Correspondence

Normalizing Photocatalysis

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On the Problem of Comparing Rates or Apparent Quantum Yields in Heterogeneous Photocatalysis

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In a recent essay Maschmeyer and Che proposed a "simple and practical way towards a normalization" of apparent quantum yields for hydrogen photogeneration catalyzed by semiconductor powders.[1] The proposal is based on the well-known observation that with increasing photocatalyst concentration the apparent quantum yield (AQY) increases first linearly before reaching a constant value. By analogy with heterogeneous catalysis in the dark the authors assume that in the plateau region diffusion and not intrinsic photocatalyst properties control the AQY. Therefore it was recommended that comparison of various photocatalysts is meaningful only when the reaction is conducted in the linear regime. However, the underlying premise 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 diffusion limitations (Figure 1, regions B to C). It appears then more meaningful to conduct any photocatalytic reaction at the onset range of the plateau region as explained in more detail below.

The true quantum yield of any photochemical reaction is given by the ratio of reaction rate to light intensity absorbed at a given wavelength per volume and time (I_a, photon flux). Since the absorbed photon flux depends on the intensity of the light source, absorption coefficients of the photocatalyst and substrates, and the photoreactor, only quantum yields, that is, rates divided by I_a, can be used for a reliable and quantitative comparison of various photoreactions. Whereas the measurement of I_a is easy in homogeneous systems, it is a difficult procedure for heterogeneous reactions like hydrogen evolution photocatalyzed by aqueous semiconductor suspensions.[1] In this case light is not only absorbed but also scattered and reflected by the suspended particles, and it is extremely tedious to correct for this loss of absorbed light intensity.[2–4] The loss may reach 13–76 % of the total incident photon flux.[5] Most authors therefore compare simply rates or even rate constants tacitly assuming that the absorbed photon flux is the same in each reaction. But this assumption in general is not justified since even minor changes in the nature of the suspension and irradiation setup may considerably alter I_a and therefore the reaction rate.

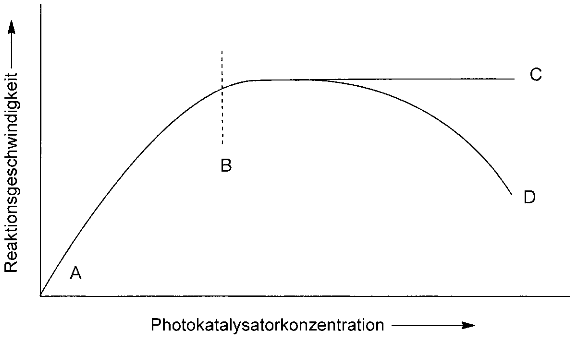

Figure 1. Dependence of reaction rate on photocatalyst concentration.

To overcome this basic problem of a heterogeneous photoreaction it was proposed already many years ago[6–9] to replace the absorbed photon flux by the incident photon flux, that is, the number of photons arriving at the reactor surface as proposed again in the Essay.[1]It is obvious, however, that the rate- and AQY-determining absorbed photon flux may differ considerably from experiment to experiment although the incident flux is the same. Therefore apparent quantum yields are not a reliable basis for comparing various photocatalytic reactions.[10] Furthermore, the rate of any catalytic photoreaction, irrespective of whether homogeneous[11] or heterogeneous,[4] initially increases linearly with photocatalyst concentration (Figure 1, curve A–B) owing to the increase of absorbed photon flux and then stays constant in the region of B to C representing concentrations of constant and optimal light absorption. In the case of a heterogeneous system a rate decrease may occur in region from B to D as a result of reduced penetration depth and increased scattering of the incident light beam.[12,13] Thus, in contrast to heterogeneous catalysis in the dark, in heterogeneous photocatalysis

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the plateau region originates from the saturation of light absorption. Only in special cases like high concentrations and slowly diffusing intermediates may the reaction be diffusion controlled.[14] This seems very unlikely for photocatalytic hydrogen evolution.

As follows from the experimental observations summarized above, a photocatalyst concentration around the plateau onset should be selected in order to ensure optimal light absorption. Only in this case is a comparison of apparent quantum yields or rates of various photocatalytic reactions meaningful. For titania powders of specific surface areas of about 50–200 $m^2 g^{-1}$ the optimum concentration is in the range of 0.5–3.0 $g L^{-1}$ depending on chemical and technical details of the irradiated system. In view of these basic considerations the recommendation to operate photoreactions catalyzed by semiconductor suspensions in the linear regime of the plot of AQY versus photocatalyst concentration[1] should not be accepted.[15]

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[1] T. Maschmeyer, M. Che, *Angew. Chem.* **2010**, *122*, 1578; *Angew. Chem. Int. Ed.* **2010**, *49*, 1536.
[2] J. C. Colmenares, R. Luque, J. M. Campelo, F. Colmenares, Z. Karpinski, A. A. Romero, *Materials* **2009**, *2*, 2228.
[3] B. Ohtani, *Chem. Lett.* **2008**, *37*, 217.
[4] D. F. Ollis, *Top. Catal.* **2005**, *35*, 217.
[5] M. Schiavello, V. Augugliaro, L. Palmisano, *J. Catal.* **1991**, *127*, 332.
[6] M. R. Hoffmann, S. T. Martin, W. Choi, D. W. Bahnemann, *Chem. Rev.* **1995**, *95*, 69.
[7] N. Serpone, R. Terzian, D. Lawless, P. Kennepohl, G. Sauve, *J. Photochem. Photobiol. A* **1993**, *73*, 11.
[8] N. Serpone, G. Sauvé, R. Koch, H. Tahiri, P. Pichat, P. Piccinini, E. Pelizzetti, H. Hidaka, *J. Photochem. Photobiol. A* **1996**, *94*, 191.
[9] H. Tahiri, N. Serpone, R. Le van Mao, *J. Photochem. Photobiol. A* **1996**, *93*, 199.
[10] A comparison seems meaningful by referring a set of reactions performed in the same photoreactor to a standard system obtaining thereby “relative photonic efficiencies”, see Refs. [6–8].
[11] H. Einaga, M. Misono, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 3435.
[12] P. Johne, H. Kisch, *J. Photochem. Photobiol. A* **1997**, *111*, 223.
[13] D. Curcó, J. Gimenez, A. Addardak, S. Cervera-March, S. Esplugas, *Catal. Today* **2002**, *76*, 177.
[14] A rare case for a diffusion-controlled semiconductor-photocatalyzed reaction was reported for an organic addition reaction: A. Reinheimer, R. van Eldik, H. Kisch, *J. Phys. Chem. B* **2000**, *104*, 1014.
[15] It is noted that the use of a factor of two in the equation for the apparent quantum yield is justified only if the reducing agent does not exhibit current amplification properties.