Normalizing Photocatalysis

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Intrinsic Catalytic Activity versus Effective Light Usage—A Reply to Professor Kisch's Comments

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We would like to thank Prof Kisch[1] and others[2] for their interest in our article[3] and appreciate their concern as to the proper use of (at times still evolving) terms and experimental protocols, so as to obtain meaningful data. It appears that our article, which was written from the viewpoint of strictly traditional heterogeneous catalysis, was not met with unqualified approval as it seemed to contradict some of the established views and practices of that section of the photocatalysis community which is represented by Prof. Kisch. It is our conclusion that this impasse (or misunderstanding) has arisen, in part, because of a lack of unequivocal consensus on the terms used in the field, but principally from different aims regarding the objectives of the measurement.

It is a happy coincidence that the latest IUPAC *Glossary of Terms Used in Photocatalysis and Radiocatalysis*[4] will soon be published. This very useful IUPAC initiative tracks and tries to unify literature developments as they evolve. Although in our original article the term apparent quantum yield (AQY) is used, this is a good opportunity to adopt IUPAC's coming suggestions and use the term photonic efficiency (PE) instead, which is defined in Equation (1) for the purposes of this particular discussion.

$$PE = \frac{(\text{moles of } H_2 \text{ evolved}) \times 2 \times 100}{\begin{array}{c}(\text{moles of photons reaching the internal}\\ \text{surface of the irradiation window})\end{array}} \qquad (1)$$

The principal disagreement seems to be centered on which catalyst loading/concentration should be used to compare catalysts so as to rank their activity. Professor Kisch's assertion is: „*…the underlying premise*[3] *that in any heterogeneous catalytic reaction a doubling of the catalyst concentration leads to a doubling of the observable rate in the non-diffusion-limited regime does not hold for a heterogeneous photocatalytic reaction. This arises from the fact that the rate of any photoreaction is given by the product of quantum yield and absorbed light intensity, and the latter factor exponentially depends on the concentration of the light-absorbing species. In general, therefore, the plateau region of a diagram of reaction rate versus photocatalyst concentration corresponds to the saturation of light absorption and not to diffusion limitations. It appears then more meaningful to conduct any photocatalytic reaction at the onset of the plateau region as explained in more detail below.*“

In fact, our underlying view is that the literature currently does not allow for meaningful comparisons between different photocatalysts active in the generation of hydrogen from aqueous media, and that to rank them the catalytic sites must be measured when they are performing at their optimum capacity. This can only occur when the catalyst concentration is such that it lies in the linear regime of light absorption. As can be seen in Figure 1 (taken from a recent IUPAC Technical Report, Ref. [5]), a significant part of the concentration range can display linear behavior, and catalytic activity can easily be measured at these concentrations. Only after scattering starts to have an impact does that linearity give way to other nonlinear behavior, as shown in, for example, Figure 2 (taken from Bickley et al.[6]). This is, of course, reflected in the observed rate, as in, for example, Figure 3 (taken from Ref. [5]), as the catalytic sites are not provided with sufficient light to work at their optimum capacity.

Measurement of the highest possible activity of the active site of a heterogeneous catalyst is the only way in which ca-

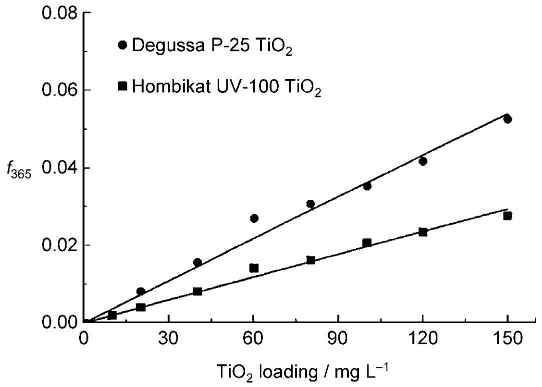

Figure 1. Fraction of the photon flow f_{365} absorbed at 365 nm versus concentration of the titania solution for the Degussa P-25 TiO_2 and the Hombikat UV-100 TiO_2 specimens, according to Ref. [5].

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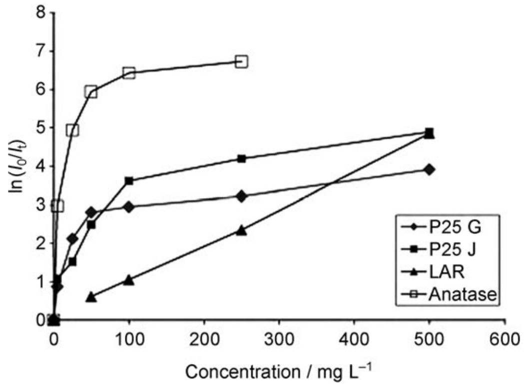

Figure 2. Beam intensity attenuation ($\ln(I_0/I_t)$) versus dispersion concentration for different TiO_2 photocatalysts. P25 G (Degussa Germany) (◆), P25 J (Degussa Japan) (■), anatase (□), low-area rutile (LAR) (▲), according to Ref. [6].

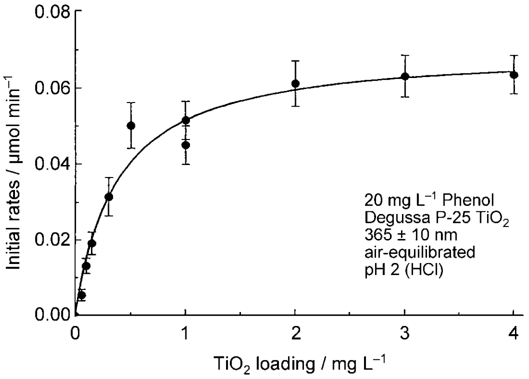

Figure 3. Initial rate of the photooxidative degradation of phenol versus TiO_2 loading for the Degussa P-25 TiO_2 specimen, according to Ref. [5].

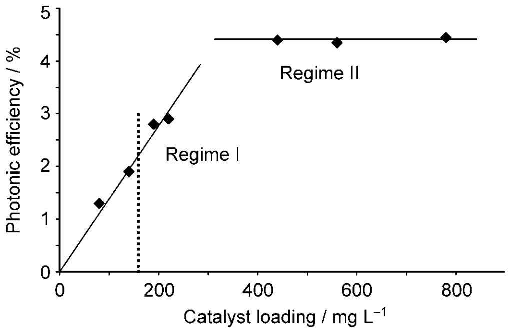

Figure 4. Photonic efficiency versus catalyst loading, indicating the regimes where the catalytic sites can operate at their highest turnover rate (regime I) and where they operate at a lower turnover rate (regime II), adapted from Ref. [3].

talytic materials can be ranked in terms of their intrinsic turnover rate (of course, additionally they may be ranked using other parameters such as selectivity, longevity, cost, etc.). This means that each active site, or ensemble of active sites, needs to experience the fullest access to all reactants possible (we include here water, sacrificial reagent, if applicable, and photons). Therefore, we suggest that the photonic efficiency (PE) needs to be measured in a regime where there is a linear variation of light absorption with catalyst concentration (i.e., regime I, see Figure 4, adapted from Ref. [3]), such that this parameter can be used to rank photocatalytic materials in terms of their intrinsic activity. In addition, other parameters (e.g. chemical substrate concentrations, temperature, pressure, etc.) must be chosen in such a way that a doubling of catalyst concentration does, indeed, lead to a doubling of the observed rate.

Employing catalyst concentration regimes that are in the plateau region of the absorption vs. catalyst concentration plot, either at the very edge or further along, can be useful in determining how much light is needed to, for example, completely destroy an organic contaminant in the presence of a particular catalyst, or to measure the amount of a catalyst needed to achieve such an outcome. However, these results are very dependent not only on the catalyst employed, but also on reactor geometry, as nicely pointed out by Bahnemann and co-workers.[7]

Therefore, we proposed a different measurement in our article that separates these two aspects and allows for a materials ranking only. We set out to, as a first screen, rank materials based on the intrinsic maximum activity (i.e. turnover rate) of a catalyst. Depending on the level of understanding of how a particular catalytic system works, this may be expressed in a variety of units—the most basic being moles converted/amount of catalyst (discussed more extensively in Ref. [3]). This simple approach should translate fairly easily across different groups and laboratories, thereby addressing the problem of incomparable published data sets for different catalytic materials.

We hope that this explanation clarifies the issues sufficiently well to allow some degree of adoption of our proposal by the community as how to rank photocatalytic materials for the generation of hydrogen from aqueous media. We sincerely thank the editor for stimulating this discussion and the opportunity to reply.

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