Structure Sensitivity in Heterogeneous Catalysis: Activity and Yield/Selectivity

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The relationship between exposed *catalytic* sites ($\underline{a}$) and exposed *catalyst* sites ($\overline{A}$) was postulated to be in accord with (J. J. Carberry, *J. Catal.* **107**, 248 (1987))

$$\underline{a} = D_0(\overline{A})^{d+1},$$

where D_0 is a site discrimination coefficient and d the exponent of structure sensitivity. Recently assembled data of D. Farin and D. Avnir (*J. Amer. Chem.* **110**, 2039 (1988)) which support the postulated activity–yield/selectivity structure-sensitive relationships are cited. In sum a vast corpus of data supports the law (J. J. Carberry, *J. Catal.* **107**, 248 (1987))

$$\frac{\text{Rate}}{\overline{A}} = K(\overline{A})^d = N, \text{ turnover number}$$

for a given site type at a fixed fluid-phase composition. When two or more site types are involved in a complex (multipathed) reaction network, not only is activity (conversion) affected by structure sensitivity but yield/selectivity (the ratio of turnover numbers) can also be influenced. Comments on the significance of the exponent d which suggest a distinction between demanding/facile and structure sensitive/insensitive behaviors are offered. Simple geometric argument predicts $d = 0$ to 2 while a value of $d \gtrsim 0$ can be rationalized if morphological/chemical changes accompany crystallite size variation. A turnover velocity, N_0, independent of fluid-phase composition (conversion x) is suggested, for reactant order n, as

$$N_0 = \frac{\text{Rate}}{\overline{A}\, C^n} = \frac{N}{(C_0(1 - x))^n} = k_v D_0(\overline{A})^d,$$

where C_0 is feed concentration and k_v the intrinsic reaction velocity per active site per exposed site. © 1988 Academic Press, Inc.

INTRODUCTION

The notion of the turnover number, N, while utilized in analyses of enzyme kinetics, was most fruitfully invoked by Boudart (2) in heterogeneous catalysis. That insight gave rise to the concept of structure-sensitive/insensitive reactions (or demanding/facile reactions (2)).

If we define $\underline{a}$ as the area/volume of *catalytic* surface sites and $\overline{A}$ as the area/volume of *catalyst* surface sites, there follows the logical query, How does $\underline{a}$ vary with $\overline{A}$?

$$\frac{\text{Rate}}{\overline{A}} = \frac{k_v \underline{a} f(C)}{\overline{A}} = N = \text{turnover number.} \quad (1)$$

In earlier reports (1) we suggested the $\underline{a}$–$\overline{A}$ relationship

$$\underline{a} = D_0(\overline{A})^{d+1} \quad (2)$$

or

$$\frac{\text{Rate}}{\overline{A}} = K(\overline{A})^d = N. \quad (3)$$

(Note that N, as generally defined, is a function of reacting fluid-phase composition.)

When $d = 0$ we witness structure insensitivity or facile reaction; for $d \neq 0$ demanding or structure sensitivity is manifest.

Since *catalyst* exposed area per unit volume, $\overline{A}$, is inversely proportional to average crystallite size, L, and directly propor-

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tional to dispersion $\mathscr{D}$ (or fraction exposed) then

$$N \propto (\mathscr{D})^d \text{ or } (L)^{-d}. \qquad (4)$$

For a reaction catalyzed by a surface site, say e, which differs from site d then

$$N_d \propto (\mathscr{D})^d \text{ and } N_e \propto (\mathscr{D})^e. \qquad (5)$$

Hence yield/selectivity will be governed by the ratio of turnover numbers for this two-site situation, i.e.,

$$\frac{k_d}{k_e} = \frac{k_1}{k_2} \propto (\mathscr{D})^{d-e} \text{ or } (L)^{e-d}. \qquad (6)$$

In any multipathed catalytic reaction network, e.g.,

$$A \xrightarrow{1} B$$
$$ \searrow_{2}$$
$$ C$$

where B is the desired product, the yield (B/A_0) or selectivity (B/C) will be dictated by k_1/k_2 or, as Eq. (6) teaches, by

$$N_1/N_2 \propto (\mathscr{D})^{d-e} \text{ or } (L)^{e-d}. \qquad (7)$$

MODEL AND REALITY

In the wake of the original postulate (1)

$$\underline{a} = D_0(\overline{A})^{d+1} \qquad (8)$$

or

$$N \propto (\overline{A})^d$$

a preprint of work by Farin and Avnir (3) of the Hebrew University of Jerusalem was kindly made available to us by Professor Avnir. In their work a notion of structure sensitivity/insensitivity is now presented which is, in spirit, identical to that offered in Refs. (1). Farin and Avnir suggest

$$\text{Activity, } \frac{\text{moles}}{\text{time} \cdot \text{particle}} \propto (R)^{D_R} \qquad (9)$$

for particle (crystallite) average radius, R. The Carberry model (1) and that of Farin-Avnir (3) are related by (since exposed area per particle is $\propto R^2$)

$$d = 2 - D_R. \qquad (10)$$

A vast corpus of data on structure-sensitive/insensitive reactions is set forth by Farin and Avnir (3) who provide, *it must be emphasized,* rational models for the prediction of their observed values of D_R.

The experimental data are presented in Table 1. Values of d, the exponent in Eq. (3), are given for each of the reported studies; i.e., d is obtained from the values of D_R reported by Farin and Avnir (3). Values of

TABLE 1

Values of d for Eq. (3) Calculated from Reported D_R values (3) by $d = 2 - D_R$
(Data Assembled by Farin and Avnir (3))

No.	Reaction	Catalyst	Value of $\underline{d}$ in $N = K(\overline{A})^d$	Particle size or dispersion range (No. of data points)	Data source
1	Ethane hydrogeno-lysis	Pt/Al_2O_3	-0.8	10–118 Å (8)	Ref. (8, Table 1 and Fig. 1)
2	Ethane hydrogeno-lysis	Pt/Al_2O_3	-0.9	32–147 Å (5)	Ref. (8, Table 2)
3	Ethane hydrogeno-lysis	Pt/Al_2O_3	-1.1	23–150 Å (9)	Ref. (8, Table 3)
4	Ethane hydrogeno-lysis	Pt/Al_2O_3	-1.1	0.07–0.81 (12)	Ref. (9, Fig. 1)
5	Ethane hydrogeno-lysis	Ir/Al_2O_3	-1.3	0.08–0.67 (9)	Ref. (9, Table 1 and Fig. 1)
6	Cyclopropane hydrogenolysis	Pt/Al_2O_3	-0.3	13–175 Å (7)	Ref. (10, Table 1)

TABLE 1—*Continued*

No.	Reaction	Catalyst	Value of d in $N = K(\bar{A})^d$	Particle size or dispersion range (No. of data points)	Data source
7	Cyclopentane hydrogenolysis	Pt/Al$_2$O$_3$	−0.2	0.08–0.42 (5)	Ref. (*9*, Fig. 2)
8	Cyclopentane hydrogenolysis	Pt/Al$_2$O$_3$	0	19–175 Å (6)	Ref. (*11*, Fig. 1)
9	Cyclopentane hydrogenolysis	Pt/Al$_2$O$_3$	0	66–150 Å (5)	Ref. (*11*, Table 1)
10	Cyclopentane hydrogenolysis	Ir/Al$_2$O$_3$	0	0.08–0.67 (9)	Ref. (*9*, Table 1 and Fig. 2)
11	Cyclopentane hydrogenolysis	Rh/Al$_2$O$_3$	−1	0.21–1.00 (6)	Ref. (*12*, Fig. 2)
12	Propene hydrogenation	Ni/Al$_2$O$_3$	+3.5	8–224 Å (4)	Ref. (*13*, Fig. 4)
13	Benzene hydrogenation	Rh/Al$_2$O$_3$	−0.25	0.20–0.87 (7)	Ref. (*14*, Table 4)
14	Benzene hydrogenation	Pd/charcoal	+0.4	23–213 Å (7)	Ref. (*15*, Table 1 and Fig. 1)
15	Benzene hydrogenation	Pt/SiO$_2$	+1.0	66–379 Å (5)	Ref. (*15*, Table 1 and Fig. 1)
16	Ethylene oxidation to ethylene oxide	Ag/Cab-O-Sil	+0.8	61–290 Å (5)	Ref. (*4*, Table 3)
17	Ethylene oxidation to ethylene oxide	Ag/Cab-O-Sil	+1.3	200–450 Å (7)	Ref. (*17*, Tables 1 and 5)
18	Ethylene oxidation to ethylene oxide	Ag/silica Z	+0.4	66–392 Å (5)	Ref. (*4*, Table 3)
19	Ethylene oxidation to CO$_2$	Ag/Cab-O-Sil	+1.6	61–290 Å (5)	Ref. (*4*, Table 3)
20	Ethylene oxidation to CO$_2$	Ag/Cab-O-Sil	+1.8	200–450 Å (7)	Ref. (*17*, Table 1 and 5)
21	Ethylene oxidation to CO$_2$	Ag/silica Z	+1.3	66–392 Å (5)	Ref. (*4*, Table 3)
22	Electroxidation of hydrogen	Pt–Pd/C	≈0	0.01–0.55 (4–5)	Ref. (*18*, Table 1)
23	Electroreduction of oxygen	Pt–Pd/C	−0.3	0.01–0.55 (4–5)	Ref. (*19*, Table 1)
24	Ammonia synthesis	Fe/MgO	−3.8	10–110 Å (17)	Ref. (*20*, Fig. 5)
25	CO methanation	Ni/Al$_2$O$_3$	−0.8	21–144 Å (5)	Ref. (*21*, Table 1 and Fig. 4)
26	Epimerization of *cis*-1.2-dimethyl-cyclohexane	Pt/Al$_2$O$_3$	0	11–118 Å (8)	Ref. (*22*, Table 1)
27	Photocatalytic decomposition of MeOH	Pt/TiO$_2$	+0.6	50–350 Å (15)	Ref. (*23*, Fig. 3)
28	Coke deposition	Pt/Al$_2$O$_3$	−0.3	0.04–1.00 (5)	Ref. (*24*, Fig. 2)

$d = 0$ are evident, i.e., cases of structure insensitivity as well as examples of turn-over numbers which decrease ($d > 0$) and other cases where N increases ($d < 0$) as average crystallite size increases. More on this point anon.

Of particular interest is the issue of yield/selectivity (ratio of rate coefficients, $k_1/k_2 \equiv$

N_1/N_2) as a function of dispersion. Consider the two cases of selectivity: In hydrogenolysis of ethane and cyclopentane (8, 9, 11), hydrogenolysis of cyclopentane is facile ($d = 0$), that of ethane demanding ($e = -1.3$). Hence, by Eq. (6),

$$\text{Selectivity} \propto \frac{k_p}{k_E} \propto \frac{N_p}{N_E} \propto (\mathscr{D})^{+1.3} \text{ or } (L)^{-1.3},$$
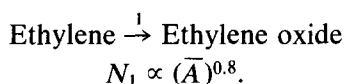
where, of course, dispersion $\mathscr{D} \propto 1/L$.

Another yield/selectivity network which is structure sensitive is that of epoxidation of ethylene as catalyzed by supported silver. Although a triangular network, at ethylene conversions less than ca. 30%
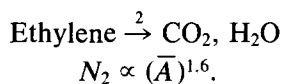
$$\text{Ethylene} \xrightarrow{1} \text{Ethylene oxide}$$
$$_2 \searrow^{O_2}$$
$$CO_2, H_2O$$
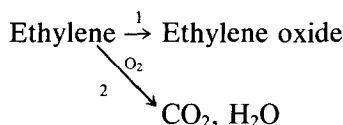
As the data in Table 1 indicate, turnover number behavior is not the same for steps 1 and 2:

For

$$\text{Ethylene} \xrightarrow{1} \text{Ethylene oxide}$$
$$N_1 \propto (\overline{A})^{0.8}.$$

For

$$\text{Ethylene} \xrightarrow{2} CO_2, H_2O$$
$$N_2 \propto (\overline{A})^{1.6}.$$

Selectivity (rate of ethylene oxide to that of CO_2, H_2O formation) is then governed by

$$\frac{N_1}{N_2} \propto (\overline{A})^{d-e} \propto (\overline{A})^{-.8} \propto (L)^{0.8}.$$

Thus in the case of selectivity in hydrogenolysis of cyclopentane relative to that of ethane, high dispersion is desirable, while in contrast, a low dispersion of silica-supported silver favorably affects selectivity in epoxidation of ethylene, as the experimental work of Wu and Harriott demonstrates (4). Insights regarding structure sensitivity in epoxidation of ethylene over Ag, its alloys, and promoted formulations are pro-

vided in a quite recent review by Sajkowski and Boudart (5).

DISCUSSION

While a vast body of structure-sensitive/insensitive data is apparently well organized by the proposed relation (1)

$$N \propto (\overline{A})^d \propto (L)^{-d} \qquad (11)$$

or its equivalent as proposed in the recent publication (3), the matter of the significance of a power law relationship between *catalytic* (active) surface sites $\underline{a}$ and total *catalyst* surface sites $\overline{A}$ invites clarification.

One might suggest that the issue of structure sensitivity or lack of same is best viewed in two ways.

I. With a change in crystalline dimension, L, the ratio of corner, edge, and planar surface sites per unit volume will change (or not) as dictated by simple geometry *without changes in surface morphology*. So then, if we consider a simple cubic crystallite it is evident that if the preferred (demanded) catalytic sites are corner, c, atoms

$$\underline{a}_c/\overline{A} \propto (1/L)^2$$

or

$$N_c \propto (\overline{A})^2, \quad \text{i.e., } d = 2.$$

If edge atoms are preferred

$$\underline{a}_e/\overline{A} \propto (1/L)^1$$

or

$$N_e \propto (\overline{A}), \quad \text{i.e., } d = 1.$$

Should all exposed surface atoms be demanded by the reaction

$$\underline{a}_0/\overline{A} \propto (1/L)^0$$

or

$$N_0 \propto (\overline{A})^0, \quad \text{i.e., } d = 0.$$

Note that this reasoning, which has also been presented by Farin and Avnir (3), does not require a change in shape or surface structure (morphology) or surface chemistry with a change in crystallite size. Yet this simple reasoning predicts values of the ex-

ponent of site discrimination between 0 and 2. In this case we can have demanding reaction ($d > 0$) yet one which is *not* structure sensitive, *since structure does not change with L.*

II. With a change in crystallite dimension, L, morphological and/or surface chemical changes may be induced. Changes in coordination number with crystallite size come to mind. Erasure of defects, impurities, may well accompany crystallite size variations. Thus should active catalytic site population $\underline{a}$ decrease with an increase in dispersion (i.e., $\overline{A}$) we would observe negative values of the exponent of discrimination ($d < 0$). This event would then be truly an instance of structure sensitivity. Obviously morphological changes can also inspire $d > 0$; i.e., $\underline{a}$ increases with dispersion.

In sum, case I involves demanding ($d > 0$) or facile behavior ($d = 0$), while case II addresses structure-sensitive behavior ($d \gtrless 0$) or structure insensitivity ($d = 0$).

It would seem that the original terms— demanding/facile—are not necessarily interchangeable with structure sensitive/insensitive.

COMMENT ON THE TURNOVER NUMBER DEFINITION

As defined

$$N = \frac{\text{Rate}}{\overline{A}} \equiv \frac{\text{molecules}}{\text{time} \cdot \text{site}}. \quad (12)$$

Since

$$\text{Rate} = kf(C) = kC^n$$

and as we noted (1)

$$k = k_v\underline{a}$$

it then follows that N is concentration dependent. We free ourselves of such dependency by defining a turnover velocity

$$N_0 = \frac{\text{Rate}}{C^n\overline{A}} = \frac{k_v\underline{a}}{\overline{A}} \quad (13)$$

or

$$N_0 = k_vD_0(\overline{A})^d \quad (14)$$

or in terms of the composition-dependent turnover number N, our turnover velocity N_0 is

$$N_0 = \frac{N}{(C_0(1 - x))^n}. \quad (15)$$

Note that the intrinsic velocity coefficient is k_v = velocity per active site per exposed site, for order, n.

PRACTICAL IMPLICATIONS

In terms of activity and yield/selectivity the fundamental query is, How does one favorably affect the exponent(s) of site discrimination (or exponent(s) of structure sensitivity)?

Signal enhancement of catalytic activity by alloying an active catalyst agent (e.g., Pt, Pd, Ag) with inert or less-active species (e.g., Au, Cu) has been noted by Boudart and co-workers (6) and in our laboratory (7). Nor is surface enrichment in alloys to be dismissed as a means whereby N or relative values of N (yield/selectivity) might be manipulated (1).

An excellent case is that of ethylene expoxidation as the recent review of Sajkowski and Boudart attests (5). Their analyses suggest the telling influences of promoters, alloying, and dispersion upon relative values of N.

As was noted earlier the turnover number functionality can exert a signal influence upon catalytic reactor time-on-stream behavior when supported crystalline sintering occurs. In such an instance we showed that the principal reaction rate coefficient would behave with time-on-stream, t, in accord with

$$k = \frac{\overline{k}_0}{(1 + \overline{K}t)^{(s-1)(d+1)}}, \quad (16)$$

where s is a phenomenological sintering order and d is, of course, our exponent of structure sensitivity.

So long as d is positive, activity, k, declines with time-on-stream, t, since s is always positive and greater than unity. *However, should $-d > 1$, one can see that*

on-stream activity could actually increase with time in spite of catalyst area reduction due to sintering.

In the light of Table 1, $d = -3.8$ for Fe/MgO. Reduced Fe is an NH_3 synthesis catalyst. Whatever be the value of s in Eq. (16), it is apparent that the synthesis rate would *increase* with time-on-stream as the Fe sinters in an Fe/MgO catalyst.

CONCLUSIONS

Extant data apparently support the turnover number model (*1*)

$$N \propto (\overline{A})^d.$$

$\overline{A}$ is the exposed catalyst area/volume and d the exponent of site discrimination or structure sensitivity.

Simple geometric arguments predicted $d = 0$ to 2 (facile to demanding behavior) while values of $d \gtreqless 0$ can be rationalized if morphological/chemical changes occur with crystallite size variation.

A fluid-phase composition (conversion, pressure)-independent turnover velocity is defined as

$$N_0 = \frac{\text{Rate}}{C^n \overline{A}} = k_v D_0 (\overline{A})^d.$$

APPENDIX: NOMENCLATURE

A, B, C	species concentrations
$\underline{a}$	exposed *catalytic* (active) sites per volume of dispersed catalyst agent
$\overset{\circ}{A}$	Angstrom
$\overline{A}$	exposed *catalyst* sites/volume
C_0	key reactant feed concentration
d	exponent of site discrimination or structure (demanding) sensitivity Eqs. (2) and (3)
D_R	fractal exponent in Ref. (*3*)
D_0	coefficient of site discrimination in Eqs. (2) and (3)
$\mathscr{D}$	dispersion or percentage exposed
e	exponent of site discrimination
f	a functionality
k_i	rate coefficient for reaction step i; equal to $k_v \underline{a}$
k_v	velocity coefficient, cm/time
K	coefficient in turnover number relation (Eq. (3))
L	crystallite *average* dimension
n	reaction order
N	turnover number, molecules/t site (Eq. (3))
N_0	concentration-independent turnover velocity, cm/time
R	crystallite radius
s	sintering order
t	time-on-stream
x	conversion

Greek

$\propto$	proportional to

REFERENCES

1. Carberry, J. J., *J. Catal.* **107**, 248 (1987); see also 25th CONICET Anniversary Reactor Design Conf., Santa Fe, Argentina, 1982 *in* "Concepts and Design of Chem. Reactors" (S. Whitaker and A. Cassano, Eds.), Gordon & Breach, New York.
2. Boudart, M., *AIChE J.* **18**, 465 (1972).
3. Farin, D., and Avnir, D., *J. Amer. Chem. Soc.* **110**, 2039 (1988).
4. Wu, J. C., and Harriott, P. J., *J. Catal.* **39**, 395 (1975).
5. Sajkowski, J., and Boudart, M., *Catal. Rev. Sci. Eng.* **29**(4), 325 (1987).
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. Barbier, J., Morales, A., and Maurel, R., *Bull. Soc. Chim. Fr.* **1–2**, I-31 (1978).
9. Barbier, J., and Marecot, P., *Nouv. J. Chim.* **5**, 393 (1981).
10. Barbier, J., Marecot, P., and Maurel, R., *Nouv. J. Chim.* **4**, 385 (1980).
11. Barbier, J., Marecot, P., Morales, A., and Maurel, R., *Bull. Soc. Chim. Fr.* **7–8**, I-309 (1978).
12. Fuentes, S., Figueras, F., and Gomez, R., *J. Catal.* **68**, 419 (1981).
13. Takai, Y., Ueno, A., and Kotera, Y., *Bull. Chem. Soc. Japan* **56**, 2941 (1983).
14. Fuentas, S., and Figueras, F., *J. Catal.* **61**, 443 (1980).

15. Benedetti, A., Cocco, G., Enzo, S., and Pinna, F., *React. Kinet. Catal. Lett.* **13,** 291 (1980).

16. Dorling, T. A., and Moss, R. L., *J. Catal.* **5,** 111 (1966).

17. Jarjoui, M., Gravelle, P. C., and Teichner, S. J., *J. Chim. Phys.* **75,** 1069 (1978).

18. Barbier, J., Lamy, E., and Outiki, O., *React. Kinet. Catal. Lett.* **18,** 127 (1981).

19. Outiki, O., Lamy-Pitara, E. and Barbier, J., *React. Kinet. Catal. Lett.* **23,** 213 (1983).

20. Topsoe, H., Topsoe, N., Bohlbro, H., and Dumesic, J. A., *Stud. Surf. Sci. Catal.* **7,** 247 (1981).

21. Bhatia, S., Bakhshi, N. N., and Matthews, J. F., *Canad. J. Chem. Eng.* **56,** 575 (1978).

22. Barbier, J., Morales, A., and Maurel, R., *Nouv. J. Chim.* **4,** 223 (1980).

23. Harada, H., and Ueda, T., *Chem. Phys. Lett.* **106,** 229 (1984).

24. Barbier, J., Corro, G., Marecot, P., Bournoville, J. P., and Franck, J. P., *React. Kinet. Catal. Lett.* **28,** 245 (1985).