x, y of H into a subset $x \circ y$ of H (32,33).

This map is written as follows

$$\circ : H \times H \rightarrow P(H) - \{\emptyset\} : (x,y) \rightarrow x \circ y \in H$$

where $P(H)$ is the power set of H . Thus, a hyperstructure (H, \circ) is a hypergroup if (\circ) is an associative hyperoperation for which the reproduction axiom:

$$hH = Hh = H, \forall h \in H$$

is valid (in Marty's definition) (32).

Later, in the 1990s, T. Vougiouklis discovered the H_v -structures which have enumerated by N. Lygeros (33-35), the largest classes of hyperstructures. The essential idea which allows the existence of these H_v -groups is the weak associativity.

Then, the hyperoperation is called weak associative (WASS) if

$$(xy)z \cap x(yz) \neq \emptyset, \forall x, y, z \in H$$

This axiom means that the two sets $(xy)z$ and $x(yz)$ have at least one common element for all x, y, z in H (33, 34).

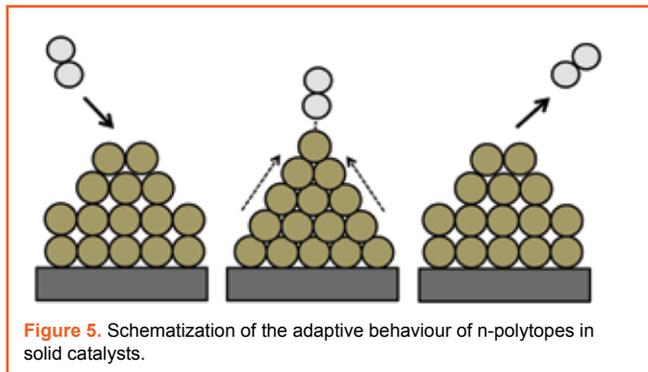
The hyperstructure (H, \circ) is defined H_v -semigroup if it is WASS, whereas it is named H_v -group if it is a reproductive H_v -semigroup according to the reproduction axiom (vide supra) (35).

Since their discovery, the H_v -structures have proved to have applications in several fields (e.g. linguistics, biology, chemistry, physics, and so on) and many papers have been written on this topic (36-39). In the science of catalysis, hyperstructures have recently been proposed to describe the complexity of heterogeneous catalysts (14). In fact, the complexity structures of active sites belong to the H_v -structures, the largest class of hyperstructures which satisfy the weak properties.

During a reaction, the catalyst acts as a hyperoperator, mapping reactant molecules (e.g. x, y) into the class of n -polytopes (= subset $x \circ y$ of H_v). Hence, the products of the catalytic reaction belong to a set which is not a singleton. This hyperoperation is a weak associative because distinct complexity structures (sets) created by the catalytic reaction, contain n -polytopes as common elements. This allows the condition required for the existence of the H_v -structures to be satisfied.

The concept of polytopes has been well established in heterogeneous catalysis. We know that (active) sites are packed into polygonal (2-D) or polyhedral (3-D) shapes, namely n -polytopes, having several planes of symmetry and high packing efficiency. For instance, metal/metal oxide nanoparticles are shaped through the assembly of atoms in three dimensions, and hence their geometrical structures are reflected by 3-D polytopes (3-polytopes). However, small particles are not static but change over time, depending on the reaction conditions, and as a result their geometrical structures may be better described by polychorons (4-polytopes) since they are time related.

Thus, spatio-temporal self-organizing phenomena (e.g. self-repair of surface atoms, concentration patterns, etc.) taking place locally on vertices, edges and terraces during a reaction can be structurally denoted by polytopes variable over time, having 1, 2 and 3 dimensional structures, respectively. In fact, n -polytopes may adapt themselves to the reaction conditions, leading to an optimum fit between the adsorbed species at the surface (Figure 5). As a result, the overall reaction pathway requires lower activation energy in order to occur. Similarly, various self-organizing phenomena may occur in multicomponent catalysts, such as zeolites, and their geometrical complexity can be described through polytopes acting in a discrete 3-D space, as reported elsewhere (14). Since n -polytopes are related to



the geometrical structures of solid catalysts, varying both in space and time, they represent the initial set of the action of hyperstructures (Hv-structures). Because the catch the information created by the hyperoperation, Hv-structures give a manner to compute correctly and simultaneously the products of the catalytic reaction.

CONCLUDING REMARKS

The recent development of *in-situ* characterization techniques has revolutioned our knowledge about the physico-chemical properties of solid catalysts. Nowadays, thanks to advanced experimental techniques, a great deal of information can be obtained at femtosecond time scale about the molecular mechanisms of catalytic processes. However, it is often difficult, and sometimes impossible, to obtain a precise picture of the reaction mechanisms at molecular level, since non-linear dynamics govern self-organization phenomena in catalytic systems. In fact, reactions at solid surfaces typically result in a non-linear combination of complexity structures of active sites. In this context, the algebraic hyperstructures (namely Hv-structures) have been proposed as a model to describe the complex behaviour of solid catalysts.

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