Turnover Rates in Heterogeneous Catalysis

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Contents

I. Introduction

Fifty years ago, the rate of heterogeneous catalytic reactions was frequently expressed in so-called arbitrary units. Activity was commonly expressed by conversion plotted *vs* time at a given temperature. In either case, the information made it impossible to reproduce the work, even if enough details were provided on the preparation of the catalyst. This tradition was so ingrained that arbitrary units were used by Otto Beeck in a famous paper[1] reporting his extensive work on evaporated metal films of transition metals used as catalysts for the hydrogenation of ethene. Yet, Beeck had measured the area of his films and he could have reported *areal* rates, i.e., rates per unit surface area of the films. These were communicated privately later by one of Beeck's collaborators and used in a comparative study of various platinum catalysts.[2]

The measurement of areal rates on supported metal catalysts became possible after the first attempt in Boreskov's laboratory to obtain the area of supported metal particles by chemisorption of dihydrogen.[3] In this way, areal rates for silica gel supported platinum catalysts were obtained for the oxidation of sulfur dioxide[4] and of dihydrogen.[5] Boreskov's technique was then applied for the first time to η-alumina-supported platinum-reforming catalysts containing a much smaller weight fraction of metal than was the case for Boreskov's catalysts: that study in the Esso (now Exxon) laboratories revealed that the metal clusters were about 1 nm in size.[6] Sinfelt *et al.* at Esso then used the technique to report for the first time areal rates on reforming catalysts.[7-9] In fact, these were called specific rates, but this expression is now reserved to rates per unit mass of catalyst. The systematic use of areal rates in comparing catalytic activity of metals used in the form of evaporated films, large single crystals and supported particles or clusters ushered in the era of quantitative measurements of catalytic activity. Yet, ultimately the rate should, if possible, be referred to the number of active sites, because such a rate expresses the rate at which the catalytic cycle turns over: it is a *turnover rate* or *turnover frequency*.

The purpose of this review is to examine the definition, determination, limitations, and advantages of turnover rates in heterogeneous catalytic reactions. Brief remarks will also be made on kinetic coupling of elementary steps in catalytic cycles, i.e., the mechanism that helps these cycles to turn over in spite of thermodynamic obstacles along the way.

A. Definition of Turnover Rate

The definition goes back to the early days of enzyme catalysis when the rate of reaction was referred to the amount of enzyme and called *turnover number*.[10] This appellation was unfortunate, as *turnover number* is not a number but has the dimension of one over time. Besides, *turnover number* in enzymatic catalysis usually denotes the maximum value of the rate per catalytic site, at saturation of the enzyme by the reacting substrate, as defined by Michaelis–Menten kinetics.[10] This unfortunate limitation is totally unnecessary and provides another cogent reason to avoid completely the use of turnover number in catalysis.

To the extent of my knowledge, the *turnover number* first appeared in the literature of heterogeneous catalysis to denote the rate of reaction referred to the number of surface platinum atoms titrated with dihydrogen on a supported platinum catalyst.[11] Subsequently, the rate referred to the number of catalytic sites became known as *turnover rate*, v_t, or *turnover frequency* (TOF). It is simply defined as the number of revolutions of the catalytic cycle per unit time, generally the second.[12] It is a chemical reaction rate, a differential quantity depending on temperature, pressure, and concentrations. Like all catalytic rates, it is hard to measure. Frequently, turnover rate is replaced by a related, but generally not identical quantity, the *site time yield*[13] (STY), defined as the number of molecules of a specified product made per catalytic site and per unit time.

B. Reasons for the Review

The difficulty in measuring a TOF is not only in determining the rate but in counting active sites. Besides, sites may not be all identical. In spite of

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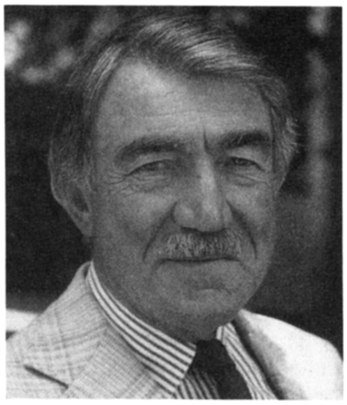

Michel Boudart was born in Brussels. He graduated from the University of Louvain with a B.S. degree (Candidature Ingenieur) in 1944 and an M.S. degree (Ingenieur Civil Chimiste) in 1947. In 1950 he received his Ph.D. degree in Chemistry from Princeton University. After graduation, he remained at Princeton University until 1961, first at the Forrestal Research Center as a research associate (1950–1953) and assistant to the director of Project SQUID (1953–1954) and then in the Department of Chemical Engineering as Assistant Professor (1954–1958) and Associate Professor (1958–1961). After a three-year stay at the University of California at Berkeley as Professor of Chemical Engineering, he became Professor of Chemical Engineering and Chemistry at Stanford University in the Department of Chemical Engineering, which he chaired from 1975 until 1978. He was the Keck Professor of Engineering from 1980 to 1994 and is now Emeritus. Michel Boudart is a founder of Catalytica, Inc. He belongs to American Chemical Society, American Institute of Chemical Engineers, and Sigma Xi. He is a member of both the National Academy of Sciences and the National Academy of Engineering of the United States of America, and a foreign member of the Académie Royale des Sciences, des Lettres et des Beaux-Arts de Belgique and its Royal Belgian Academy Council for Applied Sciences. He is also a Fellow of the American Association for the Advancement of Science, the American Academy of Arts and Sciences, and an Honorary Fellow of the California Academy of Sciences. He has received a doctorate *honoris causa* from the University of Liège, the University of Notre Dame, the University of Ghent, and the Institut National Polytechnique de Lorraine. He serves on a scientific advisory board for the Brookhaven National Laboratory and is a member of the Technology Advisory Board for British Petroleum. Boudart's textbook, *Kinetics of Chemical Processes* (1968), has been translated into Japanese, Spanish, and French and was reprinted (1991) in the Butterworth-Heineman Series of Chemical Engineering Reprints. He is also the author of *Kinetics of Heterogeneous Catalytic Reactions* (with G. Djéga-Mariadassou), Princeton University Press, 1984, originally published as *Cinétique des réactions en catalyse hétérogène* (Masson, Paris, 1982). He is co-editor (with J. R. Anderson) of *Catalysis: Science and Technology*, Vol. 1–9 (Springer-Verlag). He has published more than 250 journal articles and holds four US patents. His honors include Belgian American Educational Foundation Fellowship, 1948; Procter Fellowship, 1949; Curtis McGraw Research Award of the American Society for Engineering Education, 1962; the R. H. Wilhelm Award in Chemical Reaction Engineering of the American Institute of Chemical Engineers, 1974; the 1977 Kendall Award and the 1985 Murphree Award, both of the American Chemical Society; the 1991 Chemical Pioneer Award of the American Institute of Chemists; and the International Precious Metals Institute 1994 Tanaka Distinguished Achievement Award. The Symposium "Advances in Catalytic Chemistry III" (May 1985, Salt Lake City, Utah), was organized in his honor, as was the Catalysis Symposium of the 68th ACS Colloid and Surface Science Symposium (June 1994, Stanford University). The Catalysis Society selected him as the 1986 Ciapetta Lecturer. Michel Boudart has been a Visiting Professor at the Universities of Louvain (1969), Rio de Janeiro (1973), Tokyo (1975), Paris (1980), Cambridge (1984), and the National University of Salta (Argentina, 1994), and is currently a Fairchild Distinguished Scholar at the California Institute of Technology (1994–1995). As a participating scholar in the Chinese University Development Project of the World Bank, he has visited Fudan University (Shanghai), the Wuhan University of Technology (Wuhan Hebei), and Beijing Polytechnic University in the People's Republic of China.

these experimental and conceptual difficulties, there are many *advantages* in attempting to report a TOF.

First of all, if the method and conditions of measurement of the rate are fully described, together with the method of counting sites, a value of TOF can be reproduced in different laboratories. It can be compared to a value of TOF obtained on a different catalyst, e.g., the same metal but a single crystal, or a different metal, or a different material. In a theoretical or mechanistic sense, such comparisons are much more incisive than those made with specific or areal rates.

As a second advantage, even if a value of TOF is only approximate because of the approximations made in counting sites, it can immediately reveal whether the catalyst is truly a catalyst, i.e., whether it turns over more than once, or is merely a reagent. At the other extreme, the number of turnovers during which the catalyst has lasted is a direct measure of the potential lifetime of the catalyst.

A third advantage of measurements of TOF on catalytic samples that differ in the amount of active materials that they contain is that they provide a clear experimental test of the absence of artifacts in the rate measurements as a result of heat and mass transfer.

Fourth, values of TOF measured under identical conditions on samples of a catalytic material exposing different crystallographic planes or containing clusters of different size, indicate the importance or nonimportance of crystalline anisotropy, as reflected eventually in the size of clusters. This is useful information in theory and in practice.

Last, values of TOF are useful in assessing the potential of new catalytic materials in relation to catalysts in current use.

II. Measurement of Turnover Rate (or Frequency) or Site Time Yield

A. Solid Acids

The arduous problems faced in the correct measurement of the rate of heterogeneous catalytic reactions in the absence of heat and mass transfer, poisoning, activation, and deactivation, are not considered in this review. The focus is on the determination of the amount of catalytic sites. Clearly the first task is that they be identified. Next come two questions: are the sites identical and do they interact? Generally, there exists no unambiguous answer to these questions, especially because identification and counting must be ideally carried out *in situ*, i.e., during the catalytic reaction.

But in spite of the difficulties, there seem to be cases for which turnover rates have been determined successfully. An example deals with zeolites and reactions catalyzed by their protonic Brønsted acidic sites.

Catalysis by zeolites is a vast subject recently summarized in its science and technology by Haag.[14] Zeolites are silicoaluminates that are available by synthesis in the form of pure single crystals of micrometric size. Their crystallinity can be excellent. If the atomic ratio of Al to (Si + Al) remains small, i.e., below ca. 0.1, interactions between Al ions and also interactions between their associated protons remain negligible. This situation has been examined and reviewed by Barthomeuf: it depends on the topology of the zeolitic framework.[15] With sodium-free ZSM-5 (MFI) zeolites, the lack of interaction between protonic sites has been checked by measurements of the specific rate for *n*-hexane cracking on samples with Si/Al atomic ratios between 15 and almost 100000, a range of almost 4 orders of magnitude.[14] In that range, rate, at constant temperature and pressure, was found to be strictly proportional to the Al content. Clearly, all catalytic sites are identical and noninteracting, in the range of composition covered in this study. For seven other acid-catalyzed reactions, a linear correlation between activity and concentration of Brønsted sites was also found, albeit in a more limited range of Si/Al ratios. Haag concludes, "The possibility to synthesize zeolite catalysts with a well-defined pre-determined number of active sites of uniform activity is certainly without parallel in heterogeneous catalysis." Haag also adds, "Turnover frequencies (TOF's) for a variety of acid catalyzed hydrocarbon reactions could be determined for the first time." It must be noted that this achievement in catalytic science was driven by its many industrial applications, yet was made possible by the synthesis of pure single crystals of the catalytic material.

B. Metals

The situation depends on whether a given reaction is structure insensitive or structure sensitive. An operational definition of structure sensitivity is that the areal rate of the reaction or its TOF depends on surface crystalline anisotropy revealed by working on different faces of a single crystal or on clusters of varying size between 1 and 10 nm. Historically, the lack of effect of particle size was first noted for the hydrogenation of cyclopropane on supported Pt.[11] The effect of particle size was first observed for the synthesis of ammonia on supported iron.[16] But the concept of structure insensitivity and sensitivity received unequivocal confirmation from studies of the two above reactions on single crystals of platinum[17] and iron,[18] respectively.

1. Structure-Insensitive Reactions

For a number of well-investigated reactions catalyzed by metal, the areal rate or the TOF under fixed conditions does not depend or depends only slightly on surface crystalline anisotropy as expressed on clusters of varying size or on single crystals exposing different faces. Moreover, in many cases, identical or almost equal values of TOF were obtained with metal clusters supported on one or several carriers and on single crystals of the same metal. These striking results have been discussed in detail elsewhere.[12]

How is it possible to avoid significant effects of surface crystalline anisotropy on areal rates of values of TOF? *First of all*, the catalytic site involved in the rate-determining step, if there is one, should consist of only one surface metallic atom or of two adjacent ones at the most.[19] Otherwise, structure sensitivity should be recognizable. But even with a catalytic site consisting of a single metal atom, structure sensitivity might still be observable.

Maybe, *in addition*, the surface coverage during reaction should be close to saturation and surface reconstruction at the few remaining isolated sites might have erased surface anisotropy altogether. Such an explanation has been proposed to account for the structure insensitivity of palladium in the oxidation of carbon monoxide on single crystals and supported clusters at pressures between 10^{-1} and 10^2 mbar.[20] Indeed, the surface of a Pd tip used in field ion microscopy reconstructs as a result of CO adsorption at 1 mbar.[21]

Reconstruction of catalytic surfaces in adsorption or catalysis so as to minimize surface free energy was indeed proposed and advocated by Boreskov as a general principle in heterogeneous catalysis.[22] More recently, surface reconstruction has been shown to be one of the possible mechanisms accounting for chemical oscillations in heterogeneous catalysis.[23] In every case, the question is whether surface reconstruction, if thermodynamically favored, can be reached kinetically in a catalytic run. This question will be reexamined below in connection with structure sensitive reactions.

Another possible explanation of structure insensitivity is based on the formation of a reactive hydrocarbon overlayer on a metal surface during a catalytic reaction involving hydrocarbons.[24] If, for instance, the rate-determining step in the reaction is the dissociation of hydrogen on this overlayer, insensitivity to the subjacent metal structure becomes understandable.[12]

But whatever may be the explanation of structure insensitivity when it is observed on a supported metal, a single crystal or both, the areal rate does not seem to be the best way to report the rate data. Indeed, on certain faces of a crystal, there may be sites that are inaccessible to reactants. Why not report a turnover frequency referred to the number of one or several types of surface atoms? For supported metals, it is not the surface area of the metal that is measured, but rather the number of surface atoms counted by a fully described titration by chemisorption following a method that has been calibrated by means of independent physical techniques. Such a value of TOF may be considered as a true one, just as in the case of zeolites discussed above. Indeed, for a structure-insensitive reaction, all accessible surface atoms can be considered as equally active sites. But again, the strength of such a statement relies on the fact that the same, or a very close, turnover frequency has been measured for the same reaction under identical conditions on several faces of a single crystal of the same metal. The availability of TOF values on single crystals at pressures equal to those used with supported metals, as pioneered by Kahn, Petersen, and Somorjai,[17] must therefore be regarded as a critical step forward in the evolution of catalysis by metals toward a quantitative science. Indeed, even with the best reproducible work on supported metals, it is not possible to be sure that all of the possible support effects[12] have been eliminated, both in the measurement of rate and in the counting of sites. Thus, work with large single crystals becomes the standard by which the quality of the work on supported metals can be judged.

2. Structure-Sensitive Reactions

The best example is ammonia synthesis on iron, a reaction that continues to be of great industrial importance. It is also another example of the decisive results that can be obtained by studying a catalytic reaction on large single crystals at high pressures as started in the Somorjai laboratory.[18] Thus, it was shown that by far the most active face of iron single crystals in ammonia synthesis at 20 bar was the (111) plane by more than 2 orders of magnitude for the areal rate.[18] This was attributed to special sites with a coordination number equal to 7, the C_7 sites, as suggested earlier in work on supported iron clusters.[25] With these results, a value for the TOF on Fe(111) can be obtained and extrapolated to TOF data on ammonia synthesis at 1 bar on a multiply promoted industrial catalyst. The two TOF values agree within a factor of 2.[26] Because of the uncertainties in the extrapolation and in the counting of iron sites on the industrial catalyst, this comparison suggests that the industrial catalyst exposes predominantly the optimum C_7 sites that are by far the most active ones in the reaction.

If this tentative conclusion is firmed up by further observations on a working industrial catalyst,[27] it will be the first time that a true TOF has been reported for a structure-sensitive reaction on a complex commercial metallic catalyst. This will be also the first documented example of a structure-sensitive reaction on a metal surface that is reconstructed so as to expose the most active sites. This reconstruction is brought about or stabilized by catalyst promoters and/or by ammonia used in the reduction of the catalyst. The surface reconstruction of supported iron clusters with appearance of (111) facets after exposure to ammonia was reported earlier following studies with Mössbauer effect spectroscopy. [25] Surface reconstruction again leads to the possibility of reporting what is believed to be a true TOF.

3. How to Measure Upper Values of TOF

There exists a technique that measures directly an upper value of the TOF without the necessity of identifying and counting active sites. This technique is called steady state isotope technique for kinetic analysis (SSITKA), in which the steady state of a catalytic reaction running in a continuous reactor with complete mixing is suddenly perturbed by a sudden switch of reactants, say from $^{14}N^{14}N + H_2$ to $^{15}N^{15}N + H_2$ and the relaxation of the composition of the product expressed as $[^{14}NH_3]/[^{14}NH_3] + [^{15}NH_3]$ from unity to zero as a function of time. The area under the exponential relaxation curve is a relaxation time τ.[28] Ideally, the TOF is equal to θ/τ, where θ is the fraction of active sites covered with the most abundant reactive intermediate involved in the rate-determining step. If θ is assumed to be unity, one obtains an upper limit to the TOF: $(TOF)_{max}$. On the other hand, if the number of sites is assumed to be equal to the total number of surface atoms counted, say, by the chemisorption of hydrogen, one obtains a mean or apparent value of the TOF that is a lower limit, $(TOF)_{min}$, since there may be a distribution of activity among sites.[26]

Indeed, assume that 50% of the sites counted by a chemisorption method have a TOF of 1 s^{-1} while 50% have a TOF of 10^{-2} s^{-1}. The average measured TOF would be 5×10^{-2} s^{-1}, clearly a minimum value. In their application of SSITKA to ammonia synthesis on supported Ru catalysts, Goodwin and Nwalor report the following:[28] on an unpromoted Ru catalyst, what we call $(TOF)_{min}$ and $(TOF)_{max}$ differ by a factor of 10 but on an Ru catalyst promoted with potassium oxide, $(TOF)_{min}$ and $(TOF)_{max}$ differ only by 10%. Within the latter approximation, it may be concluded[27] tentatively that the potassium promoter has brought about a reconstruction of the Ru surface to expose almost exclusively the most active sites, as in the case of the iron industrial catalyst for ammonia synthesis. If so, the reported value of $(TOF)_{max}$ must also be close to the true TOF for ammonia synthesis on the promoted catalyst. This also suggests saturation of the active surface with adsorbed nitrogen ($\theta = 1$). Further applications of SSITKA to the direct determination of TOF *without* counting sites may well be another significant advance in the quantitative kinetics of catalytic cycles, although possible complications may arise.[28]

III. Applications of TOF Values

A. Comparisons of Rate Data

Today, rate data in arbitrary units or plots of conversion *vs* time are becoming the exception rather than the rule in the scientific literature of catalysis. With only one unit, namely the second, a value of turnover frequency offers a straightforward way to compare data obtained in different laboratories. Comparisons between supported and Wilkinson homogeneous rhodium catalysts for the hydrogenation of cyclohexene show very close values of TOF under similar conditions.[29] For the oxidation of carbon monoxide on palladium, TOF values at low and high pressures and low and high temperatures have been compared in the case of large single crystals, and of clusters supported both on α-Al_2O_3 single crystals and on high specific surface area γ-Al_2O_3.[20] These comparisons have led to the discovery of a new support effect consisting of the surface diffusion of CO adsorbed on the support to the interface with supported palladium and subsequent reaction with oxygen.[30] It is hard to imagine how this effect would have been identified without the use of TOF values. Indeed, it is because of anomalous TOF values that the supply of molecules of CO by surface diffusion could be assessed and explained quantitatively.

Another application of TOF values deals with the frequent occurrence of poisoning. Thus, for the hydrogenation of cyclohexene, some supported Pt/γ-Al_2O_3 catalysts were found to be poisoned with sulfur originating from sulfates on the support. For the hydrogenation of cyclohexene, a typical structure-insensitive reaction,[12] values of TOF calculated by counting surface platinum atoms not covered with sulfur by means of hydrogen adsorption were found to remain constant.[31] Again, it must be pointed out that the extensive TOF data for the hydrogenation of cyclohexene on many platinum catalysts supported on different supports and consisting of metal clusters of size between 1 and 10 nm, agreed under identical conditions with TOF values obtained on a platinum single crystal.[12]

By contrast, values of TOF obtained for a given reaction on a given supported metal are sometimes in striking disagreement[32] for a reaction that has been identified as structure insensitive. This is a reminder of the exacting work demanded in catalytic rate measurements and another example of the application of TOF values in the assessment of catalytic rate data.

A major obstacle in the correct measurement of intrinsic kinetic data in heterogeneous catalysis is the ubiquitous parasitic effect of heat and mass transfer, especially inside the pores of high specific area materials. Here again, values of TOF come to the rescue. Thus, in the case of supported metals, if the same value of TOF is obtained for a given reaction at fixed conditions on two catalytic samples containing different amounts of metal on the porous support, the kinetic data are not disguised by heat or mass transfer.[33] To be on the safe side, the TOF should be measured at two different temperatures on both samples.

Another application of TOF deals with new catalytic materials. It is frequently said that a new material is attractive because of its high activity in a certain catalytic reaction. What kind of activity is it? And how does that activity compare with that exhibited by prior catalysts? While a comparison of specific rates may be adequate, the use of TOF values gives a more direct comparison, for instance in the case of molybdenum carbide as compared to ruthenium for the hydrogenolysis of alkanes.[34] In each case, of course, the method used in counting sites must be fully described, especially with new materials for which there is little information on the nature of the sites.

Finally, TOF values are most helpful in assessing the role of promoters in catalysis. The classical example is ammonia synthesis on metallic iron. Values of TOF reveal that promotion by alumina is only *textural*, i.e., it maintains higher specific area without changing the rate per exposed iron atom. By contrast, potassium oxide promoters do change the TOF for the reaction, per iron atom exposed, at least at high pressure and high values of conversion.[27]

B. Catalytic Cycles

Until recently, a catalytic reaction was presented as a *closed* sequence of elementary steps, closed in the sense that the entity called the catalyst was consumed in the first step of the sequence and regenerated in the last step. Kinetic analysis of closed sequences in catalysis or chain reactions was developed by Christiansen, Temkin, and Horiuti.[35] It was Chad Tolman's idea to represent the closed sequence as a cycle turning clockwise from twelve o'clock, through the hours representing the active intermediates and back to the starting point. This representation of catalytic cycles has become the rule in homogeneous catalysis with organo-metallic coordination compounds, thanks to the well-known electronic rules describing their behavior. Although the Tolman cycle has been adopted so far only sporadically in heterogeneous catalysis, the notion of catalytic cycle has taken hold largely as a result of the use of the measure of the catalytic rate as a turnover frequency. Since catalysis is a kinetic phenomenon, the rate at which catalytic cycles turnover is the essential goal of catalytic research, insofar as it gives detailed information on *how* the cycle turns over.

Thus, the mechanistic question is *how*, but only after the cycle has been found to turnover at a rate measured by its TOF. An important consideration in the understanding of what makes a catalytic cycle turnover is also a kinetic one. It is the *kinetic coupling* between the elementary steps of the cycle. Thus, a particular step in the cycle that could be *equilibrated* so as to be severely limited by equilibrium if taken in isolation may actually proceed in a one-way direction if the next step in the cycle proceeds in the forward direction at a rate that exceeds sufficiently the rate of the preceding step in the reverse direction. This may explain why so many catalytic cycles do proceed with a high TOF in spite of the fact that some of the component steps would be disfavored thermodynamically in the absence of kinetic coupling. These ideas have been developed previously.[36-38]

IV. Conclusion

We conclude that the concept of TOF is paramount in any form of catalysis. In heterogeneous catalysis, this is also the case in spite of the special problem presented by solid surfaces. This problem is closely related to the model of a Langmuirian surface consisting of adsorption and catalytic sites, all identical and noninteracting. In spite of all accumulated knowledge that makes this model generally unacceptable, Langmuirian kinetics is used almost universally in heterogeneous catalysis.[12] Why it works so well in practice has led to controversies that flare up periodically.[39] In a similar way, serious questions have been raised about the applicability of the concept of TOF in heterogeneous catalysis.[40,41] What is a site? How do we define and count them? If they are not all the same, what is the value of reporting a TOF?

In this review, cases are presented for which both *Langmuir kinetics and values of TOF* appear to describe data in a manner that is correct if not rigorous. In the case of catalysis with micrometer-size single-crystal zeolites exhibiting identical and noninteracting sites, TOF values are true values. Values of TOF can also be obtained in the case of structure insensitive reactions on metals, as studied with large single crystals or supported clusters, with original surface crystalline anisotropy in both cases. Finally, values of TOF can be obtained even in the case of a structure-sensitive reaction on model and real catalysts, when surface reconstruction under high surface coverage obliterates non-Langmuirian behavior.

In the last analysis, the concept of TOF forces investigators to make a hypothesis concerning the nature of the active centers and to measure their

Table 1. Turnover Frequency (s^{-1}) for Hydrogenation of Cyclohexene, at 298 K, H_2 at Atmospheric Pressure, Gas Phase or Liquid Phase[a]

supported metal	% metal exposed[b]	TOF, s^{-1}	
		gas phase	liquid phase
Ni	36–100	1.53–2.44	0.32–0.66
Rh	5–100	5.13–7.17	1.16–1.36
Pd	11–76	2.38–3.98	1.35–1.72
Pt	14–100	2.72–2.94	0.55–0.66

[a] In the latter case, cyclohexane was the solvent, and the rate was zero order with respect to cyclohexene. [b] Determined by H_2 chemisorption, as spelled out in the published papers extracted from Stanford investigations by R. J. Madon, E. Gonzo, W.-C. Cheng, and D. J. Sajkowski; all pertinent references given in: Boudart, M.; Sajkowski, D. J. *Faraday Discuss.* **1991**, *92*, 57.

amount in a way that can be reproduced from laboratory to laboratory. It is generally agreed upon that the nitrogen BET method of measuring the surface area of solids is based on Langmuirian assumptions that are totally unacceptable. Yet the BET method is the universally accepted method of measuring the specific surface area of a catalyst: it can be reproduced from one laboratory to the next.

Similarly, the concept of TOF is a useful one in heterogeneous catalysis. Even when it is not rigorous, it leads to values that can be reproduced in different laboratories, and it provides quantitative insights into the working of catalytic cycles. An example of the type of comparison that becomes possible with TOF values is shown in Table 1 where the catalytic activity of four different metals for the hydrogenation of cyclohexene is compared both in the gas phase and in the liquid phase. Two facts emerge. First, the TOF values for Ni, Rh, Pd, and Pt differ by less than 1 order of magnitude in the gas phase and even less in the liquid phase. Second, for a given metal, the TOF in the gas phase is higher than that in the liquid phase by less than 1 order of magnitude.

In Practice. A reaction rate, a differential quantity, is always hard to measure. In heterogeneous catalysis, it is even harder because of problems of heat and mass transfer, and catalyst deactivation. A turnover rate is even harder to obtain because of the necessity to determine or estimate the number of sites. If they are not all equally active, the turnover rate will have an average value.

Turnover frequency is by definition identical to a turnover rate. Many prudent investigators omit to report a TOF even when they could estimate one because the rate may have been *disguised* by mass and heat transfer.

In the absence of a TOF a site time yield, STY, can be reported more safely. As defined in the Introduction, it is the number of molecules of a specified product made per catalytic site per unit time, real time in a batch reactor or space (residence) time in a flow reactor. For those who hesitate to estimate the number of sites, there is a last alternative: the space time yield, i.e., the number of molecules of a specified product made per unit volume of reactor per unit time. In the units popularized by Paul Weisz, the space time yield for large catalytic processes is, *in order of magnitude*, 1 μmol cm^{-3} s^{-1}, which translates roughly into a STY equal to 1 s^{-1}, also in order of magnitude.[42] These values are dictated by two limiting considerations when porous catalysts are used. First, if rates were much smaller, the reactor would have to be too expensive for a given productivity. Second, if rates were much larger, the catalyst and thus also the reactor volume would be poorly utilized because the heterogeneous reaction would be confined to the mouth of the pores of the catalyst, as a result of diffusional limitations into and out of the catalyst grains. Thus, the order of magnitude values suggested above have been said to be at the center of a window on reality.[43]

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