

HETEROGENEOUS CATALYSIS BY METALS

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Summary

Catalysis by metals will be reviewed in this paper because of the progress in this sub-field of heterogeneous catalysis since 1965. Preparation of supported metals has become reproducible under controlled conditions, and reaction rates can now be measured in the absence of limitations by mass and heat transfer. With correct rates obtainable on reproducible catalysts, it is increasingly common to report rates not as an ill-defined 'activity' but as turnover rates, *i.e.*, molecules reacting per second per surface metal atom titrated by standardized methods of selective chemisorption.

Turnover rates for a number of reactions on several metals have been reproduced by different investigators using different preparations. Agreement has been found between turnover rates on catalysts with 100% of metal exposed and on large single crystals. Hence, for reactions that are called structure-insensitive, no bulk metal (subsurface atoms) is needed to obtain the surface behavior of bulk samples. It is also clear that metal-support interactions can be totally absent. For other reactions, *i.e.* those which are structure-sensitive, certain *sites* consisting of ensembles of surface atoms exhibit enhanced turnover rates. Identifying and counting these metallic sites are challenging tasks that have been tackled successfully only in the case of the synthesis of ammonia on iron.

Introduction

In heterogeneous catalysis many simple questions have long been asked, and until recently the answers have often been contradictory. This is because a measure of catalytic activity is not quantitative unless it is reported as a turnover number, N , more appropriately called a *turnover frequency*, or turnover rate, which is the number of molecules transformed per unit time per catalytic site. Without a knowledge of N , catalytic data cannot be reproduced and remain qualitative. In enzymatic and homogeneous catalysis, values of N have been reported for many years, as it is easy in principle to count the number of catalytic entities in solution. In heterogeneous catalysis, counting sites remains a formidable obstacle to scientific advances. Yet, over the past twenty years, much progress has been made in counting the

atoms on metallic surfaces, or in using single crystals, for which counting surface atoms is trivial. However, the number of surface atoms is not necessarily equal to the number of catalytic sites. Moreover, even on a perfect single crystal surface, a molecule can be bound in different ways. Thus carbon monoxide can be held on a single atom or it can bridge two or more adjacent atoms, and react in these various binding states at different rates. Thus, even in an ideal situation, a value of N might be only an average one. If the surface is not perfect, there is always the chance that the reaction will take place, in whole or in part, on a small number of defects, *e.g.* steps, kinks, edges and corners.

In spite of these difficulties, values of N obtained by counting metallic surface atoms have proved immensely useful over the past 20 years in comparing data obtained in different laboratories and in answering an old question in heterogeneous catalysis: as particle size grows from that of a small cluster to infinite value for a single macroscopic crystal, how does the value of N change for a given reaction on a given metal? Does it change at all? If it does not change appreciably, as has been repeatedly found in the past 15 years, what does this behavior tell us about the mechanism of the reaction?

Counting surface atoms

To prepare a stable collection of catalytic metal particles for the study of size effects, use is made of a carrier or *support* consisting of a porous matrix which allows in-and-out flow of reactants and products, contains the metal particles in its pores and itself takes no direct part in the catalytic reaction on the metal. The support may be alumina, silica, amorphous or crystalline (zeolitic) aluminosilicates, magnesium oxide or carbon. The appropriate metal salt is introduced into the support by adsorption or ion exchange, and then is reduced, usually in flowing hydrogen, to form zero-valent metallic clusters or particles. The size of the latter depends on the details of the preparation. Its determination by physical tools such as X-ray diffraction or transmission electron microscopy is usually cumbersome and is carried out mainly as a check of the chemical technique chosen to obtain not the size but the *dispersion* of the metal in the sample, *i.e.*, the *fraction of metal atoms exposed*. Dispersion is defined as the ratio of the number of surface metal atoms to the total number of metal atoms. The number of surface atoms is equal to the number of molecules of a chemisorptive gas, *e.g.* H_2 , O_2 , CO , held to the metal and to the metal only ('selective chemisorption') at a suitable temperature and pressure, multiplied by an empirical coefficient which takes into account possible dissociation of the adsorbed molecule, *e.g.* H_2 into $2H$, as well as the stoichiometry, *i.e.* the number of atoms or molecules bound per surface atom. The latter must be determined separately by chemisorption and physisorption or physical tools on samples used for calibration. To relate the calibration data to dispersion, assumptions must then be made to translate measured particle surface area or size or

volume of the calibration samples into number of surface atoms. It must also be assumed that the adsorption stoichiometry does not change with particle size, as calibration is done by necessity on larger particles. No wonder that adsorption stoichiometries are still in doubt, even for the most studied metal, platinum, and the most common chemisorptive gases H_2 , O_2 and CO . There is an additional difficulty to be taken into account, namely the shape of very small metallic particles, their change of shape as a result of chemisorption [1] and the unknown relationship between shape and adsorption stoichiometry. At the present time, comparisons of turnover frequency must be made on the basis of the same assumed adsorption stoichiometry. At worst, this may lead to consistent errors by a factor of two in reported values of dispersion.

Because the shape of very small particles is unknown, the relationship between size and shape is not clear. This was first pointed out in an early study of platinum dispersion in commercial platinum reforming catalysts [2]. In that study, it was reported that the metal was present in the form of small *clusters* which, in spite of a dispersion approaching unity, were probably not *atomically* dispersed, but were in the form of rafts, which have recently been identified by electron microscopy in the case of ruthenium on silica gel [3]. In fact, there is no authenticated case of *atomic* dispersion in which a single accessible zero-valent metal atom is known to be *stable* on a support. For instance, it was claimed that zero-valent platinum could be atomically dispersed in the supercages (1.3 nm in diameter, accessible through 0.8 nm windows) of a Y-zeolite [4]. Later work could not find evidence in favor of atomic dispersion, but suggested the existence of platinum clusters *ca.* 1 nm in size [5 - 7]. A recent study of Pt/Y-zeolite by X-ray scattering reveals that the platinum clusters in the supercages of Y-zeolites possess the normal face-centered cubic structure of the bulk metal with lattice spacing the same as for bulk platinum [8]. This is true when the clusters are covered with hydrogen. When they are bare, there appears to be a slight contraction in the lattice parameters, and when they are covered with oxygen, the crystalline structure of platinum is almost completely destroyed [9]. Although not atomically dispersed, these clusters exhibit a measured dispersion of unity. Yet they may contain quite a few atoms, as a tetrahedron of close-packed spheres having four spheres on each edge of the tetrahedron contains 20 spheres, with 19 of them exposed at the surface. If the spheres are platinum atoms, the edge of the tetrahedron measures 1.35 nm, but its dispersion is virtually unity. In reality, no crystalline shapes can be recognized on high resolution electron micrographs of small metallic clusters; rather, they look like irregular spheres. Crystal habit is seen only for particles *ca.* 3 nm in size or more.

Thus any relation between dispersion D and spherical size d is obscured by the shape factor. For convenience, the conversion formula $d = (1/D)$ nm is adequate for transition metals, *e.g.*, a dispersion of one-half corresponds to a size equal to 2 nm. The formula fails if the clusters exhibit an extended raft structure.

Measuring turnover frequency

In heterogeneous catalysis, the usual problems of measuring rates of reactions are compounded by the necessity of transferring heat and mass to and from the catalytic surface at a rate fast enough so that these physical rates do not interfere with the chemical one. To cope with these effects, chemical engineers have evolved elaborate theories with practical experimental criteria [10]. With supported metals, a particularly simple criterion first proposed by Koros and Nowak [11] provides a test of good kinetic behavior. The method is simple: prepare two or more catalysts with metal loadings as different as possible, measure the number of surface atoms and the rate of reaction at two temperatures [12], and calculate the turnover frequency N . If N is the same at each temperature for the two or more samples, the kinetic measurement is correct. The criterion of course works as well for homogeneous catalysts attached to a solid surface.

With proper safeguards, it is now possible to reproduce the value of N on a given metal, under identical conditions of pressure, temperature and composition, measured on different catalysts, prepared in different laboratories by different methods with different supports. An example, that of the hydrogenation of cyclopropane to propane, will be discussed below. The quantification and duplication of reaction rates on metals is perhaps the most significant recent advance in heterogeneous catalysis, a field of chemical reactivity with an ingrained reputation for qualitative and irreproducible results.

Expectations for particle size effect

First of all, as we grow a cluster starting with one atom, the coordination number, *i.e.* the number i of nearest metal neighbors, of an exposed surface atom clearly goes up steadily until it reaches average values of six to nine, characteristic of low-index faces on large crystals [13]. Similarly, the relative fraction of exposed atoms C_i with coordination number i changes with particle size, as will the relative fraction of surface sites B_j defined as locations above the surface with j nearest metal neighbors [14]. The effects measured by C_i and B_j will be called *structural*. They should vary more markedly as a 1 nm cluster is grown up to a size of 5 nm, a range which is critical for the observation of such effects. Above 5 nm little effect is expected, as regular crystallographic habits become fully developed. In a way, changing particle size in the range from 1 to 5 nm is similar to looking at different crystallographic planes on a macroscopic single crystal. But below 1 nm, other effects, not observable on large crystals, may become important as the relative proportion of surface atoms with very low coordination numbers becomes appreciable, if not dominant. This is the essence of the concept of Taylor's *active center*.

Calculations of the electronic structure of clusters of transition metals support the expectation of their anomalous properties [15], and many results have been obtained by means of the fruitful X_α Scattered Wave SCF Method of Slater and Johnston [16]. Experiments reveal chemical and physical properties of metallic clusters that differ from those of bulk crystals [17]. For example, palladium particles supported on silica gel in the dispersion range from 0 to 0.8 exhibit a spin paramagnetism [18] and a hydrogen solubility [19] which both decrease linearly with increasing dispersion.

Different properties of supported clusters are also expected as a result of their possible interaction with the support. As metallic clusters below 3 nm change shape readily [1], depending on their contact angle with the support, they will change their surface structure together with their shape [3]. They may also exhibit preferred or anomalous structures because of epitaxial growth on the support [20]. Finally, there may be an electronic charge transfer between the metal and the non-metallic support, an effect well-known in solid state physics and first formulated by Schwab and co-workers in the case of supported metal catalysts [21, 22]. Depending on whether the effect is observable as a change in catalytic activity of the support or of the metal, it is convenient to refer to it as the Schwab effect of the first kind or of the second kind, respectively. Clearly, if they exist, these metal-support interactions must become more important as cluster size decreases. There are also cases where the support participates in the catalytic reaction by transfer of a reaction intermediate from the metal to the support, as in dual-function catalysis [23] or hydrogen spillover [24]. Artefacts may also arise due to the transfer of impurities from the support to the metal [25, 26].

In brief, particle size should affect binding energies of reactants, catalytic intermediates and products and, hence, the turnover frequency. How important the effect will be and to which of its many possible causes it can be ascribed are questions that can be answered today only by experiment. Some of the evidence will now be reviewed.

The hydrogenation of cyclopropane

This reaction, when leading to propane, resembles the hydrogenation of alkenes and not hydrogenolysis, the latter reaction leading to methane and ethane. At low temperatures, hydrogenation is the sole reaction on platinum, and isomerization of cyclopropane to propene on the support can also be neglected. An early study of the reaction on platinum unsupported and supported on alumina or silica gel showed, to our surprise, that when the dispersion of the metal was varied essentially between ~ 0 and ~ 1 , the turnover frequency did not vary by more than a factor of two, being larger for the catalysts with the larger dispersion [27]. The same conclusion has been reached qualitatively and quantitatively in a particularly careful and exhaustive check of the work of our group by another group [28]. The turnover

frequency reported by both groups has also been obtained on a macroscopic single crystal of platinum, when the reaction was studied at pressures comparable to those used by the other two groups [29]. It is in excellent agreement with the other results, the margin of error being due to an extrapolation in temperature (not pressure) necessary to compare the results on the macroscopic single crystals and the microscopic single crystals of platinum. That the turnover frequency is virtually the same on a large crystal and on crystallites 1 to 1.5 nm in size supported on alumina or silica is a result that deserves further discussion [30].

In our earlier paper [27], it was said that because of the lack of effect of particle size on the rate of hydrogenation of cyclopropane, the reaction was a *facile* one. This was an unfortunate choice of adjective because *facile* simply means easy to the organic chemist. At the suggestion of Charles Kemball, it was switched from *facile* to *structure-insensitive*, in keeping with the rationale expounded in the previous section [31]. Correspondingly, reactions that were called *demanding* [27] became known as *structure-sensitive* [31].

Structure-insensitive and structure-sensitive reactions

In a critical review, I have collected information pertaining to the effect on turnover frequency of three factors: first, the effect of particle size in the critical range and of crystallographic orientation for macroscopic single crystals; second, the effect of alloying an active Group VIII metal such as nickel with a less active Group Ib metal such as copper; and third, the effect of changing from one Group VIII metal to another of the same group [32]. More recent references are found in [30]. Reactions have been classified into two groups. In Group I are reactions involving breaking (or making) of H—H, C—H, or O—H bonds, and in Group II are reactions involving breaking (or making) of C—C, N—N, or C—O bonds [33]. Reactions of Group I are less sensitive than reactions of Group II to changes of structure, to alloying, or to the nature of the metal. It is proposed that these three changes cause changes in binding energy that are magnified for reactions of Group II since these require surface sites consisting of more metal atoms than do reactions of Group I, which may necessitate only one surface atom. The advantages of this explanation are its simplicity and its ability to predict behavior. For instance, it predicts that reactions of Group II require a homogeneous transition metal catalyst containing more than one metal atom [34]. It suggests that dihydrogen may require only one surface atom for its dissociation, and not two adjacent ones as traditionally assumed [35]. Similarly, it favors formation of a π -complex between an alkene and a single metal atom [36] rather than that of an eclipsed 1,2-diadsorbed alkane on two adjacent metal atoms [37]. Nevertheless, it would be foolhardy to claim that the proposed explanation of structure-insensitivity, if correct, is unique. In fact, three other plausible explanations of structure-insensitivity will be considered below: surface reconstruction [39], extractive chemisorption [40], and

formation of a catalytic metal-alkyl overlayer [41]. This wealth of speculation underscores the usefulness of studies on the effect — or *lack of effect* — of particle size on turnover frequency.

Alternative explanations of structure-insensitivity

In heterogeneous catalysis by metallic chlorides, oxides and sulfides, there are many examples of extreme anisotropy in which a particular crystallographic orientation does all the catalytic work. This is especially marked with catalysts which consist of layer lattices: only the planes exposing coordinatively unsaturated transition metal ions are catalytically active. There are also examples of such catalysts where only a minute concentration (1 in 10^5) of surface defects is catalytically active. By contrast, structure-sensitivity with metals, when it exists, is much less dramatic, involving changes in turnover frequency by a factor of not more than 10 - 100 in order of magnitude. Much more surprising are the recent studies with metallic catalysts exhibiting structure-insensitivity. Note that insensitivity does not mean invariance. There is a fuzzy area between insensitivity and sensitivity. Differences in reactivity are magnified by operation at low temperatures and smoothed out at high temperatures. To draw the boundary in the fuzzy area clearly requires a value judgment.

Thus, in the more recent study of hydrogenation of cyclopropane on supported platinum, it is concluded that a factor of two in turnover frequency means structure-sensitivity [28], whereas in the older study the same factor of two was interpreted as a case of structure-insensitivity [27]. It is a tribute to progress in experimentation that a monotonic increase of turnover frequency with dispersion by a factor of only two can be considered significant enough to deserve an explanation, namely that corner and edge atoms are more reactive than other atoms with higher coordination numbers. It is truly surprising to find a reaction which exhibits structure-insensitivity within the experimental error of less than 5% in turnover frequency. This is the case for cyclohexene hydrogenation, which will be discussed later in this paper.

The hydrogen-oxygen reaction on platinum: surface reconstruction

When the reaction between H_2 and O_2 on supported platinum is studied on the same catalysts in the same apparatus, it is found that the reaction is structure-sensitive in excess hydrogen but structure-insensitive in excess oxygen [38]. Since the kinetics indicates that the rates under these conditions are determined by chemisorption of dioxygen and dihydrogen respectively, the general explanation mentioned earlier would suggest that more surface atoms are required for splitting dioxygen than for splitting dihydrogen. While this is reasonable, another explanation can be suggested [38]. In excess oxygen, the surface is probably covered with an almost complete monolayer of oxygen. This monolayer may reconstruct the platinum surface so as to obliterate the structural details originally present on particles of different dimensions [8]. By contrast, in excess hydrogen, a hydrogen-

covered surface would remain unreconstructed. Hence structure-insensitivity in one case and sensitivity in the other. Support for this view is provided by an X-ray scattering study of 3 nm platinum particles in a Y-zeolite, in atmospheres of both hydrogen and oxygen [8]. In oxygen, the successive peak intensities in the radial distribution function for the platinum structure are diminished by an amount corresponding to the amount of destruction of the normal platinum lattice in the outermost metallic layer of the particle. More strikingly, exposure to oxygen at room temperature of 1 nm clusters of platinum in the supercages of the zeolite almost completely destroys the normal lattice structure exhibited by the same platinum clusters when covered with a layer of hydrogen. Quite recently, the reaction between H_2 and O_2 on supported platinum catalysts has been reinvestigated by the Boreskov Group [39]. Their data show structure-insensitivity in both excess H_2 and excess O_2 . The difference between the results of both this investigation and those found by us may be due to a substantial difference in pretreatment of the catalysts. The effect of these pretreatments on surface composition or structure needs further study.

Hydrogenation of di-t-butyl acetylene on platinum: extractive chemisorption

The idea behind such a study of liquid-phase hydrogenation is that the triple bond of the substrate is so shielded by the bulky substituents that it cannot approach surface atoms of a flat crystal plane. Hence it may well react only, or preferentially, at corner and perhaps edge atoms of very small particles. This logic was contradicted in a study [40] using cyclopentene as a reference compound: all runs with di-t-butyl acetylene were sandwiched between two runs with cyclopentene, and runs were discarded when the two cyclopentene runs of the sandwich gave a turnover frequency differing by more than 5%. Not only does the hindered substrate get hydrogenated almost as fast as cyclopentene, but if there is a significant trend in this apparently structure-insensitive reaction, it is the opposite of that expected; namely, the particles with the lower dispersion (flatter planes) are more reactive than the particles with high dispersion (edges and corners). The ingenious explanation of the authors of this fascinating study is *extractive chemisorption*. If the metal atoms are extracted from their normal metallic habitat during the formation of the catalytic intermediate, structure-insensitivity becomes understandable. Another possible explanation [41], to be discussed next, is considered briefly by the same authors but dismissed.

Hydrogenation of cyclohexene on platinum and palladium: formation of a metal alkyl catalytic species

This reaction has been studied in both liquid and gas phases on supported palladium and platinum catalysts [42 - 44]. The reaction was structure-insensitive. In particular in the liquid phase, the turnover frequency remained remarkably invariant as the metal dispersion was varied over the critical range. This was especially striking for the data concerning liquid phase reaction on platinum; these data remained the same irrespective of

support, metal loading or dispersion. The unusual reporting of rates with three significant figures was justified by the reproducibility of the data and by the fact that the rate, at constant pressure, was strictly zero-order with respect to hydrocarbon, and hence a constant very easily measured with precision and accuracy. Two of the catalysts studied exhibited a platinum dispersion of unity, thus having a characteristic dimension of 1 nm or less. These results can be explained by the assumption that a reaction will be structure-insensitive if the critical intermediate requires only one surface atom, or perhaps two adjacent ones. Yet the remarkable insensitivity of the reaction to structural changes brought about by variation in particle size makes it attractive to consider another explanation, which may also be an alternative to that of extractive chemisorption discussed above. This interpretation, advanced to explain a large number of observations on the catalytic hydrogenation of olefins [41], suggests that the metal is covered with a partially dehydrogenated adsorbed olefin, whose role is to transfer dihydrogen from the fluid phase to the substrate to be hydrogenated. The elaborate mechanistic interpretations [37] carried out since 1934 to check the original mechanism of Horiuti and Polanyi [45] for hydrogenation of alkenes on metals remain unchanged; however, the nature of the catalytic entity is postulated to be not a site at the metallic surface, but an alkyl-metal complex formed by interaction between the metal and the substrate. Such a view might be helpful for understanding the relative success of asymmetric hydrogenation performed on ordinary metal catalysts pretreated with optically active chemisorbed molecules [46, 47].

Structure-sensitive reactions

The exploration of the effect of particle size on the crystallographic orientation of supported metals has revealed that the nature of the reaction clearly influences the magnitude or trend of the effect. Thus, as discussed above, some reactions have a turnover frequency which is little or even negligibly affected by the structural details of the surface. In contrast, ammonia synthesis on supported iron has a turnover frequency which *increases* monotonically as dispersion increases [48]. This was interpreted as reflecting the need for special surface atoms, C_7 , with coordination number seven to chemisorb dinitrogen in or prior to the rate-determining process. According to theoretical considerations [14], the relative concentration of C_7 atoms is less on small particles than on larger ones. The assignment of enhanced activity to C_7 atoms has been recently supported by findings on single crystals of iron [49]. In a high-pressure study of ammonia synthesis, it was found that the (111) planes of iron which expose C_7 atoms are more active by two orders of magnitude than are other planes of iron. When these data on Fe(111) are extrapolated down in pressure and temperature to the conditions corresponding to those of a study of ammonia synthesis on a commercial catalyst [50], it is found [51] that the turnover frequency is identical (to within less than a factor of two) on Fe(111) and on the commercial catalyst.

The reaction between H_2 and O_2 in excess H_2 on supported platinum is an example of a reaction for which the turnover frequency is larger on larger particles than on smaller ones [38]. This may be explained by the fact that the dissociation of O_2 on platinum is more rapid on surface atoms of lower coordination than that found on smaller particles or on stepped single crystals of platinum, exposing active steps with lower coordination numbers among inactive terraces having atoms with higher coordination numbers [52].

Conclusion

In summary, the study of particle size effect on turnover frequency has proved to be an incisive tool in heterogeneous catalysis. The largely unexplored domain involving particle sizes *below* 1 nm appears the most challenging for the future in terms of preparation, characterization and potential enhancement of reactivity [6]. Moreover, *here the domain of heterogeneous catalysis rejoins the domain of homogeneous catalysis* or that of heterogeneous catalysis by free or immobilized organometallic metal cluster complexes [53]. Finally, in this size range metal-support interactions are expected to be particularly important. Much remains to be done to understand the nature of these interactions [54].

For the future, three other avenues of research appear promising. First, the symmetry and size of the ensembles responsible for the activity of metals in structure-sensitive reactions must be determined, and the number of active sites must be counted. Progress toward that goal has been achieved in the case of ammonia synthesis on iron. Second, the nature of the Schwab effect of the second kind must be understood and exploited in the case of metal-support interactions that involve the support as a ligand to modify the activity of metal clusters. Such interactions have been identified in the case of platinum clusters in acid Y-zeolites. Third, new materials must be explored, including new supports such as those exhibiting basic properties, new metals such as molybdenum, and metals modified with non-metallic (*e.g.* carbon) or metallic additives. In all three categories, it is expected that model systems will play an increasing role. These model systems consist of metal particles deposited on non-porous supports by methods used in the microfabrication of electronic devices. Such systems can be characterized by the large range of instruments used in surface science.

In closing, let us discuss some recent results obtained with the model systems just mentioned, dealing with another example of a structure-insensitive reaction, namely the low pressure oxidation of carbon monoxide on palladium clusters deposited on single crystals of $\alpha\text{-Al}_2\text{O}_3$ [55]. It was found that at 445 K, the turnover frequency for CO oxidation remained unchanged on clusters between 1.5 and 8 nm in average size, and under identical conditions was also the same as that reported on large single crystals of palladium [56]. The apparent increase in turnover frequency by a factor of three on

particles of palladium smaller than 3 nm when the CO oxidation was run at 518 K [55] disappears when the sites responsible for the reaction are properly counted [57]. It is interesting to note that the subsequent re-investigation [57] led to interesting facts concerning a structure-sensitive side reaction, namely the disproportionation of CO to CO₂ and surface carbon, which is favored on palladium clusters less than 3 nm in average size. The re-investigation in turn was prompted by the difficulty to explain the previous observations suggesting that CO oxidation was structure-insensitive at 445 K but structure-sensitive at 518 K.

Whatever the ultimate explanation of these findings, it appears that the concept of structure insensitivity or sensitivity can be fruitful in spotting anomalous behavior, the understanding of which is always of scientific or practical interest. The concept can also be applied to suggest that homogeneous transition metal catalysts with only one coordinated metal are suitable for structure-insensitive reactions, while metallic clusters are necessary in the case of structure-sensitive reactions.

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