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Remarks on the Issue of Structure Sensitivity in Heterogeneous Catalysis: Activity and Selectivity

INTRODUCTION

Sir Hugh Taylor noted (in 1925) that the nature of the solid catalyst would be governed by the nature of the reaction catalyzed (*1*). Surely an extraordinary insight, one which, it is fair to say, has inspired generations of provocative research. Indeed it would seem meet and just that one of his former students, Boudart, has set forth the notion of the turnover number, N, i.e., the number of molecules reacting per second per site (*2*). This fruitful insight provides a measure of intrinsic catalytic vigor (i.e., velocity per exposed site) and so frees us of the ambiguity implicit in what I would term, global rate formulations, i.e., velocity per gram of *total* catalyst formulation. For Boudart's insight focuses upon intrinsic catalytic site dispositions *and*, in consequence, reveals much about potential variations in catalyst site dispositions as catalyst crystallite size is varied, by whatever means (preparation, loading, sintering).

In terms of the fundamental aspects of heterogeneous catalysis, per se, the concept of the turnover number is most potent in that variations in morphology (nature and structure) of surface sites with crystallite size variations (or for that matter alloying, heat treatment, etc.) are made manifest by measurements of N: And, as we shall shortly suggest, signal practical consequences with respect to catalytic reactor analysis and design, for catalyst systems prone to sintering emerge in the light of the turnover number concept. Finally, the potential importance of relative turnover numbers in affecting selectivity is noted.

STRUCTURE OF THE CATALYTIC RATE

Let us assume that we are witness to a simple first-order, diffusionally undisguised, supported solid catalyzed reaction (the assumption of linear kinetics alters not the general teachings set forth here)

$$\text{Rate, } R = k_0 F. \qquad [1]$$

k_0, for this heterogeneous (fluid–solid catalyst) system, is in fact,

$$k_0[\mathrm{s}^{-1}] = k_\mathrm{v}\mathbf{a}, \qquad [2]$$

where k_v is the catalytic velocity coefficient (cm/s), and $\mathbf{a}$ is the *catalytic* area per unit volume of catalytic agent (cm^{-1}). In fact, of course, we know not the true value of $\mathbf{a}$, i.e., actual *catalytic* area per unit of catalyst agent volume. What we know by, for example, chemisorption and titration is the "exposed" area of the catalytic agent (hereafter called the catalyst). The actual *catalytic* area, $\mathbf{a}$, may or may not equal "exposed" *catalyst* area (*3*). Let us call "exposed" measurable area per volume of catalyst agent, $\bar{A}$. What then is the relationship between the measurable, $\bar{A}$ (exposed *catalyst* area), and the actual *catalytic* area, $\mathbf{a}$?

Patently, should $\bar{A} = \mathbf{a}$, then division of the observed (diffusion uninfluenced) rate coefficient, k_0, by the measured $\bar{A}$ yields a constant (at fixed temperature); i.e., the turnover number at fixed fluid phase composition

$$N = \frac{k_0}{\bar{A}} = k_\mathrm{v} = \text{constant} \qquad [3]$$

in which case we are witness to a facile or

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structure-insensitive reaction where k_v is invariant with crystallite size.

Clearly should **a** (catalytic site area/volume) be directly proportional to $\bar{A}$ (catalyst-"exposed" surface area/volume) then Eq. [3] still prevails unless **a** is a function of crystallite size, in which case k_v varies with crystallite size and we are then witness to demanding or structure-sensitive reaction.

The issue, then, of observed structure sensitivity or insensitivity rests upon the methodology whereby $\bar{A}$ is assessed. Are we counting exposed *catalyst* sites, $\bar{A}$, or exposed sites of *catalysis*, **a**? A telling example of this critical distinction is provided by the promoted Fe catalyst employed in NH_3 synthesis (*4*). Assessments of $\bar{A}$, catalyst (Fe)-exposed sites by CO chemisorption, would teach that reaction (NH_3 synthesis) is structure sensitive. When, however, N_2 is employed as the "site counter," structure insensitivity is evidenced. Which is to say, with CO as the "site counter," all Fe *catalyst* surface atoms are measured, while with N_2 as the "site counter," only sites relevant to NH_3 synthesis *catalysis* are measured.

The tentative conclusion is that if we do our site counting properly, no reaction will exhibit *apparent* structure sensitivity (as opposed to intrinsic sensitivity (*3*)).

In principle, this tentative notion, while intellectually pleasing, may not be one readily elevated to laboratory reality. For, clearly, choosing the proper "site counter" so as to identify **a** as opposed to $\bar{A}$ presupposes an a priori knowledge of relevant catalytic mechanisms which, while available for NH_3 synthesis, are largely beyond our understanding for catalytic systems in which mechanistic inferences now escape us. In the end then, we must assume

$$k_v = k_0/\bar{A} = f(\bar{A}); \qquad [4]$$

that is, should $\bar{A}$ be directly proportional to **a**, structure-insensitive (facile) behavior will be manifest, while structure-sensitive manifestations will be evident should exposed *catalyst* sites differ from exposed *catalytic* sites as crystallite size is varied.

Pending signal advances which will specify **a** rather than $\bar{A}$, practice must rely upon the phenomenologically measured values of $\bar{A}$.

IMPLICATIONS IN SINTERING BEHAVIOR

Sintering of catalyst particles supported or otherwise (as in unsupported Fe) obviously reduces catalyst area per volume, $\bar{A}$. The sintering process is complex and to date defies unambiguous mechanistic interpretation (*5*). We are then wedded, albeit temporarily, to phenomenological description, e.g.,

$$\frac{d\bar{A}}{dt} = -k_s(\bar{A})^s, \qquad [5]$$

where s is the empirical order, t is time-on-stream, $\bar{A}$ is the measured "exposed" catalyst area per volume, and k_s is a sintering rate coefficient. For any value of s other than unity, where $\bar{A}_0$ is the initial value at $t = 0$,

$$\bar{A}/\bar{A}_0 = \frac{1}{(1 + Kt)^{s-1}}, \qquad [6]$$

where $K = (s - 1)\,(\bar{A}_0)^{(s-1)}\,k_s$.

Conventional wisdom would teach that the simple plug flow reactor continuity equation for a sintering system is then (pseudo-steady-state), for reactant, F,

$$\frac{-dF}{d\theta} = \frac{k_0\bar{A}_0 F}{(1 + Kt)^{(s-1)}} \qquad [7]$$

or for any reactor configuration, local diffusion-undisguised rate would be

$$R = \frac{k_0\bar{A}_0 F}{(1 + Kt)^{(s-1)}} = \frac{\bar{k}_0 C}{(1 + Kt)^{s-1}}. \qquad [8]$$

While Eq. [7] or [8] neatly (and empirically) describes the time dependency of activity decline due to sintering-sponsored *catalyst* area reduction, it fails to anticipate structure sensitivity, i.e., changes in N, the turnover number, with an increase in average catalyst crystallite size attendant with area reduction due to sintering.

Recall that $k_0 = k_v\mathbf{a}$ (Eq. [2]) where, we emphasize, $\mathbf{a}$ is *catalytic* area per volume. Assume $\mathbf{a}$ to be related to measurable catalyst area per volume, $\bar{A}$, by [3]:

$$\mathbf{a} = D\bar{A}. \qquad [9]$$

Two possibilities exist:

(a) D is a constant which implies that the reaction is structure insensitive or facile or

(b) D is a function of crystallite size, i.e., $\bar{A}$, in which case we have structure sensitivity or demanding behavior.

Assume then that

$$D = D_0(\bar{A})^d; \qquad [10]$$

hence Eq. [2] becomes

$$k_0 = k_vD_0(\bar{A})^{1+d}. \qquad [11]$$

Thus, in general, the sintering-affected rate of catalytic reaction is

$$R = \frac{k_vD_0(\bar{A})^{1+d}\cdot F}{(1+Kt)^{(s-1)(1+d)}}. \qquad [12]$$

In this formulation D_0 is a coefficient of *catalytic* site discrimination and d is the order in *catalytic* site discrimination. In sum, per unit volume

$\mathbf{a}$ (catalytic area) = $D\bar{A}$ (catalyst area)

and by Eq. [10]

$d = 0$ structure insensitivity.

$d \gtrless 0$ structure sensitivity.

The scientific implication is evident. Division of the observed diffusion-unaffected rate coefficient k_0 by the measured *catalyst* area, $\bar{A}$, raised to the proper power d will yield a constant k_vD_0. It is in this sense that I suggest that proper *catalytic* as opposed to *catalyst* "site counting" will always reveal apparent facile behavior, which, admittedly, is to beg the question since we scarcely know d a priori, even assuming that a power law relationship exists between $\mathbf{a}$ and $\bar{A}$.

Let us, however, assume that my power law relationship (a quite tentative law of site discrimination) prevails. Then the time-on-stream, t, behavior of the catalytic global rate, R, is given by Eq. [12] for any sintering-prone system or

$$R = \frac{k^0F}{(1+Kt)^{(s-1)(1+d)}}. \qquad [13]$$

As noted, for a facile or structure-insensitive reaction, $d = 0$ and the conventional rate functionality (Eq. [8]) applies. When however demanding or structure-sensitive behavior is manifest, $d \gtrless 0$ and some rather interesting consequences emerge for the sintering catalyst system.

(a) $d = -1$. That is, the turnover number N increases with a reduction in *catalyst* area (increase in crystallite size) in which case sintering affects not at all the global rate, R, for any sintering order s.

(b) $d = -2$ (say). The global rate actually increases with time-on-stream, a consequence of a strong increase in N with crystallite growth which overwhelms catalyst area reduction due to sintering.

(c) $d > 0$. Global rate reduction with t is exacerbated as both N and catalyst area decline with sintering-sponsored crystallite agglomeration.

Thus we can now appreciate the quite practical importance of respecting turnover number behavior. The overall (scientific and technological) import is the implicit challenge; How might we tailor the catalyst (alloying, promotion, preparation, pretreatment) such that the exponent of discrimination, d, be negative?

To be sure, one may properly ask, what promising means are available to realize some control of d, which is to say, turnover number behavior? To date said behavior is observed but not dictated. Some provocative studies are at hand. Lam *et al.* (*6*), in a study of the H_2–O_2 reaction over Pd–Au alloys, report signal enhancement of the turnover number of Pd in the presence of inert Au (alloyed), which they attribute to a ligand effect. In their study a 50-fold increase in turnover frequency is found between pure Pd and Pd alloys containing 40 to 60% Au. Would it not be of interest to explore this fascinating phenomenon as a function of alloy dispersion as induced by preparation, pretreatment, and/or sintering?

In our study (*7*) of CO oxidation over Pt/Cu alloys interesting effects of alloying and sintering were observed which when translated into turnover numbers suggest the ultimate possibility of favorably affecting the turnover numbers by proper alloying and sintering.

Nor is the role of surface enrichment in alloy catalysts to be ignored since recent theory (*8*) points to the critical role of surface tensions of the pure components in dictating enrichment. Thus is invited the possibility of fashioning alloys whose surface character and sintering behavior may well exhibit desirable features.

SELECTIVITY IMPLICATIONS

Catalytic selectivity or yield involves two or more reaction pathways, each governed by a specific rate coefficient, k. In general the selectivity or yield of a desired species will always be dictated by ratios of rate coefficients, e.g.,

$$K_1 = k_1/k_2; \quad K_3 = k_1/k_3,$$

and so on. To address the influence of turnover number upon selectivity, i.e., the influence upon K_1, K_3, etc., in a complex reaction network, it proves fruitful to rephrase the argument set forth above in terms of site area per unit volume of the catalyst crystallite. So, for example, in terms of $\mathbf{a}$ and $\bar{A}$,

$\mathbf{a} \equiv X$, active *catalytic* sites

$\bar{A} \equiv X + Y$, total surface *catalyst* sites,

or in general, for several site types

$$\bar{A} = X + Y + Z, \text{ etc.} \qquad [14]$$

Equation [11] so rephrased becomes

$$k_0 = k_v D_0 (X + Y)^{1+d}. \qquad [15]$$

The turnover number, at fixed fluid phase composition is then

$$N = \frac{k_0}{(X + Y)} = k_v D_0 (X + Y)^d \qquad [16]$$

or in general

$$N = k_v D_0 \, (\bar{A})^d.$$

For, for example, a simultaneous network

$$\begin{tikzcd} F \arrow[r, "1"] \arrow[dr, "2"'] & B \quad \text{on site } X \\ & C \quad \text{on site } Y \end{tikzcd}$$

$$\begin{aligned} N_1 &= k_1 \, (\bar{A})^d \\ N_2 &= k_2 \, (\bar{A})^e. \end{aligned} \qquad [17]$$

At fixed fluid phase composition the point selectivity or yield is

$$\frac{dB}{dC} \propto \frac{N_1}{N_2} \propto K_0 (\bar{A})^{(d-e)}.$$

That is, the selectivity determining rate coefficient ratio, $K = k_1/k_2$, can be influenced by differences in turnover number–crystallite size dependency when more than one site type is involved. Or in terms of dispersion $\mathcal{D} \equiv \bar{A}$

$$K = K_0 (\mathcal{D})^{d-e}. \qquad [18]$$

An interesting and industrially important case of selectivity in which, evidently, $d \neq e$ is that of ethylene oxide selectivity variation with supported Ag crystallite size, in epoxidation of ethylene (*9*). A reduction in ethylene oxide yield occurs with an increase in dispersion ($d < e$ in Eq. [18]). The existence of a CO_2-producing site (O^-) and ethylene oxide-generating site (O_2^-) on supported Ag in epoxidation has long been championed.

Insofar as Eq. [18] may govern any solid-catalyzed rate coefficient ratio, then any complex selectivity/yield-sensitive reaction network can be influenced by crystallite size by reason of differences in turnover number behavior, should more than one site type be involved. Once again, as in the sintering example cited above, the turnover number, particularly relative turnover number for multisite catalysis, promises to be of enormous practical consequence. Preparation, pretreatment, and alloying can dictate performance in terms of selectivity as well as overall activity even in the absence of time-on-stream sintering.

CATALYTIC/CATALYST AREA

It is now evident that if one uses the proper surface site counter, N will be constant.

By Eq. [16], for example, where we recall $(X + Y) \equiv \bar{A}$, and X is the *catalytic* site while $(X + Y)$ is the total *catalyst* surface site number, if our measuring agent counts only X, then by our premise (Eqs. [9] and [10]) ($\mathbf{a} \equiv X$)

$$X = D_0(X)^{(d+1)} \qquad [19]$$

so that $d = 0$, or facile reaction, as is demonstrated in the use of N_2 as *catalytic* site counter for Fe/MgO (*4*). If not X but $\bar{A}$ (Eq. [14]), i.e., *catalyst*, sites are counted

$$X = D_0(\bar{A})^{(d+1)} \qquad [20]$$

and demanding behavior may be manifested, as is demonstrated in the use of CO as *catalyst* site counter for Fe/MgO (*4*).

$\bar{A}$ represents the sum of all surface *catalyst* sites both active and inactive (for particular reaction steps), while X represents the active sites for a particular reaction—the latter are, I suggest, Taylor–Boudart sites.

CONCLUSIONS

In the spirit of the Taylor–Boudart teaching, the distinction between *catalytic* and *catalyst* surface sites suggests a power law relationship between the two which leads to some provocative practical consequences with respect to turnover number behavior in sintering as well as selectivity.

APPENDIX: NOMENCLATURE

$\mathbf{a}$	exposed *catalytic* active area per volume
$\bar{A}$	exposed total *catalyst* area per volume $= X + Y + Z \cdots$
B, C	product species
D_0	coefficient of site discrimination
d	exponent of site discrimination
e	exponent of site discrimination
F	reactant species or concentration
k_0	first-order rate coefficient (s^{-1})
k_s	sintering rate coefficient
k_v	first-order velocity coefficient (cm s^{-1})
k_i	rate coefficient for species i = 1,2, etc.
K	ratio of rate coefficients
N	turnover number at fixed fluid composition (moles/s site)
R	reaction rate
s	sintering order
t	time on stream
X, Y, Z	surface area per volume of sites X, Y, Z, etc.
$\propto$	proportional to

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REFERENCES

1. Taylor, H. S., *Proc. R. Soc. London Ser. A,* 108 (1925).
2. Boudart, M., *AIChEJ.* **18,** 465 (1972).
3. Boudart, M., and Dijega-Mariadassou, G., "Kinetics of Heterogeneous Catalytic Reactions," p.170. Princeton Univ. Press, Princeton, NJ, 1984.
4. Topsoe, H., Topsoe, N., Bohlbro, H., and Dumesic, J. A., "Proceedings, 7th International Congress on Catalysis, Tokyo, 1980" (T. Seiyama and K. Tanabe, Eds.), p. 247.
5. Wanke, S. E., "Progress in Catalyst Deactivation" (J. L. Figueiredo, Ed.). NATO Advanced Study Series, E: Applied Sciences, No. 54, Nijhoff, The Hague, 1982.
6. Lam, Y. L., Criado, J., and Boudart, M., *Nouv. J. Chim.* **1**(6), 461 (1977).

7. Liao, P. C., Fleisch, T. H., Carberry, J. J., and Wolf, E. E., *J. Catal.* **74**, 307 (1982).
8. Kuczynski, G. C., and Carberry, J. J., *Chem. Phys. Lett.* **111**(4, 5), 445 (1984).
9. Wu, J. C., and Harriott, P., *J. Catal.* **39**, 395 (1975).

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