

## Thermodynamic Analysis of the Stability of Supported Metal Catalysts

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The stability of the bidimensional dispersed state of metal on a support is analyzed by comparing its free enthalpy with the free enthalpy of the state in which the metal atoms are agglomerated in the form of crystallites. The chief result of the analysis is the existence of a critical crystallite radius  $r_c$  given by the equation

$$r_c \equiv \frac{5\delta}{1 - \cos \theta},$$

where  $\delta$  represents the diameter of a platinum atom and  $\theta$  the wetting angle of the metal on the support. For crystallite radii smaller than  $r_c$  the bidimensional dispersed state is more stable, while for radii larger than  $r_c$  the crystallite state is more stable.

### INTRODUCTION

The activity of supported metal catalysts is strongly dependent upon the degree of dispersion of the metal and, of course, is greater when the exposed surface area of metal is larger, hence when the size of the crystallites is smaller. As concerns the nature of the crystallite size effect, experimental evidence shows that for some reactions (facile reactions) it is only a surface effect, but that there are reactions (demanding reactions) for which the decrease in activity is accelerated by the increase of the size of the crystallites (1). It is probable that for a facile reaction a single metal atom acts as an active site, while for demanding reactions a group of metal atoms having a special configuration plays such a role. In the first case the specific activity of the catalyst (defined as the rate per unit exposed surface area of metal) is independent of the crystallite size; in the second case the decrease of the number of privileged groups of atoms caused by the increase of the crystallite size is associated not only with the decrease

in surface area, but also with a reduction in the number of privileged crystalline faces, defects, and edges.

Let us select from the available experimental facts the factors responsible for the degree of dispersion of the metal:

Cusumano *et al.* (2), determining the surface area of dispersed platinum by chemisorption of hydrogen at about 200°C, have observed that the adsorption of hydrogen on the platinum is about an order of magnitude smaller for platinum on silica-alumina than for platinum on alumina. The evaluations based upon the hydrogen chemisorption data indicate crystallite sizes less than 10 Å for platinum on alumina and of about 85 Å for platinum on silica-alumina. The much poorer dispersion of platinum on silica-alumina than on alumina is probably due to a lower wetting of the support by the metal in the first case as compared to the second.

Herrmann *et al.* (3) subjected various samples of platinum-alumina reforming catalysts to heat treatments. Measuring the chemisorption capacity for H<sub>2</sub> they conclude that Pt is present in the fresh non-

heated material in a bidimensional dispersed form and that heat treatment causes the formation of platinum crystallites. Dorling and Moss (4) have observed that platinum on silica prepared at temperatures less than 400°C has twice the activity for benzene hydrogenation as the same catalyst treated at 500°C. The crystallite size is less than 50 Å in the first case and substantially larger in the second. Many other experiments are available which show that heat treatment induces a loss in activity, which is associated with an increase in the crystallite size (5-8).

The aging of supported metal catalysts may also be associated with an increase in crystallite size. Some possible explanations of the aging process due to occurrence of localized hot spots (points having large temperatures) have been proposed (9-11).

This experimental evidence suggests two questions:

i. Why is the bidimensional dispersed state not stable?

ii. What is the evolution in time of the distribution function of the crystallite size during heating pretreatment and during the catalytic process?

An answer to the first question can be obtained on the basis of thermodynamic considerations, while an answer to the second needs kinetic models of the process.

In what follows, a thermodynamic stability analysis will be carried out on the basis of a comparison between the free enthalpies of the bidimensional dispersed and the crystallite states. The second problem, the kinetic one, will be treated in a future article.

#### THERMODYNAMIC ANALYSIS

The thermodynamic treatment which follows is an approximate one because the usual macroscopic quantities, valid for sufficiently thick liquid layers, will be used in the expression of the free enthalpy (Gibbs free energy) of the bidimensional dispersed state of the metal atoms, and those valid for sufficiently large liquid droplets in the expression of the free enthalpy of the solid crystallites. Neither the smallness of the system (for small systems the intensive

thermodynamic variables depend upon the dimensions of the system (12)), nor the fact that for solid bodies the usual surface tensions used for liquids on a solid surface do not provide a satisfactory thermodynamic description (13) will be taken into account. It is perhaps of interest that the variation of the surface free enthalpy with crystallographic orientation, obtained experimentally for a number of pure metals, was between 3 and 15% (14) and that at sufficiently high temperatures a solid surface underwent a cooperative phenomenon on an atomic scale (15), which led to spherical shape. Consequently, at least some of the simplifying assumptions are not too far from the reality.

The free enthalpy  $\Phi_f$  of the bidimensional dispersed state will be written as the sum of the free enthalpy of a number of  $n$  metal atoms forming a number of bidimensional islands and of the surface free enthalpies.

$$\Phi_f = n\varphi(T,p) + S_{ss'}\sigma_{ss'} + S_{sg}\sigma_{sg} + S_{s'g}\sigma_{s'g}, \quad (1)$$

where  $\varphi(T,p)$  represents the free enthalpy of one metal atom at temperature  $T$  and pressure  $p$ ,  $\sigma_{ij}$  the surface free enthalpies and  $S_{ij}$  the surface areas on which  $\sigma_{ij}$  acts. The subscripts have the following meaning:  $ss'$  support-metal;  $sg$  support-gas,  $s'g$  metal-gas.

Assuming for simplicity that the crystallites are spherical caps of equal radii, the free enthalpy of the crystallite state can be written as

$$\Phi_c = n\varphi(T,p') + Ns_{ss'}\sigma_{ss'} + Ns_{s'g}\sigma_{s'g} + S'_{sg}\sigma_{sg}, \quad (2)$$

where  $N$  represents the number of crystallites,  $s_{ss'}$  and  $s_{s'g}$  the surface areas between one crystallite and support, and between one crystallite and gas, respectively,  $S'_{sg}$  the surface areas between the support and gas. The pressure  $p'$  is different from  $p$  due to the curvature of the crystallite. It will be assumed for the time being that the function  $\varphi$  is the same in Eqs. (1) and (2). Because in the bidimensional dispersed state the atoms are grouped in islands and there are strong interactions between them, and because the crystallites are small, this sim-

plifying assumption is not unreasonable. In the last paragraph equations are established without this assumption. A further simplifying assumption implied by Eqs. (1) and (2) is that the surface free enthalpies are the same in both cases.

Let us introduce the notations

$$S = S_{sg} + S_{s'g} \text{ and } S_{ss'} = \beta S. \quad (3)$$

Because  $S_{ss'} = S_{s'g}$ , it follows that

$$S_{s'g} = \beta S \text{ and } S_{sg} = (1 - \beta)S. \quad (4)$$

The assumption of a spherical cap shape for the crystallites implies the following relations between various geometric quantities, the radius  $r$  and the wetting angle  $\theta$  (Fig. 1).

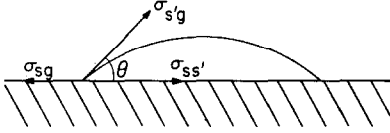


FIG. 1. Spherical cap shape of the crystallites.

$$V_p = \frac{\pi}{3} (1 - \cos \theta)^2 (2 + \cos \theta) r^3, \quad (5)$$

$$s_{s'g} = 2\pi(1 - \cos \theta)r^2, \quad (6)$$

$$s_{s's} = \pi r^2 \sin^2 \theta. \quad (7)$$

Denoting by  $\delta$  the diameter of the atoms of metal, a volume balance leads to

$$\beta S \delta = N V_p = n v. \quad (8)$$

To compare the free enthalpies of the bidimensional dispersed and crystallite states, we may first establish the conditions for which they are equal:

$$\begin{aligned} n\varphi(T,p) + \beta S \sigma_{ss'} + (1 - \beta) S \sigma_{sg} + \beta S \sigma_{s'g} \\ = n\varphi(T,p') + N\pi r^2 \sin^2 \theta \sigma_{ss'} \\ + N2\pi(1 - \cos \theta)r^2 \sigma_{s'g} + S'_{sg} \sigma_{sg}. \end{aligned} \quad (9)$$

Expanding  $\varphi(T,p')$  in series, one gets

$$\begin{aligned} \varphi(T,p') &\approx \varphi(T,p) + \frac{\partial \varphi}{\partial p} (p' - p) \\ &= \varphi(T,p) + v(p' - p). \end{aligned} \quad (10)$$

The Laplace equation leads to

$$p' - p = 2\sigma_{s'g}/r, \quad (11)$$

and Young's equation to

$$\sigma_{s'g} \cos \theta = \sigma_{sg} - \sigma_{s's}. \quad (12)$$

Since

$$S'_{sg} = S - N\pi r^2 \sin^2 \theta, \quad (13)$$

from Eqs. (3)–(11) and (13) one obtains

$$\begin{aligned} \sigma_{ss'} + \sigma_{s'g} - \sigma_{sg} \\ = \frac{\delta}{r_c} \left[ \sigma_{s'g} \frac{2(1 - \cos \theta)(2 + \cos \theta) + 6}{(1 - \cos \theta)(2 + \cos \theta)} \right. \\ \left. + (\sigma_{ss'} - \sigma_{sg}) \frac{3 \sin^2 \theta}{(1 - \cos \theta)^2 (2 + \cos \theta)} \right], \end{aligned} \quad (14)$$

where  $r_c$  represents the radius for which the two free enthalpies are equal.

Taking into account Young's equation (12), Eq. (14) leads to the unexpected simple equation

$$r_c = \frac{5\delta}{1 - \cos \theta}. \quad (15)$$

The dependence of the free enthalpy of the crystallite state on the radius  $r$  is given by

$$\begin{aligned} \Phi_c = n\varphi(T,p') + \frac{3\beta S \delta (\sigma_{ss'} - \sigma_{sg}) \sin^2 \theta}{(1 - \cos \theta)^2 (2 + \cos \theta) r} \\ + \frac{6\beta S \delta \sigma_{s'g}}{(1 - \cos \theta)(2 + \cos \theta) r} + S \sigma_{sg}. \end{aligned} \quad (16)$$

Equations (10), (11), and (12) together with (16) lead to the very simple result

$$\Phi_c = n\varphi(T,p) + S \sigma_{sg} + 5nv \frac{\sigma_{s'g}}{r}. \quad (17)$$

Eliminating the assumption that the free enthalpy  $\varphi$  is the same in both cases, and denoting by  $\varphi_3$  the free enthalpy  $\varphi$  for the tridimensional and by  $\varphi_2$  for the bidimensional case, one gets

$$\Phi_c = n\varphi_3(T,p) + S \sigma_{sg} + 5nv \frac{\sigma_{s'g}}{r}, \quad (17')$$

and

$$r_c = \frac{5\sigma_{s'g}}{\left( \frac{\sigma_{s'g}}{\delta} (1 - \cos \theta) - \frac{\varphi_3(T,p) - \varphi_2(T,p)}{v} \right)}. \quad (15')$$

A more satisfactory calculation must take into account also the fact that the surface free enthalpies  $\sigma_{s'g}$  cannot be the same in the two cases. However, in view of the lack of information concerning these surface

properties, we shall discuss only the simple equations, (15) and (17).

We would like to stress once again that in the above analysis one assumes that macroscopic thermodynamic properties such as the surface tension, volume free enthalpy and wetting angle may be applied in the description of systems composed of small crystallites, or to bidimensional dispersed systems. Because the radius of a crystallite is of the order of 10 Å and the thickness of the bidimensional dispersed state is equal to the molecular diameter, these assumptions are questionable. This "capillarity approximation" was, however, used with some success in the nucleation theory though the scales involved there are of the same order of magnitude as here (17).

#### DISCUSSION

Equation (17) shows the expected result that the free enthalpy of the crystallite state decreases with increasing  $r$ . Consequently the growth of the crystallites is a process favored from a thermodynamic point of view.

Let us now compare the free enthalpies of the crystallite state and of the bidimensional dispersed state. Equation (15) permits calculation of radius  $r_c$ . For  $r < r_c$  the free enthalpy of the crystallite state is greater than that of the bidimensional dispersed state and consequently the bidimensional state more stable. For  $r > r_c$  the reverse is true. Hence the above thermodynamic considerations impose a lower bound equal to  $r_c$  for the crystallite sizes.

If one considers a bidimensional dispersed state, the growth process will initially be slow until crystallites of radius  $r = r_c$  are generated. This is because for  $r < r_c$  the crystallite state is less stable than the dispersed state. Critical crystallite sizes of radius  $r_c$  can be generated in this case only by fluctuations. If due to fluctuations situations occur in which the dissociation time of a small crystallite is longer than the time necessary for the agglomeration of a small number of crystallites generating one of a critical size, then critical crystallites will be formed. Such

a process is highly improbable and therefore very slow. The existence of roughnesses of the support having a radius of curvature of the order of  $r_c$  or larger favors the growth. Since from Eq. (15) it follows that  $r_c$  is small (of the order of 10–30 Å) it is expected that the support should have roughnesses playing the part of nuclei of growth.

Equation (15) suggests also that if the wetting of the support by the metal measured by the angle  $\theta$  is very good, hence if  $\cos \theta \approx 1$ , then  $r_c \rightarrow \infty$  and the bidimensional dispersed state is more stable. Some information concerning the surface energies of the metals is available in the literature (16). For Pt at 1310°C it is 2340 erg cm<sup>-2</sup>, for Ni at 1250°C it is 1850 erg cm<sup>-2</sup> and for Cu at 1047°C it is 1670 erg cm<sup>-2</sup>. Because the bonds in the metals used in catalysis are stronger than in the oxides used as supports, the surface free enthalpies are larger for the metals, and consequently the wetting of the support by the metal is not too good. Of course, the wetting on one support may be better than on another one. Indeed, Cusumono's paper (2), discussed in the Introduction, demonstrates that wetting has an influence on the degree of dispersion of the metal.

#### CONCLUSION

1. The free enthalpy of the crystallite state is greater than the free enthalpy of the bidimensional dispersed state for crystallite sizes up to a critical value  $r_c$  given by Eq. (15). The reverse is true for crystallite sizes larger than  $r_c$ . Consequently, the crystallite state is more stable for radii larger than  $r_c$  and the dispersed state for radii smaller than  $r_c$ .

2. Wetting of the support by the metal has an important effect upon the degree of dispersion of the metal. The critical radius  $r_c$  becomes infinitely large for wetting angles  $\theta$  equal to zero and therefore the dispersed state more stable.

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