JOURNAL OF CATALYSIS 120, 293–302 (1989)

Some Geometric Aspects of Structure Sensitivity

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Received January 10, 1989; revised August 4, 1989

The structure of supported metal catalysts can often be related to the fraction of the total atoms which is exposed on the surface (FE). The catalytic property related to the structure is the turnover frequency (TOF), the rate per unit of surface atoms. The particular behavior of these atoms can then be expressed via their Taylor ratio, a function of the way the surface atoms form an active site. For particles of FE < 0.5, it is interesting to relate the Taylor ratio to the geometry of idealized crystallites. The relation between Taylor ratio and FE is presented graphically for some ideal crystallites, based on several possible geometrically defined active sites. Some experimental data can be explained by the analysis, but there are many exceptions. Although a graph of log TOF against log FE may sometimes produce a straight line, there is no reason to expect such a relation to be valid in general.

INTRODUCTION

The concept of structure sensitivity for metals or oxides lies at the heart of understanding heterogeneous catalysis. Once the link between structure and properties is established, the possibility of improving the properties is dramatically enhanced. This has been shown to be true in many branches of material science. In the present discussion we shall deal with catalysis by metal surfaces and in particular with small metal particles supported on supposedly inert materials. The historical development of the concept of structure sensitivity is discussed in our recent review (*1*).

For a given metal, the turnover frequency (TOF) may be a strong function of the identity of the crystal face. For iron, Spencer *et al.* (*2*) have found the relative rates of ammonia synthesis at 525°C and 20 atm to be 418 : 25 : 1 for the (111), (100), and (110) faces. For supported small metal particles, it is often considered that the change in structure of the arrays of exposed atoms is directly related to the size of the particles. Dumesic *et al.* (*3*) have explained the observation that ammonia synthesis rate (TOF) over Fe/MgO increases as particle size increases by relating this to the increase in the fraction of exposed atoms in the (111) planes.

The hydrogenolysis rates of hydrocarbons like ethane, cyclopropane, or *n*-butane also depend on the crystal face exposed, and Goodman (*4*) has shown that the (100) face of Ni is much more active than the (111) face. In the range 420–580 K, the activation energy for reaction on the two faces is about the same. This result agrees with that of Dalmon and Martin (*5*), who find that the TOF for ethane hydrogenolysis on Ni/SiO_2 decreases as the particle size of Ni increases. Once again, this result is explained by proposing that the fraction of exposed atoms which are in the (111) planes increases as the particle size increases. On the other hand, in a study of ethane hydrogenolysis on Rh/SiO_2, Lee and Schmidt (*6*) show that the TOF changes greatly as the nature of the exposed faces of Rh is changed by successive oxidations and reductions. The particles exposing mostly (100) faces are much more active than those

0021-9517/89 $3.00

favoring (111) faces, but the particle size is not changed enough to play an important role in the large difference of TOF observed.

In two of the studies mentioned above (*3, 5*), the metal particle sizes were increased by sintering at successively higher temperatures. Through a complicated interplay of kinetics and thermodynamics, difficult to quantify, the particle shapes change with size so that the (111) faces are formed as sintering proceeds. In the final example (*6*), the reconstruction is driven by chemical forces, and the particle size seems to be irrelevant. However, the changes seem to be reversible (*6*) and so perhaps amenable to analysis by thermodynamics. In any event, the explanations of the results (*3, 5, 6*) based on geometric considerations seem to be satisfactory, although there is no simple relation between structure and particle size.

In this paper, we shall concentrate on the simple type of structure sensitivity for which the geometric properties of the particles can be related by simple models to their size. In other words, in contrast to the above examples (*3, 5, 6*), we assume that the particle shape (crystal habit) stays the same as its size changes. We shall follow the models of van Hardeveld and Hartog (*7*). For example, as the size of a fcc cuboctahedron goes from 1 to 100 nm, the fraction of (111) faces exposed goes from about 1.0 to 0.8 (*7*).

In surface science a reaction is considered structure insensitive if the TOF is the same on the principal faces of single crystals. It also follows that the TOF would be the same on a polycrystalline surface. However, the TOF of small supported metal particles may be size sensitive and change as the fraction of face atoms increases with particle size. Those dealing with supported metals usually call such behavior structure sensitive. For example, the CO/H_2 reaction is classified as structure insensitive on single crystals (*8*) and as structure sensitive on supported metal particles (*1*). Of course, edge and corner atoms can also be studied by the techniques of surface science (*9*).

For supported particles so small that the fraction of total atoms which is exposed on the surface (FE) is greater than 0.5, electronic and geometric effects both are important (*1*). The number of metal atoms per particle may be so small that the separation between electronic levels becomes appreciable. Although certain geometric effects typical of these particles can be modeled by stepped single crystals, the study of their electronic characteristics requires experiments on actual small particles, either deposited on an inert support or ideally as naked clusters carried in a gas stream (*1*). Here we concentrate our attention on geometric effects, which predominate for FE $<$ 0.5. We make the conventional distinction between electronic and geometric effects, but realize that geometric arrangements are ultimately influenced also by intermetallic bond strengths, i.e., electronic effects. We shall attempt to set up a framework for the consideration of the effect of metal particle size on TOF. However, the lessons of the examples of the previous paragraphs must be kept in mind. On a truly inert support, the structure is in general directly related to particle size, but different preparation and/or pretreatment methods may sometimes complicate matters. Support effects (i.e., for a noninert support), decoration, etc., may act independently of particle size. Details are in our review (*1*).

BASIC RELATIONS

We shall characterize the structure of supported metal particles by the fraction of atoms exposed FE, sometimes called the dispersion. For particles with $d > 1.0$ nm, the approximate expression

$$\mathrm{FE} = B/d, \qquad (1)$$

where B has a value of about 1.0 nm, holds, while for particles with $d \leq 1$ nm, FE = 1.0. More precise values of B can be deduced for any particular metal and crystal form

(*10*). Equation (1) assumes that the particles can be approximately inscribed in a sphere (*11*) and thus does not apply to rafts or other unusual shapes of small particles (FE > 0.5) (*8*). Note that the existence of rafts is probably related to metal–support interactions.

Ideally we hope to determine FE by hydrogen chemisorption, experimentally determining H/M and choosing H/M_s from the literature, so that

$$\mathrm{FE} = (H/M)\,(M_s/H), \qquad (2)$$

where H, M, and M_s represent the number of chemisorbed hydrogen atoms, the total number of metal atoms and the number of surface metal atoms, respectively. The goal of the chemisorption is the physical measurement of FE or particle size d, and the result should agree with that obtained by X-ray diffraction, electron microscopy, or extended X-ray absorption fine structure (EXAFS). Although H/M_s is often taken as unity (*10*), it may vary with FE, and this problem has been carefully considered by Kip *et al.* (*12*). In any event, we need to measure FE by the best methods available.

With FE taken to represent the relation of particle size to structure, we then choose TOF to represent the property of interest, i.e., the kinetics. However, in catalysis we can measure unambiguously only the rate per total atom of metal, which we call atomic rate (AR) (*1*). Then the turnover frequency is given by

$$\mathrm{TOF} = \mathrm{AR/FE}. \qquad (3)$$

Although AR can be measured directly, TOF requires the measurement of FE also.

We turn now to the causes of the variation of TOF with FE, i.e., structure sensitivity for small metal particles on an inert support. It is important to realize that in the present discussion all other variables which may cause TOF to vary are held constant: the composition of the reactant gases, the pressure, the temperature, and the conversion. The latter is ideally as low as possible, so that the TOF measured represents that at conversion approaching zero. Clearly the method of preparation of the catalyst must be held the same to the extent that is consistent with causing FE to vary. For instance, it was already mentioned that different oxidation/reduction treatments may change TOF without much change in FE (*6*).

Since Taylor (*13*) introduced the idea that the number of active sites on the surface of a catalyst does not need to be the same as the number of atoms on the surface, it is logical to define the ratio of the number of active sites to the number of surface atoms as the Taylor ratio TR. An active site may be an atom in a particular environment on the surface, perhaps at some defect. Alternatively, it may be an ensemble of several atoms. A quantity called sites exposed can be defined,

$$\mathrm{SE} = (\mathrm{TR})\,(\mathrm{FE}), \qquad (4)$$

where SE is the moles of sites per mole of total atoms. Then the turnover frequency per site becomes

$$\mathrm{TOF_s} = \mathrm{TOF/TR}. \qquad (5)$$

If only geometric factors are pertinent (FE < 0.5), it is often postulated (*14*) that $\mathrm{TOF_s}$ is constant as FE changes. This assumption implies that the crystal shape is determined by stable low-index planes. Then Eq. (5) indicates that the TOF is directly proportional to TR.

In cases for which some surface atoms are covered by decoration or isolated by alloying, it is important to specify clearly the basis for TOF or $\mathrm{TOF_s}$. Consider for instance the comparison of TOF for a certain reaction on low-temperature-reduced (LTR) Rh/TiO_2 with that on high-temperature-reduced (HTR) catalyst (*15*). It seems preferable to base the TOF for both cases on the atoms exposed before decoration by reduction at high temperature, measured for example by hydrogen chemisorption at 298 K on the LTR catalyst. Then the TOF (HTR) may be lower or higher than the TOF (LTR), depending on how decoration

affects the dilution of sites (ensembles) by blocking and the creation of new sites at the interface between the metal and the decorating entities. The use of a TOF_s based on hydrogen chemisorption at 298 K after decoration is confusing because the remaining exposed metal atoms may offer a greatly reduced concentration of ensembles capable of dissociating and chemisorbing H_2 at 298 K (*16*). In addition, any new interfacial sites are not measured. A direct kinetic measurement of TOF_s by a pulse method has been proposed for the CO/H_2 reaction (*17*).

We emphasize the fundamental importance of determining FE, a measure related to the structure which is unambiguous and can be refined as, for instance, the techniques of high-resolution electron microscopy develop. On the other hand, the independent measurement of TR cannot be obtained by the same physical method for all catalysts. Although the chemisorption of N_2 appears to give SE for the ammonia syntheis over Fe/MgO (*18*), such a recipe is known for only a few other systems (*1*). In general, the only way to estimate TR is to use catalysis, i.e., to determine TOF, and here the result may be influenced by all the parameters which govern a rate of reaction. Adopting a pertinent concept of Carberry (*14*) to our notation, FE is a measure of the structure (with the restrictions already mentioned in discussing Eq. (2)) of the *catalyst,* and TR (or SE) is a measure of the chosen property, the rate of *catalysis.*

Some of the reasons for which the Taylor ratio is different from 1.0 are now discussed.

1. Activity may be associated with defects on the crystal faces. Then as $FE \rightarrow 0$, there will be a limiting value of TR representing the fraction of defects on an infinite face. If this defect fraction stays constant as FE increases, TR should decrease toward zero as the fraction of face atoms goes to zero (antipathetic behavior).

2. Activity may be associated with a single atom of a particular coordination (B_1 sites). Then TR will be identical to the fraction on the surface of atoms of a particular, coordination, and this changes with FE (e.g., edge, corner, or face atoms for a fcc octahedron). This is the simplest kind of geometric structure sensitivity (*7, 1*).

3. Activity may be associated with a particular ensemble of X atoms, according to the viewpoint of Balandin (*19*) or Martin (*20*). It is important to realize that as $FE \rightarrow 0$ the limiting value of TR depends on the nature of the active site, i.e., the value of X, the crystal shape, etc.

Note that a site-measuring procedure such as N_2 adsorption (*18*) is assumed to count the sites as if they were defects or atoms of particular coordination. This leads to $TR < 1.0$. However, if we consider the simple example of two-atom sites ($X = 2$) on a square planar arrangement, it does not follow that $TR = 1/X$, even if any given atom of the surface has no more than one bond to an adsorbate which assumes a bridging position. The Taylor fraction is a kinetic parameter, related to catalysis, and in general it cannot be measured by an equilibrium measurement (chemisorption), which gives a measure of the structure of the catalyst only. However, by simple reasoning we can see that a square array of 16 face atoms has 24 possible nearest-neighbor two-atom sites leading to a Taylor ratio of 1.5. Presently we shall make use of the analysis of van Hardeveld and Hartog (*7*), which shows that, for example, the limiting value of TR for a fcc octahedron as $FE \rightarrow 0$ is 3.0 for B_2 sites.

Understanding structure sensitivity is intimately related to knowing the kinetics of the sequence of steps for the catalytic reaction. For the example of B_2 sites, if a coreactant or a product is present on the surface during reaction so that a fraction of the B_2 sites is covered, then reasoning about structure sensitivity must involve both the statistics related to the crystallite and those related to the distribution of adsorbate(s),

taking into account also the mobility of the surface species. This difficult subject, for immobile adsorbates (poisons), has been considered by Martin (*20*), and Andersen *et al.* (*21, 22*). The larger the value of X (B_x-sites), the more dramatic are the effects. In order to use the simple definition proposed for the Taylor ratio, it must be assumed that the surface coverage is small so that the statistics of the metal surface is not altered by the presence of adsorbate.

In discussing kinetic effects, it should be remembered that the activation energy should not vary with FE if only geometric factors are important. The Taylor ratio is then related to the preexponential factor only.

Steady-state isotopic tracing methods are useful for determining the surface coverage of the active intermediate θ_i during reaction at steady state, as emphasized by Biloen *et al.* (*23*) for the methanation reaction on various transition metals. However, it should be pointed out that in that work a Taylor fraction is defined as θ_i, where

$$\theta_i = \mathrm{TOF}/k_i. \qquad (6)$$

This is different from our definition. Biloen *et al.* (*23*) find that θ_i may be a surprisingly small fraction of a monolayer, as confirmed later by others (*24–26*) for various systems.

A SIMPLE CORRELATION FOR STRUCTURE SENSITIVITY

Much of the data available on structure sensitivity is represented in our review (*1*) as plots of log TOF vs log FE. Most of the experimental curves can be put into one of the three categories shown in Fig. 1. The vertical positions of the curves are arbitrary, and we are interested mostly in their shapes. For FE > 0.5, where the curves are dashed, electronic factors probably lead to the general decrease of TOF as FE goes toward unity (*1*). As an approximate method of correlation, Carberry (*14*) and Farin and Avnir (*27, 28*) have assumed that lines plotted as in Fig. 1 are straight. This approximation would apply roughly to the

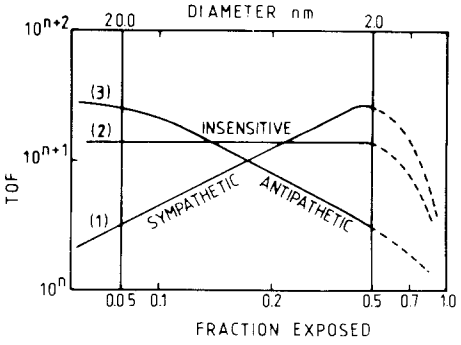

FIG. 1. Idealized behavior in structure sensitivity. Turnover frequency (TOF) in arbitrary units.

region $0.05 < \mathrm{FE} < 0.5$ if the data behave as in Fig. 1. Reference to the real data (*1*) shows many exceptions, and in particular, the maximum in curve (1) may well occur for FE < 0.5. Nevertheless, we may propose that, for the appropriate region in Fig. 1, behaviors according to curves (1) (positive slope), (2) (zero slope), and (3) (negative slope) be called sympathetic structure sensitivity, structure insensitivity, and antipathetic structure sensitivity (*1*).

We can give a more general meaning to the ordinates of Fig. 1 by normalizing the data on TOF so that $\lim \mathrm{TOF}_{\mathrm{FE}\to 0} = \mathrm{TOF}_s$ for $X = 1$ and with every surface atom being an active site. Of course in the limit of small FE the fraction of corner and edge atoms goes to zero. Then the approximately linear parts of the data on TR vs FE might be plotted according to

$$\mathrm{TR} = (\mathrm{FE})^{2-D_R}, \qquad 0.05 < \mathrm{FE} < 0.5 \qquad (7)$$

and

$$\lim \mathrm{TR}_{\mathrm{FE}\to 0} = \text{constant} \qquad (8)$$

for ensembles of atoms in a face. Clearly if only edge and/or corner atoms are active, then

$$\lim \mathrm{TR}_{\mathrm{FE}\to 0} = 0. \qquad (9)$$

In Eq. (7) we have chosen to define the exponent according to the definition of Farin and Avnir (*27*), where D_R is called the reaction dimension. When $D_R = 2$, there is

structure insensitivity, and it is convenient to associate this behavior with a dimensionality of 2, i.e., the reaction rate is proportional to the total exposed surface to a particle. Now elementary geometric reasoning leads to the following classifications. It is assumed that the crystallite shape stays the same as its size (total atoms) changes.

$D_R = 0$: Corner atoms only are active; number of active sites per particle constant.

$D_R = 1$: Edge atoms only are active; number of active sites proportional to the crystallite size.

$D_R = 2$: All surface atoms are active; number of active sites proportional to the area of the crystallite.

$D_R > 2$: Face atoms only are active; number of active sites increases faster than the total area.

If the crystal shape changes with size, then the basis for the values of D_R discussed above is invalid and D_R becomes a completely empirical quantity. The highest value reported by Farin and Avnir (*28*) is 5.8 for ammonia synthesis over Fe/MgO (*3*). Of course log TOF vs log FE may not produce a straight line at all. In any event, it is clear that it is dangerous to reason about the causes of a certain behavior without independent physical evidence (electron microscopy, microdiffraction) concerning the faces exposed or the shape of the crystallites. The effect of particle size on the coordination of exposed metal atoms has been discussed in detail by Dreschler (*11*).

The problem is further complicated by the fact that most preparation methods lead to a distribution of crystallite sizes for a given catalyst sample. Hence progress in understanding requires the use of carefully prepared model supported catalysts (*1, 29, 30*).

For values of D_R less than 2, it is also to be expected that actual data will result in nonintegral values of D_R. The lowest value reported by Farin and Avnir (*28*) is 0.7 for ethylene oxidation to CO_2 on Ag/SiO_2 (*31*).

TAYLOR RATIOS PREDICTED BY MODEL CRYSTALLITES

Let us now see how TR varies with FE according to a few of the many models worked out by van Hardeveld and Hartog (*7*). These authors used as independent variable m, the number of atoms on an edge of an octahedron, or the sum of the atoms on one (111) edge and one (100) edge of a cubo-octahedron, for example. From their tables and formulas, the total atoms N_T, the surface atoms N_S, and the surface atoms of a particular coordination $N(C_j)$ can be computed. Then FE is N_S/N_T, and the TR for a particular type of site is $N(C_j)/N_S$. When an ensemble of atoms is considered as a site, we find $TR = N(B_x(C_j, C_k \cdot \cdot \cdot))/N_S$, where a typical site may be for example $B_3(C_7, C_7, C_9)$, i.e., two edge plus one face atom along the edge of an fcc octahedron. Another B_3 site might be $B_3(C_9, C_9, C_9)$, a group of three face atoms.

The results for a few simple cases are shown in Fig. 2. Curves (1), (3), and (5) are for face atoms (C_9) for B_1, B_2, and B_3 sites, respectively. The limiting values of TR as FE goes to zero are, respectively, 1, 3, and 2. As expected, the models predict that structure sensitivity effects are shifted to lower FE as the value of X increases. As also expected, the behavior is antipathetic, as in curve (3) of Fig. 1. However, it is clear that the lines are by no means straight. For curve (5) the D_R at low FE is close to 2 and increases to about 3.4 at FE = 0.5. Reference to our review (*1*) shows that the experimental antipathetic curves are not usually straight.

Turning now to curves (2), (4), and (6) of Fig. 2, which represent sympathetic structure sensitivity that arises because only edge atoms are presumed active, we see that these model curves are approximately straight, with D_R about 1, in the region $0.05 < FE < 0.5$. Although Eq. (7) is in agreement with this result, many experimental curves show a maximum to the left of FE = 0.5 (*1*). This may appear because the en-

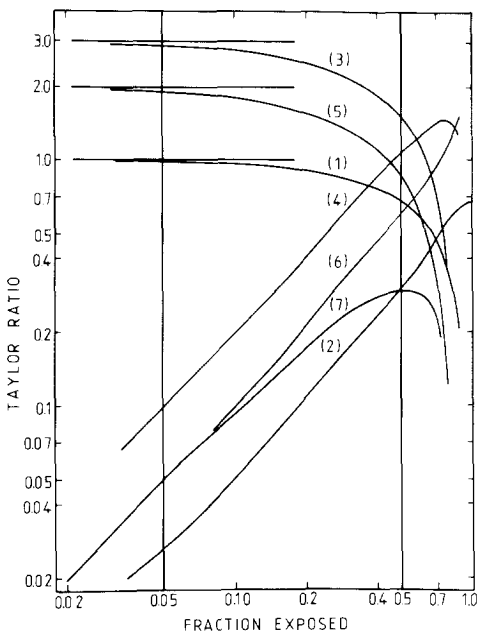

FIG. 2. Variation of the Taylor ratio with dispersion according to the models of van Hardeveld and Hartog (*7*). Curves 1–6 are for fcc octahedra and represent the following atoms or groups of atoms as reaction sites: (1) single C_9 atoms, (111) faces; (2) single C_7 atoms, edges; (3) B_2 sites, 2 C_9 atoms, faces; (4) B_2 sites, C_7, C_9 atoms, edges; (5) B_3 sites, 3 C_9 atoms, faces; (6) B_3 sites, C_7, C_7, C_9 atoms, edges. Curve (7) is for the fcc octahedron B_5-max crystal and represents the B_5 sites, C_7, C_7, C_7, C_7, C_{11} atoms, edges.

semble size is larger than those discussed so far, so let us consider B_5 sites.

Curve (7) of Fig. 2 represents the Taylor ratio for B_5 sites, defined for crystallites which are incomplete octahedra (*7*). On each face another layer of atoms (111) is added so that the B_5 sites are formed from two atoms (C_7) along the original edge of the octahedron with two atoms (C_7) from the added new edge and one central atom (C_{11}) from the original face. This type of crystal is called "B_5-max" (*7*). Now curve (7) is not straight, but passes through a maximum near FE = 0.5.

The curves of Fig. 2 show that Eq. (7) cannot in general represent the results based on the crystal models over the reasonable range $0.05 < FE < 0.5$. Of course over more restricted ranges anything is possible. In addition, a particular combination of geometric effects, electronic effects, support effects, and effects of poison may by chance produce a result fit by Eq. (7).

The curves in Fig. 2 assume that we jump from one total number of atoms to another in order to keep the crystal shapes as assumed. If one atom at a time is added, the situation is much more complicated, and oscillations may be introduced into some curves, as shown by the work of Yacaman *et al.* (*32*). In order to proceed further, modern computerized statistical procedures should be used, following for example Andersen *et al.* (*21, 22*). However, it seems to us that graphs like Fig. 2 are an effective method of presentation of such geometric results.

REPRESENTATION OF REACTION RATES

It is appropriate to consider three different representations of the reaction rate: the atomic rate, AR; the turnover rate, TOF; and the rate per particle, *a* (*28*). If a plot of log AR vs log FE over a suitably restricted range can be represented by a straight line, the slope of the line is $3\text{-}D_R$. It is important to determine the goodness of fit and the value of D_R from AR and FE, two independently measured, uncorrelated variables. It is not as precise to obtain D_R from a plot of AR/FE, i.e., TOF, vs FE, because of the appearance of FE both in the ordinate and in the abscissa. A fortiori, it is statistically unsuitable to deduce D_R from a plot of *a* (roughly proportional to $AR/(FE)^3$) vs FE. More insight into those matters can be derived from Fig. 3.

The turnover frequency for the methanation reaction over Pd/SiO_2 at 1 atm, 523 K, and $H_2/CO = 3$ has been measured as a function of dispersion by Rieck and Bell (*33*). Their results are plotted in curve (1) of Fig. 3. Typical antipathetic behavior is obtained, as typified by curves (1), (3), and (5) of Fig. 2. As FE goes to zero, the TOF should level out at a value equal to a suitable average of the rates on the (111) and (100) faces of single crystals, since it has

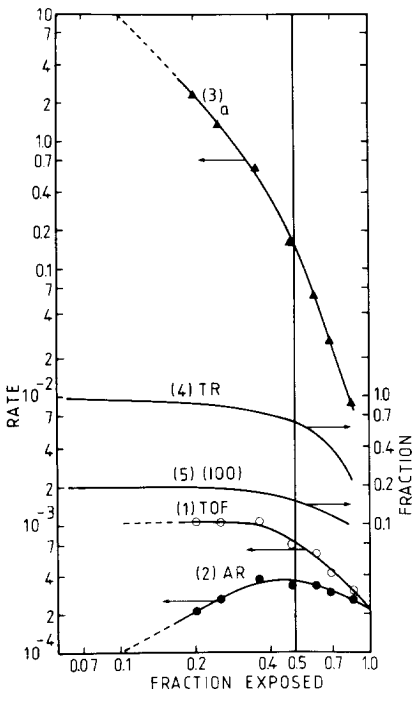

FIG. 3. The experimental data of Rieck and Bell (*31*) expressed via various definitions of the reaction rate: (1) TOF, s^{-1}, from (*31*) (○); (2) AR, s^{-1}, calculated from (*31*) by AR = (TOF) (FE) (●); (3) a, mol s^{-1} crystallite^{-1}, assuming fcc cubo-octahedra and using the models of van Hardeveld and Hartog (*7*) (▲); (4) TR, Taylor ratio of all face atoms, i.e., $[N(C_8) + N(C_9)]/N_S$; (5) (100), fraction of face atoms (C_8 + C_9) which are C_8, i.e., located in the exposed (100) faces.

been assumed that the Pd crystals are present in the form of fcc cubo-octahedra (*33*). Apparently the single-crystal rate data are not available.

Curve (2) shows the atomic rate as a function of FE. If this reaction system were of practical interest, the best use of Pd would correspond to the maximum in AR, at FE = 0.45. Note that the limiting slope of AR vs FE is 1, and AR goes to zero in the single-crystal limit. In the limit of FE = 1.0, AR = TOF.

Curve (3) of Fig. 3 shows the rate per particle a, which is calculated from the experimental data by the relation a = (TOF) (N_S). To find N_S, the particle shapes must be assumed, in the event, cubo-octahedra, as already mentioned. Ideally the morphology might be found via high-resolution electron microscopy and microdiffraction. Rieck and Bell (*33*), however, base their choice on infrared data. CO adsorbs in the linear form on Pd (111) surfaces and in the bridged form on Pd (100) faces. It is shown (*33, 34*) that the ratio of the intensities of the appropriate infrared bands is in qualitative agreement with the results based on the work of van Hardeveld and Hartog (*7*), as shown in Fig. 3 by curves (4) and (5). Curve (4) gives the Taylor ratio of the sum of the atoms in the (100) and the (111) faces, calculated from Ref. (*7*). Curve (5) shows that for large crystals, 20% of the surface atoms are in the (100) faces, and this portion decreases to zero as FE goes to 1.0.

Using then the values of N_S for a cubo-octahedron, curve (3) has been plotted. Clearly most of the change in a with FE has its origin in the increase in N_S as the crystallite size increases. For the largest particles, the slope of curve (3) becomes -2, and the value of a increases without limit as FE goes to zero.

If the data are plottd as a vs FE, without reference to curves (1) and (2), it is tempting to ignore the apparently slight curvature and to pass a best-fit straight line through the points. In this way, Farin and Avnir find $D_R = 2.9$ (*28*). It is then hardly surprising to find that curve (3) agrees with the models of van Hardeveld and Hartog (*7*).

Finally we note that if curve (4) of Fig. 3, for example, has the right shape to represent curve (1), then simple statistics can be used to find the best values of TOF_s from Eq. (5). For the data shown, TOF_s is about 10^{-3} s^{-1}.

CONCLUSIONS

1. It is logical to use fraction-exposed FE and turnover frequency or rate TOF as the measures of the structure and properties (kinetics) of catalysts. Catalytic sites, be they defects or ensembles, are related to the kinetics as measured through TOF and are rarely amenable to estimation by an equilibrium measurement.

2. The essence of structure sensitivity of the type considered here is expressed through the Taylor ratio TR. For the region of FE for which geometric effects predominate, TR can be related to FE through models of small perfect crystals. If such a representation seems experimentally justified, then it is easy to find the appropriate value of the turnover frequency per site, TOF_S, a quantity independent of FE.

3. Although the relation $TR = (FE)^{2-D_R}$ (Eq. (7)), is sometimes valid, in general even the idealized relations predicted from the behavior of perfect crystallites are more complex.

4. The atomic rate and the turnover frequency can be directly computed from experimental results. Although the rate per particle a is basically related to the reaction dimension D_R, its computation requires the knowledge (or assumption) of the crystal morphology. The TOF is to be preferred in the final analysis, for in the limit of large particles it is simple to relate it to data on single crystals. It is not appropriate in general to decide whether Eq. (7) is valid by plotting log a vs log FE as done by Farin and Avnir (*28*) and later accepted by Carberry (*35*).

5. Advances in the understanding of structure sensitivity depend on the use of model catalysts and the measurement of the morphology of the metal crystallites, and thus FE, by those methods offering atomic resolution. The measured kinetics should not be used to deduce an unknown morphology; instead, the measured morphology should be used to explain the measured kinetics.

6. Although outside the scope of this paper, the special and unusual behavior of small particles of FE > 0.5 should be mentioned. This is a field of intense research activity (*1*).

7. In our discussion we have not found it useful to refer to fractal behavior. Almost all supported particles follow Eq. (1) and thus do not exhibit fractal behavior. As the particle size changes, we use always the same atomic "measuring stick," so that the complexities of fractals are avoided.

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