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Hydrogen Generation

Catalytic Aspects of Light-Induced Hydrogen Generation in Water with TiO_2 and Other Photocatalysts: A Simple and Practical Way Towards a Normalization?

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diffusion · hydrogen · photocatalysis · titanium · water splitting

Introduction

The meaningful comparison of materials for the photocatalytic production of hydrogen from water is currently barely possible because of the lack of a standardized procedure to evaluate catalysts, hindering progress in the field.

Because of its importance for the future economy and in view of increasing societal environmental concerns, the generation of hydrogen has become a crucial challenge.[1] Since the discovery of the electrochemical photolysis of water at a semiconductor (TiO_2) electrode surface by Fujishima and Honda,[2] much work has been performed to improve our understanding of the processes involved in water cleavage[3,4] and to propose improved photocatalytic systems, particularly those operating under visible light, be they based on solid oxides[5] or non-oxides.[6]

However, because of the variety of ways in which data related to diverse combinations of the photocatalytic system, the reaction conditions, the reactor characteristics, and the irradiation system are reported across the literature, it is virtually impossible to compare the performance of the relevant catalytic materials. This holds true not only for work of different groups; sometimes even results from the same group fall into this category.

Herein, we are concerned with the evaluation of the performance of solid photocatalysts so that they can be compared in a simple and practical fashion that is applicable whether sacrificial solutions are used or not. The additional chemical potential present in a sacrificial solution will be the same regardless of the catalyst system used, so differences in the photocatalytic activity remain meaningful. Different catalysts might display varying abilities in unlocking that chemical potential, which can be accommodated in the definition of the apparent quantum yield (AQY), see below.

To a large extent, the challenge is similar to that encountered in the 1960s by researchers working in metal catalysis. In 1960, Spenadel and Boudart proposed to use hydrogen chemisorption at saturation to determine the specific surface area of alumina-supported platinum in a range of dispersion not accessible to measurements by X-ray line broadening.[7] This idea was taken further, and a new method was successfully applied to measure the surface area of the metal, namely the reaction of hydrogen at room temperature with oxygen adsorbed on supported and unsupported platinum catalysts, the so-called hydrogen–oxygen titration method.[8] This method was the key factor in the development of catalysis by oxide-supported metals.

Although much progress has been made in the understanding of light-induced generation of hydrogen from water, particularly in recent years with the introduction of sophisticated multicomponent oxides (with and without sacrificial solutions),[9–13] the state of the literature regarding the catalytic aspects of the reaction remains at times confusing, particularly regarding quantitative comparison between different catalytic systems. This brief personal view is aimed at highlighting some pertinent issues that need to be addressed, so that photocatalysts can be compared more meaningfully than is currently the case.

Catalysis Context

First of all, it is instructive to recognize that the definition of an active site in a heterogeneous photocatalytic system is a nontrivial matter. Given the many processes that occur and which finally give rise to the generation of hydrogen and oxygen (Figure 1), it is debatable whether it is sensible to try to define a single active site.

To a first level of approximation, we may think about such a catalytic system as follows. A photon, after passing through the reactor walls and water surrounding the catalyst particle, encounters the catalytic surface and gives rise to a photo-

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$$\begin{aligned}
\text{Photocat.} + h\nu &\rightarrow e^{-}_{(cb)} + h^{+}_{(vb)} \\
e^{-}_{(cb)} &\rightarrow e^{-}_{(cb)\,surf} \\
h^{+}_{(vb)} &\rightarrow h^{+}_{(vb)\,surf} \\
X &\rightarrow X_{(ads)} \\
X_{(ads)} + h^{+}_{(vb)\,surf} &\rightarrow X_{oxidized} + H^{+} / H^{\cdot} \\
H^{+} / H^{\cdot} &\rightarrow H^{+}_{(ads)} / H^{\cdot}_{(ads)} \\
2e^{-}_{(cb)\,surf} + 2H^{+}_{(ads)} &\rightarrow 2H^{\cdot}_{(ads)} \\
2H^{\cdot}_{(ads)} &\rightarrow H_2
\end{aligned}$$

Figure 1. A typical but non-exhaustive example of the processes occurring in the photocatalytic generation of hydrogen with or without sacrificial agent present.[14–17] cb = conduction band, vb = valence band, X = oxidizable species, e^- = photoelectron, h^+ = hole, surf = surface, ads = adsorbed.

excitation event, thus generating an excited photoelectron and a corresponding hole (of course, not every photon that hits the catalyst does this). The electron/hole pair will normally recombine rapidly, but some will diffuse through the catalyst and interact with interfacial water molecules. In some cases, this interaction will result in a redox reaction, in which, for example, the water gets oxidized by a photogenerated hole, thus leading to the formation of oxygen and protons that are subsequently reduced to hydrogen by the photoelectron. It has been firmly established that cocatalysts markedly aid this redox reaction, and platinum has been used to great effect by many groups.

It is clear that there are significant issues regarding mass transfer (substrate adsorption and product desorption, diffusion in general) as well as photoelectric events (electron/hole recombinations, etc.) that need to be considered when trying to define an active site. Indeed, we might best talk about a sequence of coupled reactions with a whole range of active sites working together—a cascade-type reaction system.

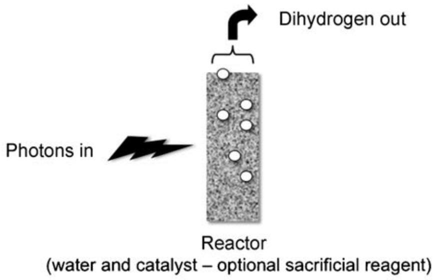
Towards a Normalization

As it is inherently very difficult to isolate the individual performances of these active sites from each other and to probe the various photonic and mass-transfer effects, researchers are presented with a rather complex task when reporting data. In other words, turnover rates based on the number of active sites are for most systems of very limited value, as not only the definition of what an active site is, but also—and as a consequence—their number is ill-defined (in contrast to, for example, acidic sites in a zeolite).

Thomas Maschmeyer was born in Hamburg in 1966. He completed his PhD at the University of Sydney and then moved to the UK for research appointments in London and Cambridge. After his positions as Professor, Head of Department, and Vice-Chairman at the Delft Institute of Chemical Technology, he returned to Australia as ARC Federation Fellow in late 2003 and was recently awarded a Professorial ARC Future Fellowship. He is also cofounder and one of the directors of Ignite Energy Resources Ltd, a low carbon footprint energy and fuels company. He serves on the editorial boards of five international journals, is President of the Catalysis Society of Australia as well as advisor and consultant to many governmental bodies and companies. He received the 2007 Le Fèvre Prize of the Australian Academy of Sciences for outstanding basic research in chemistry by scientists under 40.

Herein, we would like to suggest a systemic approach, that is, an approach that does not try to define active sites as such but looks at the overall performance of the catalytic system in such a way that the measurements reported can be easily reproduced by other laboratories. The key to this approach lies in the application of tried-and-trusted methodologies from the field of heterogeneous catalysis.[18]

When taking such a systemic approach, the whole reactor can be viewed as a catalytic space: photons and water in, dihydrogen out (Figure 2). The fate of the oxygen produced need not be considered in detail, as essentially the same principles as discussed for hydrogen apply. While simplistic, this approach allows for an easy and meaningful comparison and ranking of materials. For this purpose, we do not need to differentiate between what some refer to as "true water splitting", which results in the coevolution of oxygen at a ratio of $2\,H_2{:}1\,O_2$ and "hydrogen generation", involving sacrificial reagents. Clearly, the derived apparent quantum yields will differ significantly depending on whether or not a sacrificial reagent is used. However, the aim of our approach is to compare related systems in a meaningful way; full disclosure of experimental details will enable this comparison, irrespective of whether sacrificial reagents are used or not.



$$\text{Apparent Quantum Yield} = \frac{\text{Dihydrogen out / mol}}{\text{Photons in / mol}} \times 2 \times 100$$

Figure 2. A simple model of the reaction system to enable comparisons of catalysts, ignoring intricate reaction sequences and simply focusing on mole photons in and mole dihydrogen out. Finer experimental details regarding the use of an inert carrier gas or a partial vacuum or a combination thereof to collect the hydrogen evolved can be easily replicated across laboratories, and it is probably not necessary to be prescriptive on this point. The factor 2 in the definition of the AQY results from the fact that it takes two mole electrons to produce one mole hydrogen.

Now we can use expressions such as turnover rate and also derive an apparent quantum yield that is a measure of the efficiency with which incoming photons are used to produce hydrogen under a particular set of conditions.

There might be merit in the construction of a three-dimensional surface that plots catalyst loading versus apparent quantum yield and versus photon flux. However, in our opinion such analysis is a complication for initial screening/

ranking purposes, and it is more convenient to use solar flux, as that is the most intuitive and relevant flux as a first reference point. Thus, the simplest approach is to use a solar simulator. A range of products is commercially available. However, the particular reactor set-up must still be taken into account as well as the chosen spectral window, and the incoming photon flux needs to be established. For this task, it is insufficient to rely on a measurement external to the actual reactor (e.g. by using a thermopile), but the number of incoming photons that actually make it into the reactor must be measured. Such measurement is most easily and reproducibly achieved by actinometry (a well-established IUPAC-standardized method).[19,20] However, it is important to recognize earlier work by Schiavello and co-workers,[21] from which it can be deduced that when using supported catalysts, it is important to slurry the support with the actinometry test solution so as to take care of any light scattering. A further advantage of the use of actinometry is that as only the photons count that make the reactor internals, flux differences owing to the actual reactor design (mirrored surfaces, etc.) and the angle of incident radiation are accounted for.

The apparent quantum yield is simply defined as in Figure 2. This quantity allows for a comparison between different photocatalysts so as to be able to rank them, or for the assessment of a particular reactor configuration efficiency with a standardized photocatalyst (e.g. platinized titania Degussa P25 or CdS). The turnover rate can then be expressed as mole hydrogen per hour and gram or per hour and square meter of catalyst (which is most easily defined initially as the complete system, that is, support and active sites). A key point is that if sufficient catalyst characterization is provided, one unit can then be converted into another, and if more elaborate catalyst characterization data is available, these measurements can be converted accordingly (e.g. mole hydrogen per hour and edge site).

Reporting hydrogen production in units of $\mathrm{mol\,s^{-1}}$ is useful in areas such as spectroscopy (laser-pulse experiments, etc.), but unless identical reactors, catalysts loadings, and reaction conditions are used, these numbers cannot be translated from one catalyst to another, let alone from one laboratory to another. Furthermore, this unit is of little utility when trying to estimate the requirements of a realistic device, which has to be the final aim at some stage. In this context, catalyst stability should also be clearly reported, and an activity profile over 24 h might serve as a convenient measure.

However, the procedure set out above is in itself insufficient. The amount of catalyst used and the intensity of illumination applied strongly affect the apparent performance of the catalyst system. If homeopathic concentrations of catalyst are used and some hydrogen evolution is still observed (maybe owing to measurement error or partial decomposition of a sacrificial agent), it is possible to report quite a large amount of hydrogen generated per gram of catalyst. Equally, if very intense illumination is used, it is possible to increase the apparent reactivity unduly. To achieve a very high apparent quantum yield, quite a low level of irradiation or a very high catalyst loading might be used to maximize photon-capturing efficiency of the system, depending also on the units chosen to report the data. These different preferences make it at times close to impossible to compare and rank different catalyst systems across the literature, thus reducing the rate of progress in this area of highly topical and urgent research.

A simple way around these issues can be found when designing experiments according to the principles of heterogeneous catalysis:

1) The illumination should be set so as to mimic a realistic natural system in terms of spectrum and intensity, that is, it should be similar to sunlight. There are several ways in which to set up such a system. The simplest, most easily reproducible and therefore most practical (and flexible) for initial screening would be to use a mercury lamp (e.g. a standard 350 W Hg arc lamp), using water-cooled UV filters with different cutoff wavelengths (e.g. 305, 395, 430, 495 nm). A more sophisticated approach is to use a commercial solar simulator that employs a Xenon lamp with a monochromator crystal and filters that match the standard tables for reference solar spectra irradiances.[22,23] In both cases, photon flux should be comparable to that obtainable when using nonconcentrated sunlight directly.
2) The experiments should be performed under well-defined conditions of temperature (e.g. water-cooled reactor at 25 °C) and pressure (e.g. atmospheric).
3) It should be mandatory to establish that the system is operating in a non-diffusion-limited regime.

It is instructive to note that when discussing diffusion limitations in heterogeneous catalysis in the slurry phase under any set of reaction conditions (temperature, pressure, concentration, etc.), a doubling of the amount of catalyst should lead to a doubling of the amount of product obtained. If that is not the case, then something is preventing A and B from reacting to give C with the same efficiency as was the case at a lower catalyst loading. Diffusion to and from the active sites is this "something". We are not setting out in detail what that might be, as the answer will be very system-dependent and specific to any particular catalyst. It is easy to establish whether or not a system is operating in a diffusion-limited regime by varying the loading of catalyst (Figure 3): twice the amount of catalyst inside the reactor should lead to twice the observed rate of reaction and, in the current context, twice the AQY. The point where that curve starts to level off indicates the catalyst reactor loading below which information about the inherent catalytic activity of the system can be obtained. When going beyond that reactor loading, the turnover rate, say, per gram of catalyst, is underreported, whereas in some reactor configurations (e.g. mirrored surfaces) the apparent quantum yield (as defined in Figure 2) might be overstated. Herein lies the core issue: when measurements are taken at sufficiently different points along this curve, the resultant numbers are inherently different for the same catalyst.

Clearly, when moving to systems that are not slurries but catalysts coated onto plates, these considerations cannot be translated without some additional measures. In the case of a catalyst powder that has been immobilized on a plate, that powder can be first measured as a slurry and then its performance compared in the new reactor configuration, to

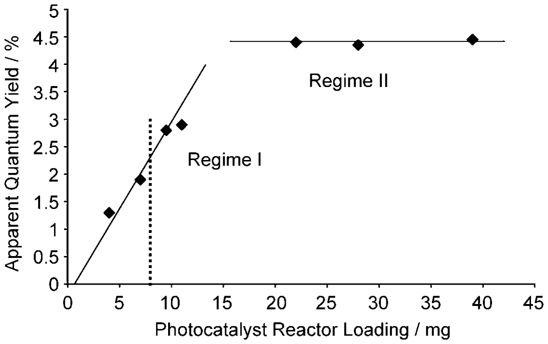


Figure 3. A typical example of baseline behavior from our laboratories, showing the apparent quantum yield of the long-established silica-supported platinized CdS photocatalyst (10 wt% CdS on SiO_2, 2 wt% Pt, relative to CdS in 50 mL aqueous 0.35 M Na_2SO_3 and 0.24 M Na_2S) as a function of the photocatalyst reactor loading, employing irradiation filtered with a 395 nm cutoff filter. As expected from classical catalysis, two regimes are clearly discernible, with the first one representing the non-diffusion-limited case. The dotted line indicates catalyst reactor loadings at which it is safe to assume linearity for this particular system, as it falls in the middle of regime I, thus reducing distortion arising from measurement error for very low levels of conversion, while still avoiding the problems associated with regime II.

see how much of the inherent activity has been lost owing to the reactor design. In cases where the catalyst is assembled onto a plate by, for example, chemical vapor deposition (CVD), it is still possible to report apparent quantum yield as defined above as well as to give a turnover rate, although now the surface area of the reactor plate might be a more useful denominator than the surface area of the catalyst.

Conclusions

We hope that the views expressed above will stimulate discussion in the research community and help to arrive at an accepted, standardized approach to photocatalyst testing and comparable reporting.

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