Normalizing Heterogeneous Electro catalytic and Photocatalytic Rates

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ABSTRACT: This short essay urges the community of those who study electrocatalysis and photocatalysis to report measures of the number of active sites in heterogeneous catalysts (especially the redox sites in an electrocatalyst) and the number of photons involved in photoconversions. An example of the former is the use of CO stripping for catalysts containing platinum-group metals and N\textsubscript{2}O titration to count redox sites in supported electrocatalysts containing base metals that do not strongly chemisorb CO or hydrogen. A minimal example of the latter is to report energy density as a way to bridge between batch photolysis and flow photo-initiated reactions.

INTRODUCTION

Only about 1% of the contributions published to date in ACS Omega deal with heterogeneous catalysis, but they all touch forefront topics in the conversion and storage of energy, particularly renewable energy, new materials, and new reactors that enable effective electrochemical and photochemical conversions. Evidently, these contributions have met the scope of ACS Omega, which is to present new findings “without any perceived evaluation of immediate impact.” This perspective addresses ways to enhance the future appreciation and utility of the information by encouraging the community, going forward, to tie the findings to the number of catalytic sites and the intensity of the process conditions, both of which are often under-reported.

DISCUSSION

Site-Counting. Counting the sites that ostensibly confer activity on heterogeneous catalysts, like all of metrology, requires bootstrapping, an initial approximation followed by successive refinements that define and realize the measurement and facilitate its traceability. The measurement is complicated by changes in, indeed generation of, the sites during reaction. Methodological deficiencies, uncertainties, and special reaction conditions notwithstanding, the reporting of some measure of the number of sites permits better comparison of results across laboratories because it provides an additional benchmark for “homemade” catalysts, which can be difficult to reproduce when synthesized at a small scale. The use of well-characterized reference catalysts may be inappropriate because they are available only for a limited range of compositions and the whole point of the reported research may be to test a composition or architecture that cannot be achieved by modifying an existing catalyst.

Unless the sites are uniform and 100% exposed, physical characterization of the sites, via bulk-averaging techniques, e.g., spectroscopy, diffractometry, or microscopy, will not necessarily correctly census them; the signature of a minority population of rare, very active sites could be overwhelmed by the signal from the majority species.

There is also no guarantee that a molecular probe, for example, titration, even one that uses a participant in the catalytic cycle, will count the sites faithfully because with the exception of populating an isotopically labeled pool or a “knockout” protocol that incrementally poisons the sites, titration must be employed outside of the catalytic cycle, i.e., ex and not in operando. Steady-state isotopic transient analyses are susceptible to error in the deconvolution of overlapping transients. The method can, in principle, be applied to reactions involving condensed media, but the high density of the intermediates may, again, impede interpretation, particularly for species that can rapidly scramble (e.g., surface- and solvent-bonded hydrogens). The knockout experiment may count readily titrated but irrelevant sites. Finally, we note that the stoichiometry of titration may be sensitive to the measurement protocol so that, in general, one can only count the sites on average or nominally.

Such cavils, however, should not dissuade researchers from attempting to normalize rates. The normalization itself is a hypothesis that needs to be reported to be disproved. Moreover, it provides further characterization of the catalyst, which should be obligate for papers published in ACS Omega because it assists future researchers who try to reproduce prior

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work, particularly in domains like electrocatalysis where the tradition of counting sites is not as strong as it is in heterogeneous catalysis.

For example, titration using H2 \(^9\) systematized the activity of a set of supported Pt electrocatalysts. In that case, the electrically conductive carrier itself had sufficient electrochemical activity to preclude the use of techniques (e.g., underpotential deposition) that serve well to estimate the electrochemically active surface area of bulk metals.

Even when special attention is paid to subtraction of background currents, the use of techniques that can work well for platinum-group metals, e.g., CO stripping or underpotential deposition of a monolayer of hydrogen or another metal, can be problematic for redox sites containing base metals that do not chemisorb CO or hydrogen at convenient temperatures. For this reason, to count the redox sites in a carbon-supported copper electrocatalyst, we adapted titration that uses N\(_2\)O to gently deposit a monolayer of oxygen on the surface of the metal. \(^12\) Electrochemical stripping of the adsorbed O then counted the sites. We believe, but have not yet shown, that the technique could be used for any reduced metal that dissociatively adsorbs N\(_2\)O (Figure 1). \(^13\)

An alternative to titrating sites stoichiometrically would be to compare the measured rate of the reaction under study to that of a fiducial reaction, one whose rate per site has only a small variability between bulk catalysts (whose surface structure can, in principle, be determined through physical measurements) and supported catalysts. In the case of metals, any structure-insensitive reaction \(^14\) should serve as a fiducial reaction for any other structure-insensitive reaction. \(^15\)

For electrochemical reductions, the electrochemically activated evolution of hydrogen \(^16\) might serve as a first guess at a fiducial reaction for other electrochemical reductions, for example, the electrochemically activated removal of heteroatoms. \(^17\) The variation of surface geometry with particle size can be calculated for compact, simply faceted particles, \(^18,19\) and the exchange current density has been measured for some metals, for example, the low-index facets of Pt \(^16\) (Figure 2).

In the case of metal oxides, the oxidation of methanol appears to serve well as a fiducial reaction because it has been shown \(^20\) to track with the number of M\(_1\)−O−M\(_2\) moieties that comprise the active sites for alcohol oxidations.

**Photon Counting.** When the source of illumination is monochromatic and tightly coupled to the reactor, it can suffice to report lamp power as a surrogate for the input flux of photons in photoconversion. For example, we have shown that photoactivated trifluoromethylation of substituted arenes, in batch \(^21\) and flow reactors, \(^22\) tracks with the density of the photon energy admitted to the reactor (Figure 3). In the case of the batch reactor, the energy density is the power of the lamp multiplied by the duration of the experiment and divided by the volume of the illuminated solution. In the case of the flow reactor, the energy density is the power of the lamp divided by the flow rate of the solution.

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**Figure 1.** Elements likely susceptible to site-counting by N\(_2\)O titration followed by electrochemical stripping of the deposited O.

**Figure 2.** Estimation of the exchange current density of small, compact, faceted particles of Pt using literature values for facet population densities \(^19\) and exchange current densities for low-index planes of the metal. \(^16\)

**Figure 3.** Yield of photoactivated trifluoromethylation of substituted arenes \(^21\) can track with lamp power in both batch and flow reactors.
that sort of correlation is convenient but does not afford the same level of insight as would knowing the quantum yield of the conversion. For example, photoconversions exhibit quantum yields, \( \Phi \), that can be less than unity, when the energy of the photon is dissipated before it affects the desired reaction, or greater than unity, when the photon initiates a chain reaction. In either case, it is good to know the value of \( \Phi \) both to explain the chemistry and to compare the conversion efficiency to other ways of deploying the photons. Moreover, lamps age and the coupling of the source to the experiment may incur losses. Therefore, it is far more instructive to report some measure of the utilization of the photons that have arrived, for example, through the results of an actinometric assay, rather than merely reporting the nameplate power of the illumination source. Several assays are available,\(^{23}\) including wet assays, which are suitable for flow photochemistry, and solid-state actinometers, which may be more convenient for testing photovoltaic devices.

### CONCLUSIONS AND OUTLOOK

Reviewers, readers, and editors of ACS Omega would certainly object if an experimental procedure only described the use of “some” catalyst, either “some type” or “some amount.” Description of the type of a catalyst is rarely omitted, but the omission of information about the number of catalytic sites is common.

Similarly, the heating of a sample described only by the wattage of the oven would raise objections. The addition of thermal energy is almost always quantified by reporting the temperature of the sample. However, the addition of photoenergy is rarely accompanied by reproducible specification of the number or flux of photons or the quantum yield of the conversion.

Adding those details, even approximately or imperfectly, will surely enhance the archival value of contributions dealing with catalysis, especially electrocatalysis and photocatalysis, by equipping future readers with metrics that can be used to quantify progress in the understanding and utilization of the materials and energy involved in the targeted chemical processes.

Intrinsic, normalized rates of catalytic conversions and photon conversions should depend on the molecular scale chemistry and imposed reaction conditions. Establishing normalized rates is a first step toward detecting (and perhaps diagnosing) scale-dependent phenomena that interfere with comparisons between laboratories and that can mask underlying trends in the targeted chemistry.\(^{24}\)

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**Notes**

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