Turnover Number in Photoinduced Molecular Catalysis of Hydrogen Evolution: a Benchmarking for Catalysts?

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CONCEPT

Turnover Number in Photoinduced Molecular Catalysis of Hydrogen Evolution: a Benchmarking for Catalysts?

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Abstract: Development of devices for production of H_2 using light and a sustainable source of electrons may require the design of molecular systems combining a molecular catalyst and a photosensitizer. Evaluation of the efficiency of hydrogen production is commonly performed in homogeneous solution with a sacrificial electron donor and the report of the maximal turnover number *vs* catalyst ($TON_{cat}^{\lim}$). This figure of merit is strongly dependent on deactivation pathways and does not by itself provide a benchmarking for catalysts. In particular, when the photosensitizer degradation is the primary source of limitation, a kinetic model, rationalizing literature data, shows that a decrease of the catalyst concentration leads to an increase of $TON_{cat}^{\lim}$. It indicates that exceptionally high $TON_{cat}^{\lim}$ obtained at very low catalyst concentration shall not be considered as an indication of an exceptional catalytic system. We advocate for a systematic kinetic analysis in order to get a quantitative measure of the competitive pathways leading to $TON_{cat}^{\lim}$ values and to provide keys for performance improvement.

Introduction

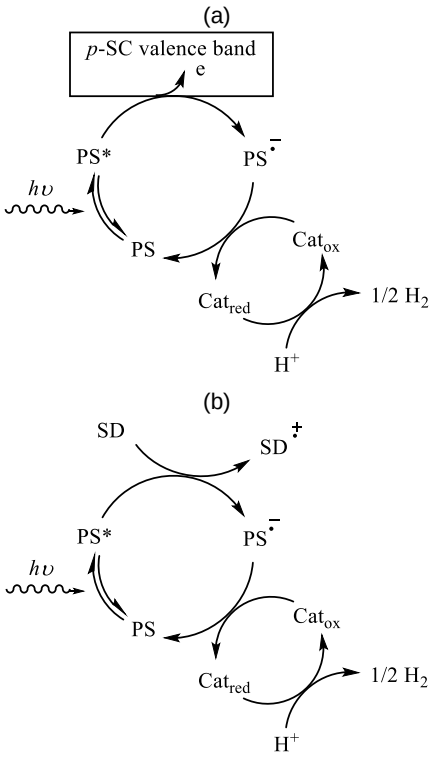
Contemporary energy issues call for the development of devices for production of hydrogen using renewable sources of energy.[1] A first step in that direction may consist in the development of molecular catalysts (Cat_{ox}) that, once reduced, can efficiently convert a source of protons into H_2.[2] The generation of the reduced form of the catalyst (Cat_{red}) can be performed *via* a photoinduced electron transfer resulting from a two steps process starting with light absorption by a photosensitizer (PS) whose excited state is quenched by a sacrificial electron donor (SD). In a device, both the photosensitizer and the catalyst could be tethered to an electrode surface being a p-type semiconductor able to transfer an electron from its valence band to the excited state of the photosensitizer (Scheme 1a). A primarily task, before even considering a device, consists in the evaluation of the performance of the photocatalytic system in homogeneous conditions using as a source of electron a homogeneous sacrificial electron donor according to the principle shown in Scheme 1b.

Homogeneous catalysis for photo-induced water reduction into H_2 under visible light dates back to the 70's.[3] Since then, many combinations of photosensitizers, catalysts and sacrificial donors have been reported, although most of the studies are conducted in organic and mixed organic-aqueous solvents because of the low stability/solubility of catalysts in pure aqueous solutions.[2a, g]

Cyrille Costentin received his undergraduate education at Ecole Normale Supérieure Paris-Saclay and pursued his graduate studies at the University Paris Diderot where he received his Ph.D. in 2000 under the guidance of Prof. J-M. Savéant. After a postdoctoral fellowship at the University of Rochester, he joined the faculty at the University of Paris Diderot as Associate Professor in 2001. He was promoted Professor in 2007. He is an expert in molecular electrochemistry and was a Visiting Scholar at Harvard University (2016-19) working with Prof. D. G. Nocera. In 2019 he joined the Département de Chimie Moléculaire at the Université Grenoble-Alpes.

Marie-Noëlle Collomb is a CNRS Research Director at the Department of Molecular Chemistry at the University of Grenoble Alpes (UGA). After completing her PhD in chemistry in 1993 at UGA under the supervision of Dr A. Deronzier, and postdoctoral fellowship with Pr. M. Fontecave, she joined CNRS in 1994 and was appointed Research Director in 2007. In 1998-99, she was a CNRS research associate in the groups of Pr. R. H. Crabtree and G. W. Brudvig at Yale University. Her current research focuses on artificial photosynthesis, with photo- and electrochemical activation of small molecules with molecular and inorganic catalysts.

Jérôme Fortage obtained his PhD in 2006, under the supervision of Dr. Fabrice Odobel at the University of Nantes. He then completed two post-doctoral fellowships in molecular photochemistry at the University of Newcastle (2007) in the group of Pr. Andrew Benniston and Pr. Anthony Harriman, and at the University Paris Descartes (2008-2010) under the supervision of Dr. Philippe Lainé and Dr. Valérie Marvaud. In October 2010, he was appointed as a CNRS researcher at the Department of Molecular Chemistry of University Grenoble Alpes. He is currently working on the development of molecular or hybrid systems for the electro/photo-catalytic activation of small molecules.



Scheme 1. Principle of photoinduced molecular catalysis for hydrogen production with a semiconductor electrode as electron source (a) and with a homogeneous sacrificial electron donor (b) Cat = catalyst, PS = photosensitizer, SD = sacrificial electron donor.

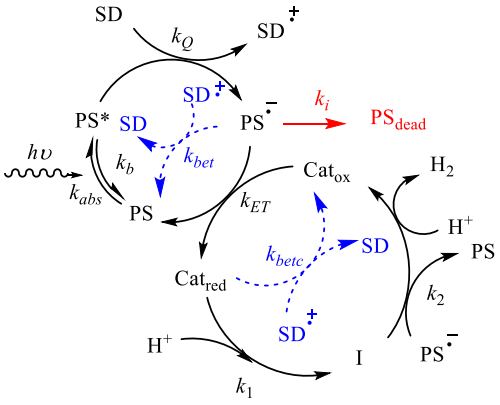
Along with the quantum yield for H_2 production, two figures of merits are usually used to report photocatalytic performances: the maximal turnover number $TON_{cat}^{\lim}$ defined as the maximal number of moles of hydrogen produced divided by the number of moles of catalyst (maximal means that it corresponds to the situation where catalysis stops; the reaction being run long enough for production of H_2 to cease) and the initial turnover frequency $TOF_{cat,0}$ defined as the initial rate of hydrogen production divided by the number of moles of catalyst. $TOF_{cat,0}$ is sensitive to the ability of the photosensitizer to absorb light and to the light source power; therefore, it is obviously neither an intrinsic characteristic of the catalyst alone nor of the photosensitizer/catalyst couple. Alternatively, $TON_{cat}^{\lim}$ is often viewed as a benchmarking value for catalysts and considered as the performance metric to be optimized. However, a survey of data available in the literature indicates that in many cases $TON_{cat}^{\lim}$ increases as the concentration of the catalyst is decreased at a given concentration of photosensitizer and excess of sacrificial donor.[2h, i, 4] In that regard, it is striking to note that, in the related field of photocatalysis reduction of CO_2, high $TON_{cat}^{\lim}$ have been reported based on the use of low concentration of catalysts leading to the claim of exceptional catalytic performances.[5] Three comments can thus be made: first, $TON_{cat}^{\lim}$ may depend on the concentrations of the component of the system (catalyst, photosensitizer,…) and therefore it is not an intrinsic figure of merit of the system; second, because it is a measure when catalysis has stopped whereas both reactants, the source of proton and the sacrificial electron donor, are still in large amount, $TON_{cat}^{\lim}$ is related to degradation processes of either the catalyst or the photosensitizer; third, performing photocatalytic experiments at a very low concentration of catalyst can lead to exceptionally high $TON_{cat}^{\lim}$ but, still, very low amount of H_2 is produced, maybe reaching detection limit, making possibility doubtful the exact nature of the catalyst or the exact origin of H_2 evolution. The same is true for CO_2 reduction as recently pointed out.[6] Indeed, at low catalyst concentration, typically one micromolar or below, coupled with a high PS concentration (several hundred micromolar), H_2 generated by the PS alone in the presence of SD could represent a significative part of the total H_2 production, without the assistance of the catalyst.[4g, i, 7] This is especially true for the least efficient catalysts. Therefore, we advocate that $TON_{cat}^{\lim}$ cannot be used as a benchmark of catalysts and that a systematic kinetic analysis should be performed to characterize the performance of a photocatalytic system. In the following we will thus first review a simple kinetic model relating $TON_{cat}^{\lim}$ to intrinsic parameters of the photocatalytic system. We will then review literature data of photoinduced molecular catalysis of hydrogen evolution and show that this simple kinetic model is indeed useful to rationalize these literature data with a particular emphasis on the evolution of $TON_{cat}^{\lim}$ as the concentration of the catalyst is changed.

Kinetic model

We recently proposed a simple kinetic model for the photoinduced electron transfer catalysis of redox reactions.[8] The basic principles are similar to the general scheme given in scheme 1b but additional steps are considered: back electron transfers from the oxidized sacrificial donor ($SD^{\bullet+}$) to the reduced photosensitizer ($PS^{\bullet-}$) or from the reduced catalyst (Cat_{red}), decomposition of the hydrogen evolution into two steps *via* an intermediate (I, presumably the hydride form of the catalyst) and degradation processes of either the catalyst or the photosensitizer. Considering only degradation of the photosensitizer as a limitation process of the photocatalysis, the kinetic scheme is shown in Scheme 2, in which all useful rate constants are defined. Note that an ECEC type mechanism is considered (i.e. the intermediate I is easier to reduce than Cat_{ox}) because such a mechanism is commonly accepted for HER cobalt catalysts.[2d] If the sacrificial donor is in large excess, as it is usually the case in practice, and assuming steady-state approximation for reaction intermediates, then the expression of $TON_{cat}^{\lim}$ is:[8]

$$TON_{cat}^{\lim} = \frac{k_{cat}}{2k_{betc}\left[\mathrm{Cat_{ox}}\right]_0}\left(-1+\sqrt{1+4\frac{k_{betc}\left[\mathrm{Cat_{ox}}\right]_0}{k_{cat}}\frac{k_{ET}\left[\mathrm{PS}\right]_0}{k_i}}\right) \qquad (1)$$

where $[Cat_{ox}]_0$ and $[PS]_0$ are the initial concentration of the catalyst and the photosensitizer respectively. k_{cat} is the pseudo first-order rate constant for catalysis corresponding to k_1 times the concentration of the actual proton donor.



Scheme 2. Homogeneous photoinduced catalysis of hydrogen evolution via reductive quenching.

Equation (1) clearly indicates that TON_{cat}^{lim} is not an intrinsic parameter characterizing the photocatalytic system because it depends on both the catalyst and the photosensitizer concentrations. In most practical cases, equation (1) can be further simplified because the degradation of the photosensitizer, although being the cause of the system efficiency limitation, is slow enough so that $4\frac{k_{betc}[Cat_{ox}]_0}{k_{cat}}\frac{k_{ET}[PS]_0}{k_i} >> 1$ and therefore:

$$TON_{cat}^{lim} \approx \sqrt{\frac{k_{cat}}{k_{betc}[Cat_{ox}]_0}\frac{k_{ET}[PS]_0}{k_i}} \quad (2)$$

This simplified expression shows that there are two bottlenecks in reaching high TON_{cat}^{lim}. One is the fate of the reduced photosensitizer ($PS^{\bullet-}$) *via* the ratio $\frac{k_{ET}[PS]_0}{k_i}$, the faster the electron transfer to the catalyst *vs.* degradation of $PS^{\bullet-}$, the larger TON_{cat}^{lim}, noting that back electron transfer from $PS^{\bullet-}$ has no effect because it just makes a non-productive loop. The other one is the fate of the reduced catalyst (Cat_{red}) *via* the ratio $\frac{k_{cat}}{k_{betc}[Cat_{ox}]_0}$, the faster the reaction with the substrate (the proton source) *vs.* back electron transfer, the larger TON_{cat}^{lim}. One could have thought that, as above, the back electron transfer from Cat_{red} (betc) would had no impact because it is just a non-productive pathway. It is not the case because it occurs after the first bottleneck where degradation can statistically occur.

Finally, the simplified expression of TON_{cat}^{lim} provides a guide to rationalize its variation with the concentration of the catalyst. It is indeed predicted that TON_{cat}^{lim} is proportional to $[Cat_{ox}]_0^{-1/2}$ in line with the qualitative observation that high TON_{cat}^{lim} are usually obtained at low catalyst loading.

Literature data analysis

Several homogeneous molecular systems for photoinduced catalytic hydrogen production working efficiently in pure aqueous solution have been reported in the last past 15 years.[2a, c, g] The purpose of the present review is not to provide a thorough description of the literature but to show that available data support that TON_{cat}^{lim} is not an intrinsic parameter of a photocatalytic system and cannot be directly used as a benchmarking value for catalysts. However, the above recalled simple kinetic model can be used toward benchmarking and rationalization of the data for future improvements of photocatalytic systems. In pure aqueous solution, studied systems typically involve the popular $[Ru(bpy)_3]^{2+}$ as photosensitizer (denoted **Rubpy**),[9] ascorbic acid as a sacrificial donor, in a pH 4 or 4.5 solution, often buffered with acetate, as proton source and a molecular catalyst. Among the non-precious metal complexes, water soluble cobalt catalysts have been the most studied.[2d, f, h, i] We have thus selected few systems for which TON_{cat}^{lim} values have been reported at various concentrations of the catalyst. The molecular structures of the selected catalysts together with the photosensitizers and the sacrificial donor are shown in Figure 1 and photocatalytic conditions gathered in Table 1. In all cases, the excess of sacrificial donor HA^- over the catalyst and adequate standard potentials makes the reductive quenching pathway (Scheme 2) dominant.

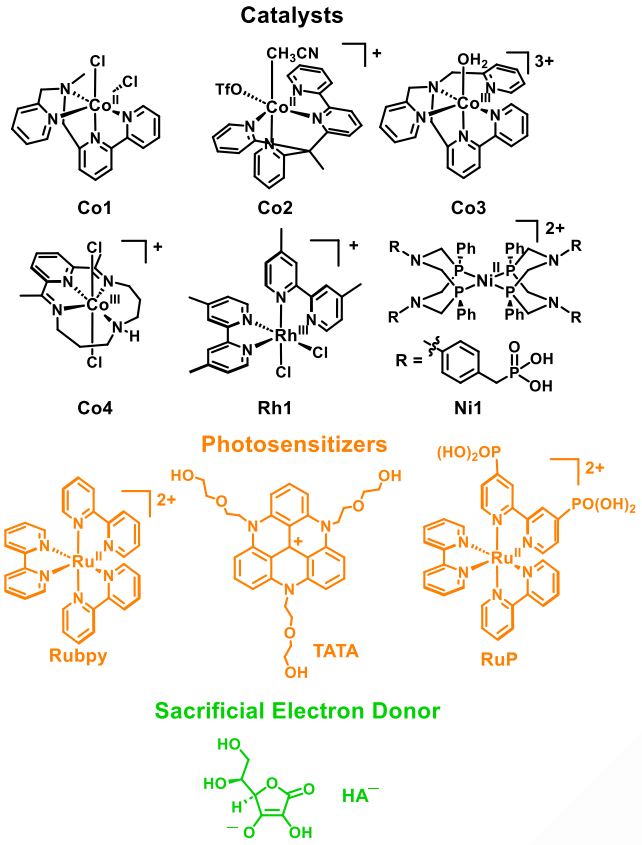


Figure 1. Molecular catalysts, photosensitizers and sacrificial electron donor for photoinduced molecular catalysis of hydrogen production in water.

For **Co1**,[4d] **Co2**,[4e] **Co3**,[4f] **Co4**[4g] and **Rh1**,[4i] with **Rubpy** as photosensitizer, experimental data show that $\log TON_{cat}^{\lim}$ decreases linearly with $\log[\mathrm{Cat_{ox}}]$ (Figure 2) with slopes around -0.5 (slopes: **Co1**: -0.5; **Co2**: -0.4; **Co3**: -0.7; **Co4**: -0.3; **Rh1**: -0.4). All trends are in line with the kinetic model based on the assumption that limitation of the photocatalysis is due to degradation of the photosensitizer **Rubpy**.[4e, f, h, 9-10] **Rubpy** is indeed known for its instability in its reduced form that can easily undergo a ligand substitution.[4g, i] In some cases,[4e, i] regeneration of photocatalytic hydrogen production was obtained from addition of fresh aliquot of **Rubpy** confirming limitation of photocatalysis by degradation of the photosensitizer.

Table 1. Photocatalytic system from hydrogen evolution in water.[a]

Medium	Catalyst (Conc./µM)	Photosensitizer (Conc./µM)	Sacrificial donor	Ref.
pH 4	**Co1** (0.5-50)	**Rubpy** (500)	HA^- 0.1 M acetate buffer 1 M	[4d]
pH 4	**Co2** (0.31-20)	**Rubpy** (330)	HA^- 0.3 M	[4e]
pH 4	**Co3** (0.5-50)	**Rubpy** (500)	HA^- 0.1 M acetate buffer 1 M	[4f]
pH 4.5	**Co4** (1-100)	**Rubpy** (500)	HA^- 1.1 M	[4g]
pH 4.5	**Co4** (5-50)	**TATA** (500)	HA^- 0.1 M acetate buffer 1 M	[4h]
pH 4	**Rh1** (1-100)	**Rubpy** (500)	HA^- 1.1 M	[4i]
pH 4.5	**Ni1** (9-45)	**RuP** (22)	HA^- 0.1 M	[4j]

[a] Irradiation conditions can be found in the corresponding references.

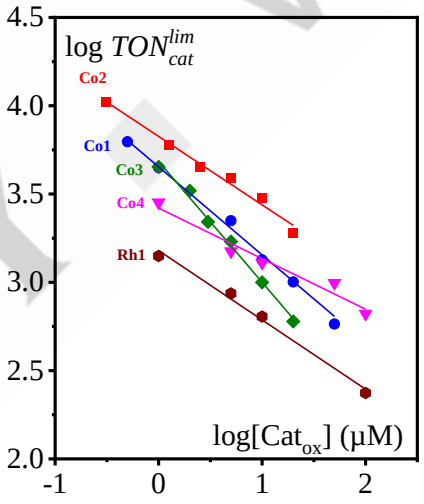


Figure 2. $TON_{cat}^{\lim}$ as function of the catalyst concentration for **Co1** (red), **Co2** (blue), **Co3** (green), **Co4** (magenta) and **Rh1** (wine) with **Rubpy** as photosensitizer. Lines: linear fitting. Experimental conditions are given in Table 1. Note that for **Co4** and **Rh1**, $TON_{cat}^{\lim}$ values are corrected from background hydrogen production.

The adherence with the kinetic model is not perfect and may be due to uncertainties in the estimation of $TON_{cat}^{\lim}$, in particular at low catalyst concentrations due to background hydrogen production, stemming from proton reduction to H_2 from $PS^{\bullet-}$, as well as to additional phenomena such as partial degradation of the catalyst. Nonetheless, for **Co4**, a thorough kinetic analysis can been performed thanks to the experimental evaluation of the relevant rate constants ($k_{cat} \approx 7100\ s^{-1}$, $k_{ET} \approx 1.4\ 10^9\ M^{-1}\ s^{-1}$ and $k_{betc} \approx 2.6\ 10^7\ M^{-1}\ s^{-1}$)[8] leading to an estimation of $k_i \approx 15\ s^{-1}$ in agreement with a similar kinetic analysis performed on data gathered at a lower concentration (0.1 M) of the sacrificial donor.[8] Taking this value of k_i, k_{ET} and k_{betc} either determined in the

literature or evaluated as similar as for **Co1**, the pseudo first-order catalytic rate constant k_{cat} can be evaluated from the data shown in Figure 2 and reported in Table 2 (see Supporting Information for details). Interestingly, although not being intrinsically the "best" catalyst ("best" being defined as the one with the largest catalytic rate constant), **Co4** has been shown to allow reaching TON_{cat} larger than **Co1**, **Co2** or **Co3** at similar concentration provided a more stable photosensitizer, such as **TATA** (Figure 1), is used instead of **Rubpy**.[4h]

Using equation (1), one can predict that, at very low concentration of catalyst, a maximal value of $TON_{cat}^{\lim}$ can eventually be reached corresponding to $TON_{cat}^{\lim} = \frac{k_{ET}[\mathrm{PS}]_0}{k_i}$ (Figure S1). These estimated values are gathered in Table 2 and correspond to very high $TON_{cat}^{\lim}$. However, we stress that such high values are not meaningful because (i) they are not characteristic of the catalytic ability of the catalysts, (ii) very low concentration of catalysts would be needed to get these values (typically nanomolar) and the amount of H_2 produced would be so small that it would be barely distinguishable from background H_2 production, that could be due to proton reduction from $PS^{\bullet-}$.

Table 2. Catalytic rate constant k_{cat} and maximal $TON_{cat}^{\lim}$ from hydrogen evolution catalysts in water

Catalyst	k_{cat} (s^{-1})	Maximal $TON_{cat}^{\lim}$	Ref.
Co1	1.1 10^4	46700	[4d]
Co2	2.5 10^4	63800	[4e]
Co3	8 10^3	50000	[4f]
Co4	7.1 10^3	46700	[4g]
Rh1	1.5 10^3	56700	[4j]

Finally, the nickel catalyst, **Ni1**, studied at pH 4.5 with 0.1 HA and 22 µM **RuP** as photocatalyst exhibits $TON_{cat}^{\lim}$ of the order of 700 at various concentrations **Ni1** (8.9 and 45 µM) with no reactivation after addition of either **RuP** or sacrificial donor.[4j] In such a case, degradation of the catalyst is the major limitation of $TON_{cat}^{\lim}$. It is in agreement with a kinetic model based on a reaction process akin to Scheme 2 but where the degradation of the reduced catalyst $PS^{\bullet-}$ is been replaced by the degradation of the reduced form of the catalyst Cat_{red}. In such case, it has been shown that $TON_{cat}^{\lim}$ is indeed independent on the catalyst concentration.[8]

Summary and Outlook

Photoinduced molecular catalysis for hydrogen production is an attractive process for conversion and storage of solar energy. Evaluation of the performance of homogeneous photocatalytic system for hydrogen production in water is thus often viewed as a step toward further improvements and development of new molecular catalysts. However, we have shown here that the commonly used metric, the maximal turnover number $TON_{cat}^{\lim}$, cannot be simply considered for a benchmarking for catalysts. Here we advocate for the development of a systematic kinetic analysis of experimental data. We show that using a simple kinetic model, the variation of $TON_{cat}^{\lim}$ the concentration of the catalyst can be rationalized and intrinsic catalytic properties of the catalyst can be extracted, hence providing a benchmark of the catalysts. The kinetic model also predicts that, at very low catalyst concentration, exceptionally high $TON_{cat}^{\lim}$ can be reached provided the reduced form of the photosensitizer transfers efficiently electrons to the catalyst, *i.e.*, faster than its degradation rate. However, we emphasize that low catalyst concentrations (below 5 micromolar) should be avoided because it would lead to $TON_{cat}^{\lim}$ not characteristic of the catalytic ability of the catalysts and the amount of H_2 produced would be so small that it would be barely distinguishable from background H_2 production.

The present analysis shows that efforts should be done to gather kinetic data for a better understanding of the processes controlling the photocatalytic responses. This can be achieved *via* the combination of long-term irradiation, transient absorption spectroscopy, fluorescence quenching experiments and electrochemical measurements. It is exemplified here on the photoinduced molecular catalysis of hydrogen production but it should be extended to the more challenging photocatalytic reduction of CO_2 reduction.

Supporting Information

Details on kinetic data and evaluation of rate constants.

Acknowledgements

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Keywords: Hydrogen Evolution • Photocatalysis • Turnover Number • Photosensitizer • Catalysis

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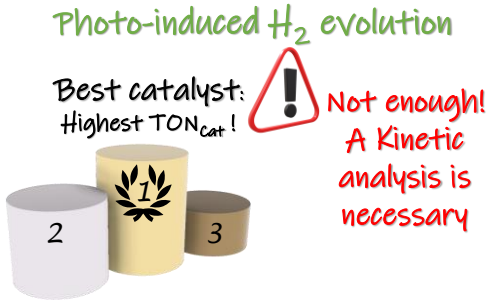

Turnover numbers cannot be directly used as a benchmarking figure of merit for homogeneous molecular catalysts in photoinduced hydrogen production. However, kinetic analysis allows rationalization of the increase of turnover numbers as the concentration of catalyst is decreased in the context of limitation of the process by degradation of the photosensitizer. This provides a way for photocatalytic systems benchmarking.

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