

Multiatom Sites and the Turnover Frequency: Reply to G. C. Bond

In the months before the submission of Professor Bond's letter (1), we exchanged several letters with him (2) and discussed our paper (3) with him in Paris. This exchange has led to a more general manner of presentation in this Letter, which includes his interpretation as a special case. These ideas are still the subject of research, so it seems premature to speak of confusion and misunderstanding.

As clearly indicated (3), we consider the limiting case of zero coverage of the surface intermediate such that the rate of adsorption controls the observed rate. We retain the notation already used (3). The predicted rate (turnover frequency, TOF) is then proportional to the probability that an incoming molecule may find a multiatom site and is thus proportional to the number of these possible sites. For $X = 2$ (an atom-pair site), this is $N(B_2^{3,9})$, as in Table 1 of Ref. (1). The original version of this table has been corrected and is presented here. The main point of contention with Professor Bond is that he prefers to set the rate proportional to the total number of atoms, $N(C_9)$, which does not change as the number of atoms in a site X (n in his notation) changes. To support this assertion, we present the following development.

As already discussed at length (3, 4), the turnover frequency or turnover rate is simply the observed rate (a function of all the usual variables) suitably normalized, and the TOF is measured per second or in molecules reacted (surface atom)⁻¹(s)⁻¹. We considered the function TOF(X , FE) in the paper on geometric effects (3) because one of our theses was that there is no theoretical reason that a plot of log TOF vs log FE should be a straight line, and indeed most of the experimental data produce curved lines

(4). Clearly the numerical values of the ordinates were not relevant to our argument.

Since the TOF clearly changes from one catalyst preparation to another, to present a general picture the rate must be normalized to a dimensionless quantity, and for this we choose

$$\text{TR}(X, \text{FE}) = \text{TOF}(X, \text{FE}) / \text{TOF}_s(X), \quad (1)$$

where we call TR the Taylor ratio. The normalizing factor TOF_s is the turnover rate per site, a quantity that generally does not have a simple relation to some kind of titration. Equation (1) corresponds to Eq. (5) of Ref. (3). For antipathetic behavior (only C_9 face atoms active), the intercept at FE = 0 is

$$\text{TR}(X, 0) = \text{TOF}(X, 0) / \text{TOF}_s(X). \quad (2)$$

Figure 2 of Ref. (3) was introduced to show that even in the absence of electronic effects and for regular crystallites, log TR vs log FE gives curved lines. In addition, $\text{TOF}_s(1)$ was set equal to $\text{TOF}(1, 0)$, so that $\text{TR}(1, 0) = 1.0$. Then to plot the other two pertinent curves of Fig. 2 of Ref. (3), we have assumed that $\text{TOF}_s(1) = \text{TOF}_s(2) = \text{TOF}_s(3)$.

TABLE 1
Statistics of Atom-Pair Sites on a Single Face of a fcc Octahedron

m	$N(C_9)$	$N(B_2^{3,9})$	$N(B_2^{3,9})_{\text{max}}$
5	3	3	1.5
6	6	9	3
7	10	18	5

Note. The following formulas, taken from Ref. (5), are adapted to refer to a single face of a fcc octahedron:

$$N(C_9) = 4(m - 3)(m - 2)/8; N(B_2^{3,9}) = 12(m - 3)(m - 4)/8; N(B_2^{3,9})_{\text{max}} = N(C_9)/2.$$

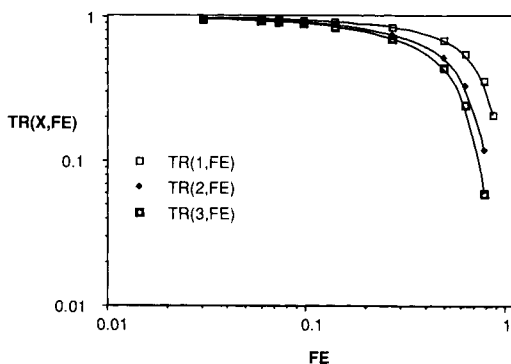


FIG. 1. Variation of Taylor ratio (TR) as a function of number of atoms per site and fraction exposed (FE), normalized so that $TR(X,0) = 1.0$. The sites are those on the faces of a fcc octahedron.

Then the formulas of van Hardeveld and Hartog (5) lead to $TR(2,0) = 3$, and $TR(3,0) = 2$. We chose this assumption so that it would be simple to plot all the lines of Fig. 2 in Ref. (3), including those for sympathetic behavior, directly from the formulas of van Hardeveld and Hartog (5).

It is not necessarily true that $TOF_s(1)$ equals $TOF_s(2)$, for the adsorbed reactant must be bound differently and have a different reactivity on the two different sites. To emphasize the arbitrary nature of the numerical value of TR, let us set $TR(X,0) = 1.0$ for all three antipathetic curves in question. In other words, $TOF_s(1) = (\frac{1}{3})TOF_s(2) = (\frac{1}{2})TOF_s(3)$. Retaining the van Hardeveld and Hartog formulas, we can construct Fig. 1 of the present Letter. The higher the value of X , the faster TR falls as FE increases. In Fig. 1, $TR(X,FE)$ can be assimilated to the ratio of rates $TOF(X,FE)/TOF(X,0)$, an experimentally measurable quantity. In principle, X can be determined by comparing the experimental data to Fig. 1. A similar quantity has been used by Andersen and Alstrup (6) and defined as TOF_m/TOF_∞ , where m is the number of atoms along an edge (3, 5).

The curves of Fig. 1 can easily be displaced by new assumptions so that $TR(X,0) = 1/X$, as Bond suggests (1). However, the

use of this procedure means that the observed rate would not be different for different values of X . In other words, if $X = 3$, $TOF(3,0)$ is the same as $TOF(1,0)$, so that $TOF_s(3)$ is three times $TOF_s(1)$.

We see that three different procedures for normalizing TR can be suggested: (a) Our original choice (3), $TOF_s(X) = 1.0$, so that $TR(X,0)$ is determined by the particular crystal model used; (b) Fig. 1, for which $TR(X,0) = 1.0$; and (c) Bond's choice, $TR(X,0) = 1/X$. The choice of one of these procedures does not constitute a conceptual misunderstanding. Since Bond gives us credit (7) for introducing Eq. (1) for the Taylor ratio, we might say with Humpty Dumpty that TR means just what we choose it to mean (8). Returning to this side of the looking glass, there is no basis for insisting that $TOF_s(2) = 2TOF_s(1)$. The way an intermediate interacts with two atoms is different from the way it would interact with one atom, and this should affect its reactivity. This problem is in a sense related to the problem of determining the radius of a given M^{n+} ion. As now known, the answer is not *unique* and depends on the number of ligands, i.e., the coordination number, around M^{n+} (9). Also, the charge carried by M^{n+} in a complex strongly depends on the number, nature, and arrangement of the ligands around it (10).

In this discussion, as in Ref. (3), we consider only the simplest case: the limit of zero coverage, for which one might except the crystal surface structure to exert the most influence on the rate. Professor Bond rejects the idea that the rate of adsorption at zero coverage (sticking probability) is proportional to the number of potential sites available. According to the formulas he proposes, all the lines in Fig. 1 would be the same as that for $TR(1,FE)$. There would be no way that a change in X would be manifested in kinetic experiments. Remember that we cannot measure the numerical value of TR, but only the ratio $TOF(X,FE)/TOF(X,0)$. We believe that the use of probability in kinetics is justified (5, 6, 11), al-

though more sophisticated statistical models might eventually be developed.

Upon studying the paper of van Hardeveld and Hartog (5) during the preparation of (3), we also were surprised that there appears to be more sites when $X = 2$ than when $X = 1$. However, we finally concluded that the initial confusion arose because of our lack of understanding that the rate as coverage tends to zero is proportional to the number of possible landing sites for the adsorbate, and not merely to the total number of sites (for $X > 1$).

The discussion can be summarized as follows:

1. In a field still subject to debate, it is not possible to expect a unique, textbook-style explanation.

2. Professor Bond's intervention has led us to the preparation of Fig. 1, which highlights the arbitrary nature of TOF_s and shows the measurable effect of the number of atoms per site.

3. Recalling the aleatory nature of the actual data on structure sensitivity (4), we fear that the lines in Fig. 1 are not separated enough to permit the estimation of X from kinetic experiments.

4. The devising of a general experiment to determine X is still an open question.

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