

Catalysis at the nanoscale level

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As the techniques presently used for routine measurements of nanoparticle size are largely unsatisfactory, especially for supported metal catalysts, new guidelines and procedures are described that allow us to obtain more accurate and reliable values of nanodimensions by chemisorption. Improved values of turnover frequencies will result, with benefit for studies on the mechanism of catalytic reactions. Examples taken from both old and recent studies show that nanoscience has been applied in catalysis for a long time. It is quite probable that an extensive use of nanotechnologies in catalyst R-D will bring unexpected industrial achievements in the future. Meanwhile, nanoscience principles can be profitably applied to the improvement of many current petrochemical catalysts.

It has been recently remarked^[1] that the addition of the “nano” prefix to many technical terms is a quite recent practice that began with the introduction of the nanometer as a microscopic length unit in place of the Angstrom. Though nanoscience was formally born with that event, it is nevertheless clear that nanosize materials were being studied much earlier, especially in the area of catalysis. A similar picture has also been recently outlined by other authors^[2,3]. In fact industrial catalysis has involved nanoparticles since its beginning at the dawn of the 20th century. For example, nanoparticles are typically present in supported metal catalysts. Here, metal particles of a size usually in the range 1–10 nm are deposited on the external surface and/or in the porous texture of inert (with some notable exceptions) materials. There is still much to improve in this area, with short-term benefits for chemical, petrochemical and refining industries. However, most of the research funds are presently set aside for very advanced, if not sometimes extravagant manufacturing techniques, which often only find industrial application after decades, and even then only in the most favorable cases. I will try to show how nanoscience concepts can be applied to the improvement of several very important catalysts presently used in the petrochemical industry, with examples mostly taken from my personal experience. Some old data will be discussed too, to demonstrate that such concepts have always been applied in industrial catalysis.

The control of metal particle nanosize is of the utmost importance for the performance of any industrial catalyst based on supported metals. Such control is currently exerted through a keen manipulation of several different variables, which are summarized in Table 1. It should be stressed that some of these variables are often interconnected,

thus making it difficult to change them one at a time. In practice, a skillful manufacturer of such catalysts must take into account a complex network of experimental variables in his work, aimed at optimizing catalyst performances. In this work he clearly needs effective and not too expensive means for a reliable measurement of the size of metal nanoparticles. As the present situation of such measurements is not satisfactory, a brief discussion of this subject now follows.

The measurement of metal particle nanosize and related properties

Physical techniques

TEM (Transmission Electron Microscopy) seems to be the optimal technique for measuring the size of nanoparticles, as it allows us to look at them directly. However its use is problematic. For example, the analysis is carried out on a microscopic amount of catalyst, hardly representative of the whole sample. Many observations must be made on each of several independently loaded samples in order to get reliable

Main variables for the control of metal particle nanosize in supported metal catalysts

- carrier surface area
- nature of the precursor
- chemical nature of the carrier surface
- metal concentration
- metal distribution
- dispersion promoters
- impregnation procedure
- thermal treatments

Table 1

data, with the considerable expenditure of time that entails. Moreover, small or flat nanoparticles may be lost, due to insufficient contrast. However, a careful use of TEM is very valuable in some cases.

XRD (X-Ray Diffraction) techniques are more practical, but they too have some specific limitations^[4]. Briefly, when the metal nanoparticles are relatively large, approaching or exceeding 10 nm, each of them may consist of several nanodomains, so that the size measured by X-ray line broadening will be smaller than the real one. In such cases, which can be recognized by HRTEM (High Resolution Transmission Electron Microscopy) analysis, SAXS (Small Angle X-ray Scattering) can be used to ensure the

intermezzo 1

How can the carrier influence the properties of metal nanoparticles?

Metal particle size is a very important property of supported metal catalysts, but several other properties are no less important, and some are even more so, such as lattice disorder or work function. The regulation of such properties can be obtained by tuning a range of variables, some of which are interconnected, thus making it very difficult to change one at a time.

The choice of the carrier plays a crucial role, of course. I do not refer to the first-step choice (among carbon, alumina, silica and so on), as it is usually straightforward for a catalyst specialist, but to the very numerous commercial or home-made samples of each type of carrier.

For example, it is a general rule that, when the surface area of the carrier is high, small metal nanoparticles are usually obtained. However it is not easy to change the carrier surface area without affecting other properties, such as the chemical nature of the carrier surface. Something can be done for oxidic carriers, in that their surface area can be decreased by suitable, not too drastic, thermal treatments, provided that surface hydroxylation does not change too much. For active carbons this approach is precluded, as the decrease of surface area is connected with graphitization, which definitely alters the physico-chemical properties of the material.

The chemical species present on the carrier surface interact, more or less, with the metal nanoparticles deposited thereon. This phenomenon is currently called “metal-support interaction” (MSI) and is usually stronger when the metal particles are smaller. It regulates the mobility of metal atoms and clusters on the carrier surface. In practice, when a strong metal-support interaction (SMSI) occurs, smaller (and more resistant to sintering) metal nanoparticles are usually obtained.

For the carriers usually employed in industrial catalysis the intensity of MSI decreases from alumina to silica to active carbon. However the surface properties of active carbons can be widely changed by proper oxidizing and reducing treatments, thus allowing us to tune the metal particle nanosize and the resistance to sintering.

correct size measurement. On the other hand, when the metal particles are smaller than about 2 nm, they do not contribute to the diffraction “visible” lines, thus giving an overestimated particle nanosize. However, in most cases it is possible to determine, using a suitably tailored Rietveld analysis^[4], the content of undetectable metal nanoparticles, to which a reasonable average size can be assigned, for example on the basis of ASAXS data^[5]. By this way a surface average size of the whole population of metal particles can be calculated. Incidentally, it can be remarked that the widely used Scherrer equation, apart from the above-mentioned problems, gives a volume average particle size, completely useless in catalysis (the difference from the correct surface average can be dramatic in the frequent cases of wide particle size distribution). In conclusion, XRD techniques, when used by qualified specialists, allow us to get reliable values of metal particle nanosize in the large majority of metal-carrier couples, the use of TEM being restricted to few cases.

For catalytic purposes, once the correct surface average metal particle nanosize Φ_{av} is known, it is convenient to calculate the number of total surface metal atoms per catalyst gram ($N_{Me,S}$), given by the equation

$$N_{Me,S} = k C_m f_m / d_m \Phi_{av} \quad (1)$$

where k is a constant depending on metal particle shape and on the extent of contact with the carrier surface (usually $k = 5$), C_m is the surface density of metal atoms^[6], f_m is the metal weight fraction in the catalyst and d_m is the metal true density. In this way an easier connection with chemisorption data can be reached.

Chemisorption

The methods traditionally used by the catalytic community for measuring $N_{Me,S}$ are based on chemisorption. In practice what is experimentally measured is the number of probe molecules that disappear from the gaseous phase in contact with the catalyst under the chosen experimental conditions (temperature and pressure). Unfortunately nobody knows what the real fate is of the disappearing probe molecules because although UHV adsorption studies on monocrystals can give some information on the geometrical aspects of the interaction with the metal surface, this can hardly be extrapolated to industrial catalysts. In practice, to calculate $N_{Me,S}$ from the experimental data (the chemisorbed STP gas volume per catalyst gram V_g) the following assumptions are currently made:

- The degree of coverage is 1 (very hard assumption, it could be much lower).
- The chemisorption stoichiometry (ratio between metal atom and chemisorbed molecule, or atom in the case of dissociation) is arbitrarily taken as 1 in most cases, probably for the sake of simplicity.
- All the disappeared probe molecules interact only with surface metal atoms (unfortunately spillover and subsurface chemisorption cannot always be neglected).

Errors as high as 100% may result, which of course are transferred to related properties such as turnover frequency (TOF). However in some cases, since (a) + (b) and (c) give opposite errors, a fortuitous compensation may occur. In other words, a wrong choice of the probe molecule, giving the problems mentioned in (c), may give an advantage.

Clearly the problem has to be approached in a different way. From the experimental value of V_g one can calculate $N_{Me,S}$ by the following equation ($N_A =$ Avogadro's number, $V_M =$ molar volume)

$$N_{Me,S} = N_A V_g S_{av} / V_M = 2.7 \times 10^{19} V_g S_{av} \quad (2)$$

S_{av} being defined as the average chemisorption stoichiometry, that is the ratio between the total number of surface metal atoms and the total number of chemisorbed molecules. Note that no assumptions like (a) or (b) have been made.

Equating (1) and (2) one obtains

$$S_{av} = k C_m f_m / 2.7 \times 10^{19} V_g d_m \Phi_{av} \quad (3)$$

which allows us to calculate S_{av} from the experimental values of V_g (chemisorption) and Φ_{av} (XRD), the other factors in (3) being known constants, for any supported metal (in the most favorable case) or for any metal-carrier couple. Now $N_{Me,S}$ can be correctly determined from chemisorption measurements through equation (2). Of course the problems mentioned in (c) remain open, but can be minimized through a good choice of the probe molecule and of the experimental conditions. Spillover is mainly given by hydrogen, which therefore should not be chosen as a probe molecule. Subsurface chemisorption is mainly given by oxygen, but in most cases a careful choice of the chemisorption temperature allows us to avoid this problem. A straightforward example has been recently given for Cu catalysts^[7]. According to the author's multi-decades of experience, the choice of the probe molecule should be restricted to between CO and oxygen.

Of course the above-discussed approach requires heavy preliminary work, to be performed by XRD specialists in cooperation with catalytic scientists, for any metal-carrier couple. This work has been started, at the University of Venice, Italy, Departments of Chemistry and of Physical Chemistry, has already been completed for Pd catalysts^[4,8,9], and is in progress for Cu^[7], Ru and Pt. For Pd catalysts it has been found that a correct measurement of Pd dispersion can be performed by CO chemisorption at room temperature with the pulse flow technique, when $S_{av} = 2$ is adopted independently on the carrier (active carbon, silica, alumina) and on Pd dispersion. Of course this does not mean that all the CO molecules are bridge-bound to the Pd atoms. To make the concept clearer, if all the CO molecules are linear-bound and the degree of coverage is 0.5, S_{av} is just 2.

It should be remarked that the value of V_g strongly depends on the experimental technique used for its measurement. This means that the experimental procedures must be carefully standardized and strictly followed in every laboratory. Moreover, as the calculation of metal dispersion is based on an S_{av} value determined through an independent physical

technique, no chemisorption method is better than another. This means that time-consuming and error-adding methods (like surface titration, for example) should be abandoned and the very simple pulse flow technique adopted.

For readers' convenience, Table 2 shows the most common relationships used in the characterization of supported metal catalysts.

Turnover frequency and active sites

In more fundamental studies the reaction rate should not refer to the mass of catalyst or metal, but to the active site. As the total number of the active sites is not known, it is common practice, as recently discussed by Boudart^[10], to substitute it with the total number of surface metal atoms, which can be correctly calculated by equation (1). The reaction rate expressed as the number of reacting molecules transformed per surface metal atom per second is often called turnover frequency (TOF) and is expressed as sec^{-1} . TOF is currently used to draw fundamental conclusions about the intrinsic activity of metals and the mechanism of the reaction. Unfortunately many TOF values have been so frequently affected by large errors in Φ_{av} , at least for supported metal catalysts, that they require a substantial revision.

It is rather obvious that the number of active sites will always be lower than that of surface metal atoms, because either the latter ones are not energetically equal in the reaction conditions or the active sites consist of nanoensembles of metal atoms (this point should be taken into account for any comparison with homogeneous or enzymatic catalysis). So it is convenient to introduce the concept of real turnover frequency, given by

$$\text{TOF}_r = \text{TOF} / f_{AS} \quad (4)$$

where f_{AS} is the fraction of surface atoms working as active sites.

Some useful relationships

average metal particle nanosize

$$\Phi_{av} \text{ (nm)} = k C_m f_m / 2.7 \times 10^{12} S_{av} d_m V_g$$

metal dispersion

$$D_m = S_{av} P_m V_g / 22414 f_m$$

metal surface area

$$SA_m \text{ (m}^2 / g_{\text{met}}) = 2.7 \times 10^{15} S_{av} V_g / f_m C_m$$

where

k is a constant (recommended value: 5)

C_m is the surface density of metal atoms, atoms / cm^2 (see ref. [6])

f_m is the metal weight fraction, $g_{\text{met}} / g_{\text{cat}}$

S_{av} is the average chemisorption stoichiometry, surface metal atoms per molecule of probe gas, calculated according to (3)

d_m is the metal true density, $g_{\text{met}} / \text{cm}^3$

V_g is the chemisorbed gas STP volume, $\text{cm}^3 / g_{\text{cat}}$

P_m is the metal atomic weight, $g_{\text{met}} / \text{mol}$

Constant 2.7 dimensions: molecules of probe gas per cm^3

Constant 22414 dimensions: cm^3 / mol

Table 2

When f_{AS} does not depend on Φ_{av} the reaction is called “structure-insensitive” and the reaction rate is inversely proportional to Φ_{av} . In fact the reaction rate, expressed as moles of reactant transformed per catalyst gram per second, is related to TOF_R by the equation

$$\text{Rate} = 5 C_m f_m f_{AS} TOF_R / N_A d_m \Phi_{av} \quad (5)$$

where N_A is the Avogadro's number. Therefore, when the reaction rate is plotted versus reciprocal Φ_{av} , for structure-insensitive reactions a straight line is obtained, from whose slope the product $f_{AS} \times TOF_R$ can be calculated. Unfortunately there is presently no way to separate the two factors.

The situation is more complex for structure-sensitive reactions. In one case f_{AS} is higher for smaller nanoparticles, for example 0.5–2 nm (Figure 1a), giving a Rate vs $1/\Phi_{av}$ plot not very different from that of structure-insensitive reactions (Figure 1b). In the other case the formation of active sites requires large nanoparticles, for example of more than 3 nm size (Figure 2a), giving a very typical Rate vs $1/\Phi_{av}$ plot (Figure 2b). As a concluding remark, in the author's opinion extensive experimentation on the dependence of the

reaction rate on metal particle nanosize could bring some advancement towards the quantitative evaluation of the Holy Grail of catalysis, the active site. Needless to say, such experimentation absolutely depends on the availability of accurate and reliable methods for the measurement of metal particle nanosize, as discussed in the previous chapter.

Some examples of nanoscience applied to industrial catalysis

As it was remarked in the Introduction, nanoscience concepts have been applied in industrial catalysis since its beginning, even if nobody was aware of that. In fact the techniques for obtaining metal particles with the required nanosize (metal dispersion) and for putting such nanoparticles in the right place throughout the porous structure of the carrier (metal distribution) are nothing other than nanotechnology. However nanoscience in catalysis is not restricted to supported metals. Both unsupported metal and mixed oxide catalysts can show situations where nanosize regions have some specific features that are key factors in the catalytic

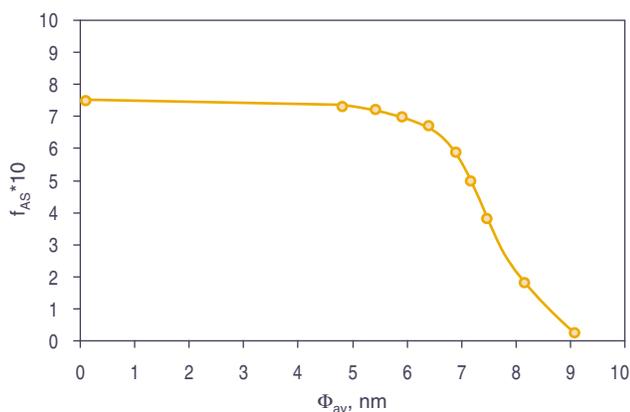


Figure 1a Possible dependence of the fraction of surface atoms working as active sites on metal particle nanosize.

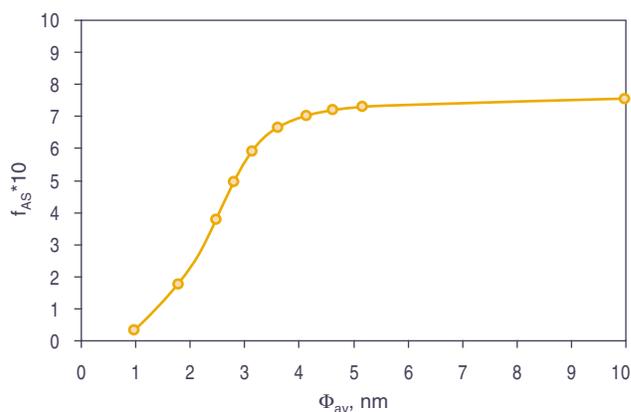


Figure 2a Another possible dependence of the fraction of surface atoms working as active sites on metal particle nanosize.

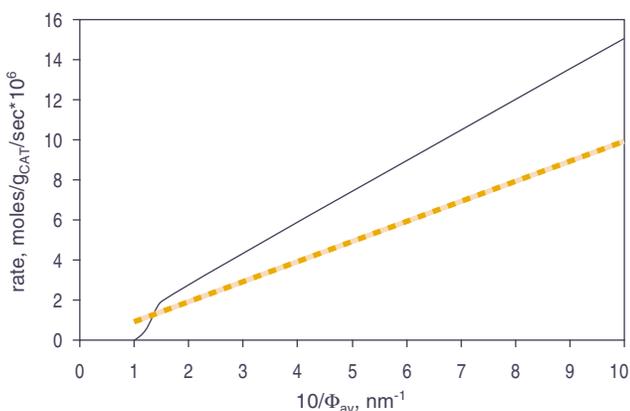


Figure 1b Reaction rate vs. reciprocal metal particle nanosize.

Dotted orange line: no dependence of the fraction of surface atoms working as active sites on metal particle nanosize (structure-insensitive reactions).

Full dark blue line: dependence of the fraction of surface atoms working as active sites on metal particle nanosize as in Figure 1a (structure-sensitive reactions).

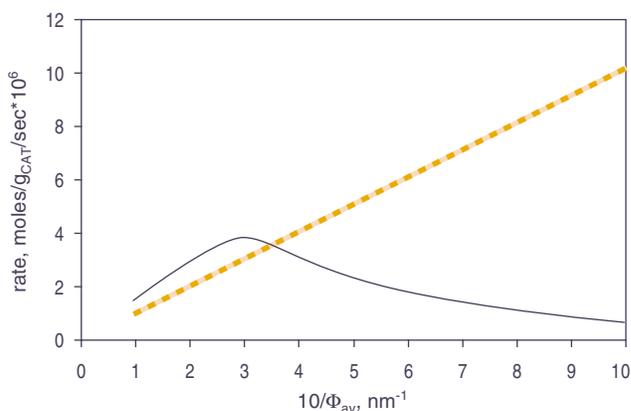


Figure 2b Reaction rate vs. reciprocal metal particle nanosize.

Dotted orange line: no dependence of the fraction of surface atoms working as active sites on metal particle nanosize (structure-insensitive reactions).

Full dark blue line: dependence of the fraction of surface atoms working as active sites on metal particle nanosize as in Figure 2a (structure-sensitive reactions).

intermezzo 2**Achieving the most suitable metal dispersion and distribution.**

(Dispersion: ratio between surface and total metal atoms.
Distribution: even, egg-shell, egg-yolk)

It is quite reasonable that, when the metal concentration on the carrier is high, large nanoparticles are obtained. So low metal contents are usually preferred, especially for precious metals, to obtain sufficiently high metal surface areas. However, attention should be paid to metal distribution, namely to the position of the metal in the carrier volume. The metal distribution in industrial catalysts is mostly egg-shell (to minimize mass transfer limitations and precious metal content), more rarely evenly distributed. In the special case of the presence of large-size poisons in the feed, the egg-yolk distribution could give some advantage, though poison withdrawing might be a better choice.

It is clear that for the egg-shell distribution the metal content in the carrier volume occupied by the metal can be much higher than the nominal one, depending on the ratio between the depth of the carrier layer where the metal is present and the size of the carrier particle. As an example, for the 0.5% Pd/C PTA catalyst the real Pd content in the Pd-containing peripheral layer is about 17%^[11]. As a practical consequence, very small metal nanoparticles cannot be easily obtained in egg-shell catalysts.

The presence of either an oxide or a second metal on the carrier surface can sometimes help the formation of small metal nanoparticles by preventing them from contacting and coalescing. A typical example has been recently reported for carbon-supported Pd, where Ru acts as a dispersing agent^[21]. It is remarkable that, starting from this academic study, some years later an improved PTA industrial catalyst was claimed to have been developed^[22].

The procedure used to impregnate the carrier with the metal salt solution also has a strong influence in sizing metal nanoparticles, mainly because it is related to metal distribution, therefore to the actual metal content. In principle, dry (or incipient wetness) impregnation should give a more homogeneous metal distribution, and therefore smaller metal nanoparticles, but reduction problems could superimpose, giving opposite results (see Table 3).

Finally, a simple way to tune nanosize metal particles consists of thermal treatments under suitable atmospheres. In most cases the temperature of precursor (oxide, hydroxide, chloride, oxychloride) reduction to metal must be carefully chosen. In general, during catalyst manufacture or "in situ" activation, one should avoid exceeding the operational reaction temperature. Of course, if the precursor species are difficult to reduce (such as chlorides), one may be forced to increase the reduction temperature. Conversely, it is useless to try to obtain very small metal nanoparticles by reduction of the metal precursor at very low temperature, unless very strong metal-support interactions will preserve them at the reaction temperature.

performances. In such circumstances again nanotechnology plays a crucial role in catalyst R-D. Some practical examples will now be discussed, showing how nanoscience concepts have already been applied, or should be applied in the future, in both the development and improvement of several industrial petrochemical catalysts.

PTA catalyst

The catalyst used for the purification of crude terephthalic acid to give PTA (Purified Terephthalic Acid) consists of 0.5% Pd on active carbon granules. Data on the industrial behavior of this catalyst have been made available only recently^[11]. This catalyst is a typical case of interconnected properties, which can be regulated by nanotechnology operations during manufacturing. For example, the three properties nanosize-content-distribution of Pd are strictly correlated. Given a prefixed Pd content (usually 0.5%), particle nanosize and distribution can be tailored, but not independently, through suitable manufacturing procedures. Such a complex situation explains why different batches of the same catalyst sometimes give very different performances in the industrial PTA plants, thus making it advisable to carry out careful quality controls before catalyst loading.

Deactivation of the PTA catalyst occurs not only by Pd sintering, but also, when traces of sulfur compounds are present in the feed, by formation of the very stable compound Pd₄S^[11], on the condition that sulfur will find correctly ordered Pd nanoregions. If this order is drastically broken through the insertion of a different element, inert towards sulfur and not decreasing Pd catalytic activity (Figure 3), sulfur-resistant PTA catalysts can be developed through another typical nanotechnology operation.

Ammonia synthesis catalyst

The precursor of the traditional ammonia synthesis catalyst consists of magnetite promoted with small amounts of irreducible oxides (Al₂O₃, CaO, K₂O). Magnetite is then reduced to metallic iron by hydrogen. If alumina is omitted, dramatic sintering of iron occurs, making the catalyst completely useless. This key role of alumina comes from the cationic substitution of Fe³⁺ with Al³⁺ ions, roughly shown in Figure 4a. When oxygen anions are withdrawn by hydrogen during catalyst reduction, except for those linked to aluminum, several iron aluminate nanoregions, roughly shown in Figure 4b, remain embedded in the structure of α -iron^[12], causing a stiffening of the latter with consequent decrease of the sintering rate. In fact, as the reduction temperature usually does not exceed 500 °C, the iron aluminate nanoregions (estimated size 2–3 nm) do not have sufficient energy to reorganize themselves in larger crystallites, which are formed only at the very high temperature (950 °C) of the α - γ iron transition^[12]. This picture has recently found further confirmation from the comparison of the reduction behavior of magnetite- and wustite-based ammonia catalysts^[13].

As a practical consequence, any catalyst manufacturer should aim at maximizing the content of iron aluminate nanoregions in the final catalyst. As there is an upper limit for the Fe^{3+} - Al^{3+} substitution, the size of such nanoregions must be as small as possible. To this purpose the special manufacturing technology of this catalyst (melting of magnetite+promoters powder mix at 1700°C and subsequent cooling) requires carefully controlled procedures, defined according to nanoscience principles.

Catalyst for the production of formaldehyde

The Fe-Mo oxide catalyst is widely used for the oxidation of methanol to formaldehyde at full methanol conversion. The catalyst consists of a mix of crystalline $\text{Fe}_2(\text{MoO}_4)_3$ and MoO_3 . Maximum activity is obtained for Mo/Fe atomic ratios in the range 1.6–1.8. It has been demonstrated^[14] that the two pure components show low activity and that a Mo-rich iron molybdate is the active phase. This is because the active site requires octahedrally coordinated Mo^{VI} , such as in MoO_3 , whereas in $\text{Fe}_2(\text{MoO}_4)_3$, Mo^{VI} has tetrahedral coordination. On the other side the presence of Fe^{3+} ions is indispensable for high activity. The formation of $[\text{MoO}_6]$ nanoregions in the structure of $\text{Fe}_2(\text{MoO}_4)_3$, giving a strong interaction with the neighboring $[\text{FeO}_6]$ octahedrons^[15], comes from special manufacturing procedures. Briefly, the precipitated (from Fe^{III} chloride and ammonium molybdate) catalyst precursor is an ill-defined amorphous material with Mo/Fe ratio in the range 2.0–2.5. The presence of the following typical species, together with similar ones, can be envisaged in such material: $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]_3(\text{Mo}_7\text{O}_{24})$ $[\text{Fe}_2(\text{OH})_2(\text{H}_2\text{O})_8](\text{Mo}_2\text{O}_7)_2$

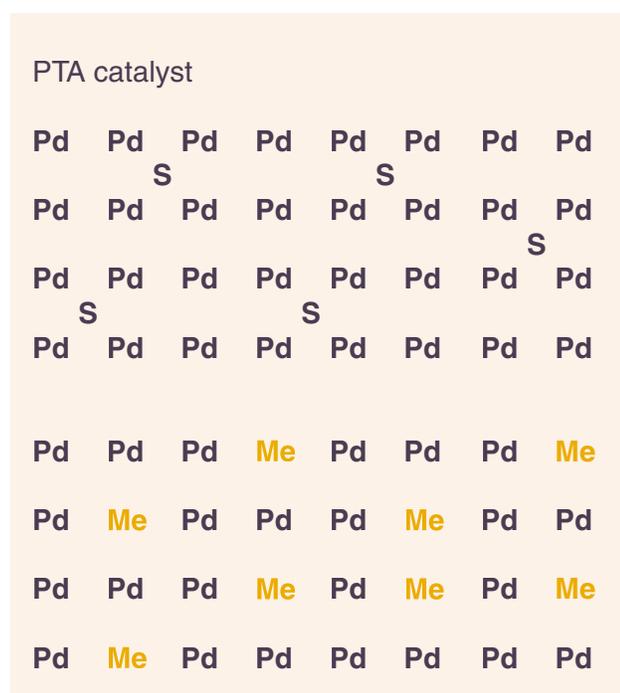


Figure 3 Simplified scheme showing formation of Pd_4S (top) and its inhibition (bottom).

At around 370°C the amorphous material decomposes with water release and formation of poorly crystalline $\text{Fe}_2(\text{MoO}_4)_3$ and MoO_3 . However, the relatively low temperature does not allow the reorganization of all the excess Mo under the MoO_3 structure, so that $[\text{MoO}_6]$ nanoregions remain included in the iron molybdate structure, giving the active sites for methanol oxidation. In practice, the composition of the active catalyst should be written as follows:



It has been experimentally found^[16] that the maximum value for x is $1/9$, but usually does not exceed 0.05. The catalytic performances strongly depend on x , that is on density and size of Mo-rich nanoregions. The optimal situation is represented by a high density of such regions, so the skilful manufacturer will tailor the production procedure to this purpose. That is not so easy, as witnessed by the large differences of catalytic performances among commercial catalysts. It should also be remarked that catalyst deactivation mainly comes from the slow destruction of the Mo-rich nanoregions^[17], shifting catalyst composition towards pure $\text{Fe}_2(\text{MoO}_4)_3$. Nanoscience should help in the research for the stabilization of such regions.

intermezzo 3

A new ammonia catalyst precursor: wustite

Can the metal surface nanostructure be drastically changed simply by using different precursors (oxides, for instance)? A striking example concerns the classical ammonia synthesis catalyst. It has been discovered^[23] and recently confirmed^[13] that a much higher activity can be obtained if the catalytic Fe surface is formed from wustite than from magnetite, thus questioning a hundred years of research and speculations on what can be called a textbook catalyst.

It is known that the presence of special nanoclusters of Fe atoms, having specific geometrical requirements, is necessary to activate the dinitrogen molecule. The same active sites are probably present also on the ex-wustite Fe surface, but are much more effective in performing the dissociation of dinitrogen. Though extensive structural and surface investigations are still to be performed on the wustite-based catalyst, it should be remarked that wustite is much more able than magnetite to dissolve Ca^{++} ions within its structure. The best proof of such an intimate interaction is represented by the very unusual stabilization of the wustite structure down to room temperature (wustite disproportionates to magnetite and iron below 575°C). After reduction, nanosize CaO particles should be present on the surface of the ex-wustite catalyst and contribute to activate dinitrogen — due to their basic nature — in addition to the well-known role of potassium. It is expected that a careful optimization of both size and distribution of such CaO nanoparticles can further increase the already considerable gap between wustite and magnetite catalysts (a good challenge for nanotechnology!).

Active phase distribution at the nanoscale

It is well known that, when the active phase or its precursor is deposited on a carrier, its particular position is a key factor for catalytic performance. From the industrial point of view the question is: Where to place the active phase in the nanosize pores of the carrier for optimal performance? For noble metal catalysts there is a clear advantage (with a few exceptions) for avoiding the deposition of the metal in the deepest part of the nanopores. This region can hardly be reached by the reactants and moreover a prolonged stay of the reaction products inside the pores could impair the selectivity.

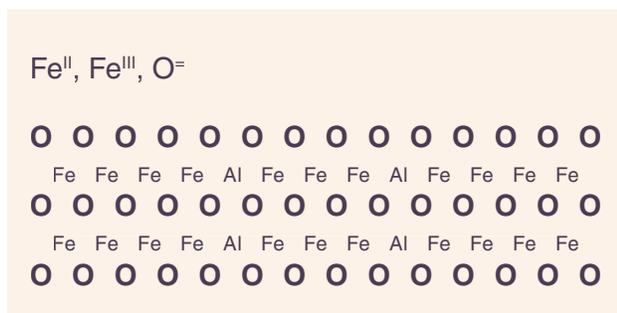


Figure 4a Simplified scheme showing Fe³⁺-Al³⁺ cationic substitution in magnetite.

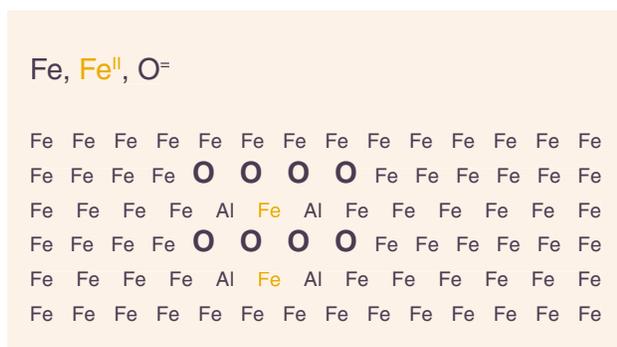


Figure 4b Formation of Fe aluminate nanoensembles embedded in metallic iron upon reduction of ammonia synthesis catalyst.

A good procedure for placing the metal only in the accessible region of carrier nanopores consists of the partial prefilling of the pores with a water-immiscible liquid, preferably high-boiling, and then impregnating with an aqueous solution of the precursor^[18]. After evaporation of the liquid phase and reduction, good catalysts can be obtained with much lower noble metal content. For example, this simple application of nanotechnology allows us to decrease from 5% to 2% the metal content in Pd on active carbon catalysts for some hydrogenations in slurry reactors.

There are also a few opposing cases, where it is advantageous to confine the active phase in the deepest nanopore region. A typical example is given by the fluid bed ethylene oxychlorination catalyst (Cu chlorides over γ -alumina). As in the industrial plant it is often convenient to run the reactor at relatively high HCl content in the feed, the Cu chlorides equilibrium is thus shifted towards CuCl₂, which easily forms polymers. If during catalyst manufacture, CuCl₂, or part of it, has been placed near the mouth of the nanopores, severe sticking phenomena of the catalyst powder may occur, sometimes even leading to plant shutdown. It is therefore necessary to employ nanotechnology to place the Cu chlorides in the deepest area of the alumina nanopores^[19], even if the catalyst suffers some decrease of catalytic activity.

The homogeneous distribution of the active phase inside the nanopores, typically reached by incipient wetness impregnation, is sometimes thought to be convenient for obtaining high dispersions. Unfortunately the final result is often exactly the opposite. A typical example is given by the PTA catalyst (0.5% Pd on active carbon granules)^[20]. While in the fresh catalyst the size of Pd nanoparticles is smaller, as expected, for the incipient wetness procedure, the reverse occurs after treatment at high temperature, (namely during catalyst running in the plant) (Table 3). This phenomenon is due to problems in the elimination of poisoning elements. Needless to say, catalyst characterization before running under industrial conditions (“fresh” catalyst) is often misleading.

Questions and answers**Are there other petrochemical catalysts that can benefit from the application of nanoscience principles?**

Yes, I think that nanoscience principles can be profitably applied for the improvement of most petrochemical catalysts. I have discussed only few of them, but I could also mention the catalysts for the production of ethylene oxide (ethylene epoxidation) and styrene (ethylbenzene dehydrogenation).

The ethylene oxide catalyst consists of alkali-promoted Ag supported on low-area alumina. Nanoscale Ag-support interactions have been found to be beneficial and can be optimized during the impregnation and calcination steps. Conversely, sodium migration phenomena from the support to the metal phase can decrease the catalyst life and should be opposed by the addition of suitable sodium nanotraps hindering its mobility.

The best styrene catalyst consists of Fe oxide (magnetite during operation), promoted by a large amount of potassium oxide and minor quantities of calcium, cerium and molybdenum (oxides, of course). Cerium promotes the activity, molybdenum the selectivity, while calcium seems to promote the stability. Basically, the activity comes from special Fe-K oxide nanoregions, which can be probably optimized, while the promoting mechanism of the other oxides is still to be clarified.

Is there an agreed definition of a nanomaterial?

It is a matter of fact that nanoscience and nanotechnology are presently attracting a huge amount of research funds, both in Europe and in the USA. Therefore, there is a clear tendency towards the proliferation of nanomaterials and nanotechnologists, in the absence

Conclusions

For the last century nanoscience principles have always been applied in industrial catalysis. In particular, supported metal catalysts are typical examples of nanomaterials.

Accurate and reliable measurements of metal particle nanosize are indispensable for both academic and industrial research on such materials. A new approach has been followed for the determination of metal particle nanosize by chemisorption. Basically the average chemisorption stoichiometry has been experimentally determined by collecting physical (WAXS, SAXS, TEM, HRTEM, depending on the specific case) and chemisorption data on suitable reference samples. For supported Pd catalysts it has been found that the average chemisorption stoichiometry Pd/CO to be used is 2.0 ± 0.1 , independently of carrier nature and metal dispersion, when the chemisorption measurements are performed at room temperature by the pulse flow technique. Such procedure opens new perspectives in fundamental studies as it allows a more precise determination of the turnover frequency.

From various practical examples for application of nanoscience principles to the improvement of several important petrochemical catalysts, it is clear that the presence of nanoensembles of either atoms or ions in the catalyst structure can play a crucial role in the tailoring of catalytic properties like activity and resistance to deactivation. The development and the preservation of such ensembles,

Example of wrong nanotechnology (0.5% Pd/C catalyst)		
<i>impregnation technique</i>	<i>reduction temperature</i>	
	25°C	400°C
<i>wet</i>	<i>Pd particle size</i>	
	3.0 nm	4.8 nm
<i>incipient wetness</i>	2.1 nm	9.0 nm

Table 3

of precise definitions. It may occur that objects larger than 100 nm are defined as nanomaterials, though they have more to do with the micron than with the nanometer. In my opinion, the maximum size for a nanomaterial should not appreciably exceed 10 nm. However, solids including in their structure or at their surface nanometric bodies of relevant importance for their performances should be considered nanomaterials too.

Some other cases are open to discussion. For instance, should solids with nanosize porosity be defined as nanomaterials? They should include zeolites and active carbons. In conclusion, there is an urgent need for internationally agreed "nanodefinitions".

requiring a strong background of solid state chemistry, is a primary target for any catalyst manufacturer.

acknowledgement

The author is very grateful to the staff of the Departments of Chemistry and Physical Chemistry of the University of Venice, who were deeply involved in the development of improved techniques for the measurement of metal particle nanosize. In particular to Alvise Benedetti, Patrizia Canton, Stefano Polizzi and Pietro Riello of the Department of Physical Chemistry and to Francesco Pinna, Carla Baldan, Tania Fantinel, Federica Mengazzo and Michela Signoretto of the Department of Chemistry. The author also thanks Francesco Ferrero, who managed the mathematical models of the turnover frequency section. Thanks are finally due to Clyde Payn, President of The Catalyst Group, who firstly invited me to speak about nanocatalysis, thus inducing me to think more deeply on this subject.

Sadly, Prof. Giuliano Fagherazzi, who was the coordinator of the key section of the project (physical techniques) untimely left us some months ago. The completion of the whole project, aiming at supplying catalytic researchers with simple but reliable procedures for the measurement of metal particle nanosize, will be performed to keep his memory alive.

Keywords

- nanotechnology
- nanocatalysis
- metal particle size
- chemisorption
- turnover frequency
- industrial catalysts

Curriculum vitae



Nicola Pernicone was born in 1935 in Florence (Italy). He received his Degree in Chemistry at the University of Florence in 1958. In 1959 he joined Edison Chemical and after two years Montecatini (later Montedison), at all times engaged in industrial catalysis. During his 32-years industrial employment he was Responsible for Catalysis Departments, R-D Manager,

Senior Scientist in various companies of the Montedison Group. Despite retiring in 1991 Nicola still works as a catalyst consultant and cooperates in catalyst research with academics in the Universities of Milan and Venice. He was a member of the Editorial Board of Applied Catalysis and of the CEE and IUPAC Committees on porous materials, and he is author or co-author of over 150 scientific papers, patents, book chapters and congress presentations on heterogeneous catalysis.

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