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Revisiting active sites in heterogeneous catalysis: Their structure and their dynamic behaviour

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ABSTRACT

This short review article aims at revisiting the description of active sites in heterogeneous catalysis on solid surfaces and their role in catalyst activity and selectivity. Special emphasis is brought to: (i) structure of the solid surface; (ii) importance of active site isolation on the surface; (iii) dynamic behaviour under reaction conditions and (iv) importance of active phase-support interaction. After a general view on active sites in heterogeneous catalyst, this article describes different case studies of metal oxide catalysts, namely MoO_3 and VPO catalysts, to exemplify the concepts, including active site description, structure and/or electronic sensitivity, synergy effects and dynamic surface behaviour during catalytic reaction. Static and dynamic models are discussed considering the many and different views expressed during the years and all considering active sites as atoms or ensembles of atoms as suggested by Taylor in 1925 and instable catalytic reaction intermediates as proposed by Sabatier in 1913. However, with the years, complex structures and dynamic behaviour with interaction between the active sites and the adsorbates (reactants and products) during catalytic reactions have been identified and characterised. In the latter case surface metalloinorganic or metalloorganic entities, designated as chemadphase, constitute the basis of reaction intermediates and are submitted to continuous oscillations on the surface under steady state. Recent developments in physical techniques used to characterise catalysts, in particular during catalytic reaction, and theoretical approach and modelling are also presented and discussed in view of improved description of active sites.

1. Introduction

Since the great world wide interest to environmental issues, catalysis has appeared as an important domain as it permits to orientate the reaction products towards desired ones, i.e. to limitate undesirable by-products, particularly in the fields of fine and pharmaceutical chemistries, but also in petroleochemistry and oil treatments such as sulfur, particulates, CO_x and NO_x limitation. This aspect of products selectivity, modulable in catalysis, is an important feature for the environmentally more friendly future. Moreover, heterogeneous catalysis, whatever gas–solid or liquid–solid, has appeared more friendly than homogeneous catalysis as it avoids to use organic solvents, although usually less selective, and it facilitates separation of used catalysts and reaction products and to be important for future developments [1].

Catalysis has been defined by Berzelius in the 19th century and the presence of more or less stable reaction intermediates have been first suggested and described by 1912 Nobel prize winner Paul Sabatier [2]. The latter has introduced the concept designated as "Sabatier principle" by which when a reactant is adsorbed on a catalyst surface, its energy of interaction should be strong enough for activation but not too strong to permit products to be desorbed (volcano curve of activity vs energy of adsorption). He has proposed a general explanation of catalytic phenomena based on the idea of the "*temporary formation of unstable chemical compounds which, serving as intermediate steps in the reaction, determine its direction and increase its velocity*". Sabatier was considering these unstable intermediates as bulk species. This was extended [3] further to reacting substances held on the catalyst surface by means of activated adsorption.

Activity and selectivity have been found in heterogeneous catalysis to be dependent on many factors, for instance on catalyst preparation, activation, chemical composition, and on bulk and/or surface crystalline structures, on electronic effects, interaction between an active phase and its support, etc., as it is developed below.

2. General aspects of active sites in heterogeneous catalysis

In 1925, in a landmark contribution to catalytic theory, Taylor [4] has suggested that a catalysed chemical reaction is not catalysed

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over the entire solid surface of the catalyst but only at certain 'active sites' or centres. He has also suggested that chemisorption may be an activated process, and may occur slowly. Moreover, he has conceived the idea that chemically active sites might be composed of an atom or an ensemble of atoms and could be sparse on the surface of a catalyst and, hence, could be inhibited/poisoned with relatively few molecules. The idea that adsorbed species and intermediates in catalysis by metals may require ensembles composed of several adjacent free-surface atoms has also been expressed at the same period by Balandin [5] who suggested that a reacting molecule may be simultaneously adsorbed on several atoms. He presented the "*multiplet theory*" which considers bond lengths and bond energies as well as geometrical forms of reacting molecules and of crystal lattice of the solid catalyst. He introduced the principles of structural and energetic correspondence between the reacting molecules and the atoms of the catalyst.

Since then, this model proves to be versatile: it is frequently invoked to account for various catalytic phenomena such as alloying effects, size sensitivity, poisoning, and compensating effects [6–8]. It is also useful in the field of kinetics, in a number of catalytic reactions involving hydrogen and hydrocarbons, such as deuterium/hydrocarbon exchange, hydrogenolysis and hydroisomerisation. Hydrogen exhibits a strong inhibiting effect, which has been accounted for assuming that the reaction takes place on patches composed of a certain number of metal atoms. The complex kinetic behaviour of the exchange reaction over Rh films [6] or Ni/SiO_2 catalysts [9] and of hydrocarbon hydrogenolysis over Ni/SiO_2 [10] have been described by using only two parameters: the true activation energy, and the nuclearity of the active site, considered as an ensemble composed of several adjacent free metal atoms. Heterogeneity of a metallic surface for active sites is well accepted. As a matter of fact, it is obvious that atoms located at surface steps or kinks are stereochemically different from one another and less fully coordinated to other atoms than those at terrace sites and flat exterior surfaces. Typically on (1 1 1) face of a face-centred cubic (fcc) metal such as platinum, there are clearly three distinct adsorption sites, namely atop, bridge, and hollow, for small molecules to be bound. It is not surprising that the enthalpy of adsorption as a function of surface coverage decreases and that a temperature-programmed desorption presents several peaks, which reflect the variety of energetic situations associated with the adsorbed species. The same kind of approaches hold true for other catalysts such as metal oxides, sulfides, etc. In such cases one speaks about defects, shear planes, etc. (vide infra) corresponding to different surface entities.

Boudart [11] has then proposed to subdivide catalytic reactions into "structure sensitive" (demanding) and "structure insensitive" (facile) reactions. In the former case the reaction rate changes with the crystallographic face exposed to the reactants. Conversely in the later case, this rate is independent. For instance, hydrogenolysis of ethane ($C_2H_6 + H_2 \rightarrow 2CH_4$) and ammonia synthesis are good examples of structure sensitivity [12], whereas CO oxidation or benzene hydrogenation have been considered at that time as structure insensitive. As a general rule C—C or N—N breaking involves structure sensitivity while breaking or formation of H—H, C—H or O—H bonds are structure insensitive. In the later case, the active sites are simpler, often as isolated atoms, while structure sensitivity involves ensembles of surface atoms. Sensitivity to such two parameters was demonstrated for metals [13], such as Pt, Ni, etc. in the 60–70s and for oxides [14] in the 80s. In reality, such a concept of structure sensitivity was first mentioned by Beeck for Ni catalysts [15] and first observed by Gwathmey and Cunningham [16]. Note also that recent papers have shown, at variance with Boudart's conclusions, that CO oxidation may also be structure sensitive on different catalysts such as Pd-Pt/Al_2O_3 [17], Au/TiO_2 [18], CeO_2 [19], Co_3O_4 [20] and many other catalysts.

For bimetallic surfaces, the environment of the metal sites has been found to be determining. The second atom, if inactive itself, reducing the number of active atoms of the first metal, permits the site to be active or not, depending on the number of atoms necessary to activate an adsorbed molecule. For instance, this phenomenon was clearly observed for Ni–Cu bimetallic catalysts for hydrogenolysis reactions [21]. Using magnetic measurement technique Martin [22] have shown that, for benzene hydrogenolysis, the reaction needs 6 surface nearby Ni atoms for adsorbed benzene and 2 for hydrogen adsorption, i.e. a surface ensemble of 8 nearby Ni atoms. When adding Cu as inert dilutant, activity rapidly decreased with Cu content as far as such ensembles of 8 Ni atoms are destroyed. At variance, for the hydrogenolysis of ethane 2 nearby Ni atoms were constituting the active sites [23,24]. The activity was found to be proportional to surface Ni content and to decrease for a given concentration of inactive Cu atom, i.e. when a number of nearby Ni atoms were replaced by Cu atoms and no more Ni dimers were present. The amount of Cu atoms necessary to deactivate Ni surface was obviously much higher in the second case than in the former case as 2 Ni nearby atoms were necessary against 8. Note that promoters are often added to solid catalysts. They can lead to either change in crystallographic phases or/and have an electronic effect and can act also as site isolation agent (vide infra). More recently, for AuPd nanoparticles with Au/Pd > 10, Pd was shown [25] to migrate to the surface under calcination and to enhance activity while maintaining the selectivity for 1–3 butadiene selective hydrogenation to butene in presence of propene. It was also suggested that dimers of Pd decreased the selectivity. This atom migration, under catalytic reaction conditions, shows the dynamic behaviour of a catalyst surface and that active site characterisation needs real "in-situ" characterisation, as we will discuss below.

According to the model of ensembles, most of the kinetic features of a catalytic reaction can be described by a simple equation involving only two adjustable parameters, the true activation energy, E_o, and the nuclearity, X, of the active site which consists of an ensemble composed of X adjacent free metal atoms. It was shown [23] that, for a given reaction, X does not change from one metal to another (CH_4-D_2 exchange over Ni and Rh). In contrast, it varies dramatically from one reaction to another, addition reaction being associated with low X values, and reactions involving C—H and C—C bond cleavage requiring progressively larger nuclearities.

The above description considers active sites as rather static. However, we have just seen above and we will see below that a catalyst surface may change under reaction conditions. Moreover, it is worth recalling that oscillations on the surface occur during catalytic reaction [26], phenomenon which is important for kinetics studies and a theory was proposed [27]. It was shown [28] that stationary heterogeneous catalytic reactions involve a gas/catalyst equilibrium, which exists always in the course of stationary catalytic reactions, acts on the rate-determining step (RDS) of the reaction. It was suggested that the gas/surface equilibrium recommences much faster than the reaction products form. Moreover, during stationary catalytic processes, the surface is covered with many two-dimensional chemisorbed crystal-like islands of different sizes rather than with isolated chemisorbed molecules. Depending on the chemical nature of the catalyst and of the reacting mixture and on the ambient conditions, these islands can be of the same or of two and more chemical compositions. Each ensemble of these islands of any one chemical composition is considered as a two-dimensional chemically adsorbed phase (chemadphase, ChPh). This phase oscillates, i.e. changes continuously its form and size, and thus moves relative to other islands over the surface of a crystal in such a way that, under stationary catalysis, the total surface area of each ChPh remains unchanged in time. In other words each of the ChPhs is in equilibrium with the reacting medium