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THE IMPORTANCE OF ACTIVE SITE STRUCTURE ON THE APPEARANCE OF PERIODIC TRENDS OF CATALYTIC PROPERTIES

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Periodic trends of catalytic properties of sulfide, oxide and metal based catalysts are proposed to result not only from an electronic effect but also from a variation of the population of surface species. A simple model is used to show that the optimum heat of formation of the compound lead to an optimum surface density of species and thus to a maximum number of site possessing an adequate structure for the reaction considered to occur.

The catalytic properties for a given reaction of transition metal sulfides [1–9], oxides [10,11] or metallic catalysts [12] with close textural characteristics are known to depend on the position of the transition metal in the periodic table. These trends lead to curves with a maximum or so-called "volcano" curves when the catalytic activity is plotted versus the heat of formation of the compounds. Usually variation of the activity over several order of magnitudes are found.

In the case of sulfides more particularly emphasized in this work, various examples of volcano curves have been reported in the literature. Either bulk [1,3,7], carbon supported [4–6,9] or alumina supported [2,8] sulfides give volcano curve for hydrogenation [7,8], hydrodesulfurization [1–5], hydrodenitrogenation [6,9] and hydrodeoxygenation [8] reactions. In addition the volcano shape is found for different experimental conditions ranging from atmospheric to high pressure and temperature of reaction from 500 K to 700 K. Similar observations can be made for oxides [10,11] or metallic catalysts [12] denoting the universality of this phenomenon.

An empirical formulation of these trends is the well known Sabatier principle stating that solids showing the maximum activity for a given reaction will have intermediate heat of formation [13]. Assuming that the metal-heteroatom bond strength is monotically dependent on the heat of formation of the compound, an other formulation of the Sabatier principle is that the more active solid must have metal-heteroatom bond energy not too strong nor too weak.

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Attempts to find a theoretical basis to such principle have been recently done by Harris and Chianelli in the case of bulk sulfides catalysts [14]. Using the Scattered Wave Xα method to study the electronic structure of series of octrahedral MS_6^{n-1} clusters these authors have been able to find a parameter following the same trend as the catalytic activity. This parameter resulted from a combination of two factors namely the number of metal d electrons in the highest occupied molecular orbital and the relative metal-sulfur d-p covalent bond strength. In view of this the electronic origin of the volcano curve was underlined.

There is however an important consequence of the variation of the metal-heteroatom bond strength that is often not fully considered which is the variation of the population or density of heteroatomic species on the surface of the catalyst. High metal-heteroatom bond strength will give higher density of heteroatomic species than small one. Therefore the necessity to get an optimum bond strength to have good activity is equivalent to the necessity to get an optimum heteroatomic species density on the surface.

The aim of this work is to give a complementary insight into the understanding of the volcano curves by taking into consideration the question of the variation of the population of surface species and using the concept of site structure or architecture [15]. Although sulfide catalysts will be mainly discussed it is meant that the approach is of interest for oxides and metallic catalysts in view of the generality of the phenomenon as underlined above.

Recent work from this laboratory have shown that the population of surface sulfur species of the MoS_2 cristallites of $MoS_2/\gamma Al_2O_3$ [16] or bulk MoS_2 [17] catalysts can be monitored by hydrogen reduction of the catalyst at increasing temperature. When probing these sulfur deficient catalysts using the low temperature (323 K) diene hydrogenation reaction, a volcano curve is obtained for the diene hydrogenation activity versus the temperature of prereduction or the S/Mo ratio. The benefit of performing the catalytic reaction at low temperature after such reduction was to keep the S/Mo ratio stable during the test.

Three types of sulfur ions have been identified on MoS_2 [16,18]. A terminal sulfur ion in the (1010) edge plane, a bridged one in the (1010) edge plane and the basal plane sulfur ion. The activity variation have been found to result from the removal of the bridged sulfur from the (1010) edge plane of the MoS_2 slabs in the temperature range 473 to 973 K. It can be shown that this edge plane is the only one containing Mo ions that can be up to 4-cus and therefore generate Mo ion possessing 3-cus and one sulfur ion which is a requirement to get a hydrogenation site according to Siegel's proposals [19].

The volcano curve of the activity versus the S/Mo ratio has therefore been interpreted as a variation of the number of diene hydrogenation sites. These sites have an appropriate structure understood in a first approximation as an optimum number of sulfur species and vacancies on a Mo ion i.e. neglecting the presence of hydrogen either in the form of SH^- group or Mo-H* species. Then it has been shown by using a simple statistical calculation that the maximum of the activity corresponded indeed to the maximum number of 3-cus Mo ions present on the active (1010) crystallographic plane of MoS_2.

Other evidence of the importance of the site structure are obtained when looking at the diene isomerization activity variation with the S/Mo ratio [20]. Both 2-cus and 4-cus Mo ions have been found necessary to get isomerization. The statistical amount of 2-cus Mo ions gives also a volcano curve whereas the statistical amount of 4-cus Mo ions gives a monotically increasing curve when the S/Mo ratio decreases. The sum of these two curves have been found to fit nicely with the experimental results.

It is straightforward from these observations that the state of the active surface of the sulfides will be an important factor to take into account when dealing with the periodic trend. Clearly for one set of reaction conditions different sulfides will have their active surface more or less populated because of the different metal-sulfur bond energy of the surface sulfur species. Therefore each of these sulfides will contain more or less sites having the appropriate structure for the reaction considered.

Qualitatively it can be said that as the heat of formation of the sulfide increases, the heat of adsorption will increase [21], as well as the metal-sulfur bond energy and the surface density of sulfur species. The consequence of this will be a volcano curve of the number of hydrogenation sites or activity variation versus the heat of formation of the transition metal sulfides.

This can be illustrated by the following model assuming a simple adsorption of sulfur species and using the Langmuir formalism. At the steady state the fraction of sulfur $\theta_s(i)$ on the surface of a given sulfide i is:

$$\theta_s(i) = \frac{K(i) \cdot p_s}{(1 + K(i) \cdot p_s)}$$

with p_s the H_2S partial pressure and $K(i)$ the equilibrium constant:

$$K(i) = K_0(i) \cdot \exp \frac{-\Delta H_{ads}(i)}{RT}$$

For the sulfide i, the steady state coverage $\theta_s(i)$ can be calculated from $\Delta H_{ads}(i)$. This allow to compute the probability of existence of k-cus metal ions on the surface of sulfide i using the following probability formula:

$$P_k(i) = C_n^k \cdot \theta_s^{n-k}(i) \cdot (1 - \theta_s(i))^k$$

with $k = 0$ to 4 and $n = 4$ i.e. assuming that the surface of the sulfide can generate metal ions up to 4-cus. Then for different sulfides having different heat of adsorption, the probability of existence of k-cus metal ions can be computed.

The numerical application given in the following has only the aim to illustrate the point. Values of $K_0(i) = 0.01$ and $p_s = 0.001$ for temperature of 623 K have been employed in order to give heat of adsorption in the range 0–100 kJ.mol^{-1}. In fig. 1 are reported the curves obtained for the probability of existence of 2 and

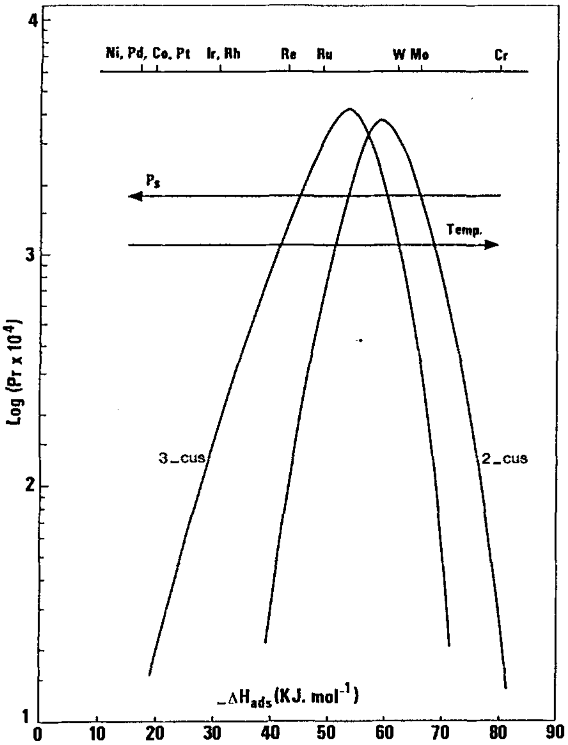


Fig. 1. Calculated variation of the probability of existence of 2 and 3-cus metal ions versus the heat of adsorption. The upper scale is displayed for application to sulfides and shows the relative position of the sulfides assuming that $\Delta H_{\mathrm{ads}} = k \cdot \Delta H_{\mathrm{f}}$ with k arbitrarily chosen equal to 0.25.

3-cus Mo ions versus the heat of adsorption of different sulfides. Clearly these curves have a volcano shape and cover three orders of magnitude as experimentally observed. The use of a dissociative adsorption would lead also to the same volcano shape of the curves.

Also reported in fig. 1 is a scale showing the relative position of various sulfides obtained by considering that the heat of adsorption is linearly dependent on the heat of formation as suggested by Benard et al. [21] for sulfur adsorption on metals. Taking Ru for example at the maximum of the 3-cus volcano curve, as observed for HDS of dibenzothiophene [1,3], shows that molybdenum sulfide will have a more saturated surface whereas Ni sulfides will have a less saturated surface. In consequence both Ni and Mo sulfides will have a smaller site density than Ru sulfide.

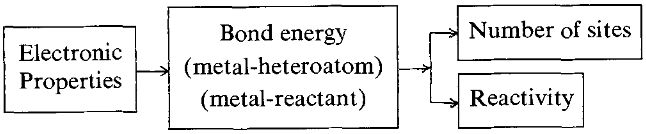
An other interesting observation derived from the above reported formulae, is that the probability (or implicitly number of sites) depend also on the reaction temperature and reactant partial pressure. Changing these experimental conditions should change the position of the maximum of the volcano curve in the way indicated qualitatively in fig. 1. An increase of the reaction temperature will increase the "optimum" heat of adsorption whereas increasing the hydrogen sulfide partial pressure will decrease the "optimum" heat of adsorption. Therefore the nature of the optimum solid will depend on the reaction conditions.

It is difficult to find rational trend in the cited literature on this point. However it is well known that for example hydrogenation reactions on MoS_2 based catalysts are poisoned by an increase in hydrogen sulfide partial pressure. In fact when considering the curve for 3-cus metal ions, fig. 1 shows that for the arbitrary position of the element chosen, all sulfides with a heat of adsorption higher than Ru sulfide will have an activity poisoned by an increase of the H_2S partial pressure whereas all sulfides with heat of adsorption lower than Ru sulfide will be promoted by such an increase of H_2S partial pressure. In the case of reaction sensitivity to 2-cus sites the same reasoning can be done in fig. 1 with tungsten sulfide taken at the optimum heat of formation.

At this stage several points need to be underligned. The description of the active sites used in this work is believed to be very crude. In the case of MoS_2 two Mo ions are concerned upon adsorption of the molecule on the bridged vacancy of the (1010) edge plane. Therefore one should consider an elementary ensemble [20,22] rather than a single metal ion as done in this work for the sake of simplicity. In addition the environment of the adsorbed reacting molecule contains not only sulfur ions and vacancies but should include hydrogens either as SH^- group or H^* species and also other adsorbed molecules. More complex probability function and kinetic equation will be required to take into account the whole environnement. There are also some limitations to the use of the probability function as it is implicitly considered that all sulfur can be removed with the same probability in accordance with the langmuir formalism used. Such uniformity is unlikely as it is well known that heat of adsorption often vary with coverage and a more complex formulation would be needed to account for the dependence of heat of adsorption with coverage. However even if all this is going to modify the curve activity versus heat of adsorption it is expected that the volcano shape will be kept because the main effect is the generation of the adequate active site structure.

The extrapolation to oxides is rather straightforward as removal of oxygen species from the active surface will generate cus metal ions and therefore sites with different structures. Again the metal-oxygen bond energy is the key factor as well recognized [11]. Similarly in the case of metal catalyst one has to consider that carbonaceous species will play the role of sulfur and oxygen in sulfides and oxides respectively with the metal-carbon bond being the important factor. The existence of carbon species on metal surface is now well established and their participation in the catalytic process recently discussed [23–25]. The volcano curve observed for metal catalyst may result in part from the existence of an optimum number of sites having the appropriate structure in terms of number of carbon and "vacancies" on single or ensemble of metal atoms.

All the above considerations about the number of site variation are not in contradiction with the electronic or energetic interpretation as both are linked as depicted in the following scheme:



The number of sites on the surface is dependent on the local metal-heteroatom bond energy which is in turn the result of the electronic properties of the transition metal ion. Similarly the reactivity of the site will be governed by the interaction between the site and the reactant molecule (hydrocarbon, hydrogen, etc...) and therefore by the electronic properties of the metal ion. Again the Sabatier principle can be applied i.e. for the same site structure, transition metal giving the optimum bond energy with the adsorbed reactant will be the more active. Therefore another volcano curve is to be expected when the activity for the conversion of a given molecule on one site structure is plotted versus the heat of formation of the active phase. Such formulation has been in particular developed by Balandin in the part of his multiplet theory dealing with volcano curves [26].

In conclusion it appears that when dealing with periodic trends one has to distinguish between the volcano curve resulting from the number of site variation (metalheteroatom bond energy variation) emphasized in this work and the volcano curve resulting from the reactivity variation (metal-reactant bond(s) energy variation). It is expected that the actual curve activity versus heat of formation is a convolution of both curves.

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