JOURNAL OF CATALYSIS **136**, 631–632 (1992)

Multiatom Sites and the Turnover Frequency

The ideal basis for comparing the activities of different catalysts would be the turnover frequency *per active centre* under specified conditions. Unfortunately there is as yet no way to estimate the number of operating active centres in a working catalyst; at least for structure-sensitive reactions, it is generally accepted that the number of atoms participating in the active centre exceeds unity, but by how much is a matter of debate. Estimates can be made, for example, from the effect of adding an inert element in lowering the activity (*1–4*), but the values derived on the assumption that the additive is randomly distributed (*4*) do not always appear reasonable; if, however, the additive is assumed to aggregate into patches, the size of the centre will be decreased (*5*). What is quite certain, however, is that the turnover frequency (TOF) estimated from the number of surface atoms titrated by H_2 chemisorption is *lower* than the true value per active centre for a reaction where the centre comprises more than one atom.

The ratio of the number of active centres to the total number of surface atoms has been called the Taylor ratio; this is a pure number, the maximum value of which will be unity, attained when (as for structure-insensitive reactions) every atom constitutes an active centre. It is therefore surprising to read in a recent paper (*6*) statements to the effect that, as the particle size increases, the limiting values of the Taylor ratio for centres containing two and three atoms are respectively three and two. This conclusion implies that the TOF *per centre* can be *less* than the TOF *per atom* or that a fraction of an atom can act as a catalytic centre. It must therefore be based on a conceptual misunderstanding.

The argument that the authors employ (*7*) in deriving their conclusion is as follows. In a fcc octahedron, exposing only (111) planes, the number of centres comprising two atoms each of coordination number 9 (i.e., excluding the apical and edge atoms) is given by van Hardeveld and Hartog (*8*) as

$$N(B_2^{9,9}) = 12(m - 3)(m - 4),$$

where m is the number of atoms along the edge of the octahedron. The total number of surface atoms of all types N_s is given by

$$N_s = 4m^2 - 8m + 6$$

so that the limit of $N(B_2^{9,9})/N_s$ as m tends to infinity is indeed three, and by a similar argument the limiting value of $N(B_3^{9,9,9})/N_s$ is two.

The confusion arises from the definition of $N(B_n^{j_1 j_2 \cdots})$ adopted by van Hardeveld and Hartog (*8*) and from their method for counting centres which leads to their equations for number of centres. They state explicitly that "when counting sites, we do not pose the condition that every surface atom belongs to no more than one site, for such a condition would make the number of sites found dependent on where one starts counting . . . ." (These authors used the term "site" where I have used "centre" or "active centre.") The equation for $N(B_2^{9,9})$ cited above thus gives *the number of different ways in which centres composed of two atoms can be made from atoms of coordination number 9* in the surface of an fcc octahedron.

This manner of computation is, however, irrelevant to the operation of a catalytic process, because it is inherent in the methodology used by Bennett and Che (*6*), originating with Taylor's view (*9*) of the nature of active centres, and implicit in the use of van Hardeveld and Hartog's statistics (*8*), that each surface atom can participate in only one ac-

0021-9517/92 $5.00

TABLE 1

Statistics of Atom-Pair Sites on a Single Face of a fcc Octahedron

m	$N(C_9)$	$N(B_2^{9,9})$	$N(B_2^{9,9})_{\max}$
5	3	3	1
6	6	9	3
7	15	18	7

tive centre at any one time. What is therefore of interest is the maximum number of ways in which atoms of a given class can form *at any one time* centres of a defined composition and geometry. Table 1 shows first how $N(B_2^{9,9})$ as calculated by the equation given above actually exceeds the total number of atoms of this class (see also Fig. 11 of Ref. (*8*)) and second that $N(B_2^{9,9})_{\max}$, the greatest number that can function at any time, approaches a limiting value of one-half the number of atoms of the relevant class as m increases. This is indeed what common sense leads us to expect.

The problem of actually counting the maximum number of centres grows greater as the number of atoms per centre is increased, especially if one distinguishes between linear and triangular B_3 sites, but the limiting values for all types of site conform to the relation

$$N(B_n^j)_{\max} = N(C_j)/n,$$

where $N(C_j)$ is the total number of surface atoms of coordination number j. The problem posed by van Hardeveld and Hartog (*8*) concerning the number of B_4 sites in a 4 × 4 array of (100) symmetry is imaginary: however many different B_4 sites may be possible, the maximum number that could act catalytically at one time is four.

In view of the widespread and continuing application of the results of the calculations performed by van Hardeveld and Hartog (*8*) to the interpretation of particle size effects and of the fact that the foregoing comments must apply to all the estimations of the populations of active centres comprising more than one atom, it is worth bringing the misunderstanding, which is clearly still current, to the attention of those interested in applying small particle statistics.

REFERENCES

1. Bond, G. C., and Turnham, B. D., *J. Catal.* **45,** 128 (1976).
2. Bond, G. C., and Yide, Xu, *J. Mol. Catal.* **25,** 141 (1984).
3. Smale, M. W., and King, T. S., *J. Catal.* **120,** 335 (1990).
4. Martin, G. A., *Catal. Rev. Sci. Eng.* **30,** 519 (1988).
5. Hoost, T. E., and Goodwin, J. G., Jr., *J. Catal.* **130,** 283 (1991).
6. Bennett, C. O., and Che, M., *J. Catal.* **120,** 293 (1989).
7. Bennett, C. O., and Che, M., personal communication.
8. van Hardeveld, R., and Hartog, F., *Surf. Sci.* **15,** 189 (1969).
9. Taylor, H. S., *Proc. R. Soc. London A* **108,** 105 (1925).

GEOFFREY C. BOND

Department of Chemistry
Brunel University
Uxbridge UB8 3PH, United Kingdom

Received January 24, 1992; revised February 21, 1992