Turnovers and photocatalysis
A mathematical description

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Abstract

In previous articles we dwelled on the usage of relative photonic efficiencies [N. Serpone, G. Suave, R. Koch, H. Tahiri, P. Pichat, P. Piccinini, E. Pelizzetti, H. Hidaka, J. Photochem. Photobiol. A: Chem. 94 (1996) 191; N. Serpone, J. Photochem. Photobiol. A: Chem. 104 (1997) 1] and quantum yields Φ [N. Serpone, R. Terziaw, D. Lawless, P. Kennepohl, G. Suave, J. Photochem. Photobiol. A: Chem. 73 (1993) 11]. Recently, we also provided an experimental protocol to measure Φ in heterogeneous media [N. Serpone, A. Salinaro, Pure Appl. Chem. 71 (1999) 303] to infer which of several photocatalyzed processes might be the more significant and efficient process. In this article we revisit photocatalysis and discuss how to describe mathematically (photo)catalytic activity and how to compare (photo)catalytic activities of various materials. Specifically, we address the usage and provide a kinetic description of the three turnover quantities: turnover number (TON), turnover rate (TOR) and turnover frequency (TOF) as they bear on the (photo)catalytic activity of a given material in heterogeneous solid/liquid or solid/gas (photo)catalysis. We argue that these turnover quantities are conceptually distinct. TON and TOR require knowledge of the number of active sites on the (photo)catalyst's surface, contrary to the requirement to determine TOF. Most significant, these turnovers also depend on the nature of the active state of the catalyst, and hence on how the active centers are described. This goes back to the differences in the nature of photocatalysis and photoinduced catalysis. ©2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Heterogeneous photocatalysis has come to describe the field of study and the technology in which irradiated semiconductor particles generate charge carriers (e^- and h^+) that are ultimately poised at the particle surface. These carriers undergo various processes, the most important of which are photoreductions (e.g. metal ions of Au, Pt, Ag, Rh, Hg, Pb, and others) and photooxidations of a large variety of organic substances (e.g. surfactants, pesticides, herbicides and others) to their complete mineralization. Our recent research efforts in this area have focussed on assessing the factors that underlie the temporal evolution of redox reactions taking place predominantly on metal oxide materials [1–5].

Understanding heterogeneous photocatalysis necessitates a suitable description of (i) what (photo)catalysis is, (ii) what turnover quantities are (numbers, TON; rates, TOR; frequencies, TOF) and (iii) how quantum yields Φ can be established. For the latter, a protocol for determining Φ in heterogeneous photocatalysis has been proposed [6] and experimental details given [7]. Relative photonic efficiencies, ξ_r, provide a method by which the work from many laboratories in environmental photochemistry can be calibrated when the more auspicious parameter Φ cannot be assessed because of certain experimental limitations [7]. The terminology 'photocatalysis' has been characterized by the continued use of labels to describe a variety of mechanistic possibilities for a given process. The turnover quantities, while being relatively understood in homogeneous (photo)catalysis, require further reflection in heterogeneous (photo)catalysis as they require knowledge of the number of (photo)catalytically active sites for TON and TOR. These turnovers depend on how the (photo)catalytic process is viewed. It is relevant therefore to revisit the description of photocatalysis briefly as it impacts on the major focus of this article.

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Table 1
Salomon's classification of photocatalysis and summary of various mechanism-specific labels [13]

Catalytic in photons	Non-catalytic in photons
Photogenerated catalysis [13]	Catalyzed photolysis [13]
Photoinduced catalytic reactions [15]	Catalyzed photochemistry [14]
(Stoichiometric photogenerated catalysis [13])	Catalyzed photoreactions [14,17]
	Sensitized photoreactions [14,15]
	Photosensitized reactions [18]
	Photo-assisted catalysis [15,19]
	(Stoichiometric photogenerated catalysis [13])
	Substance-assisted photoreactions [20]
	Substance-catalyzed photoreactions [20]

1.1. Photocatalysis

We should first recall that catalysis refers to a process in which a substance (the catalyst, Cat) accelerates an otherwise thermodynamically favored but kinetically slow reaction, with the catalyst fully regenerated at the conclusion of the catalytic cycle. When photons are also involved, the expression photocatalysis is used to describe, without the implication of any specific mechanism, the acceleration of a photoreaction by the presence of a catalyst; the catalyst may accelerate the photoreaction by interacting with the substrate either in its ground state or in its excited state and/or with the primary product, depending on the mechanism of the photoreaction [8]. Note that the latter makes no mention of whether photons also interact with the catalyst. Such a description also embraces photosensitization [9] and yet such a process, defined officially [10] as a process whereby a photochemical change occurs in one molecular entity as a result of initial photon absorption by another molecular species known as the photosensitizer, is not necessarily catalytic without assessing a turnover quantity and/or the quantum yield. The issue rests entirely on the role of the photons. Chanon and Chanon [11] suggested that the non-descriptive term photocatalysis be taken simply as a general label to indicate that light and a substance (the catalyst or initiator) are necessary entities to influence a reaction. [1] Such a broad description indicates the required reagents without undue

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[1] This cannot be a complete description of photocatalysis. An example of a photocatalytic process of a different type is the photoexcitation of surface metal-oxo complexes on some inert support, e.g. M^{2+}–O^{2-}. For example,

$$M^{2+} — O^{2-} + h\nu \rightarrow M^+ — O^-$$

$$M^+ — O + (A)(D) \rightarrow M^+(A) — O^-(D)$$
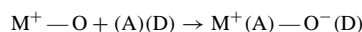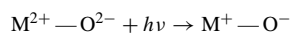
where photoexcitation of the surface metal-oxo complex leads to photoinduced electron transfer from the oxide to the metal to form the reactive state M^+–O^-. This reacts with (acceptor)(donor) molecules (A)(D) with the electron localized on the metal cation or on the hole-like state O^-. Note that there is no generation of free electrons and holes. This is local excitation. A similar process is described by mechanism I, which is also an example of local photoexcitation without photogeneration of free electrons and holes.

constraints as to the (often unknown) mechanistic details of the chemical process (Eq. (1)).

$$substrate + light + Cat \rightarrow products + Cat \qquad (1)$$

Teichner and Formenti [12] described heterogeneous photocatalysis as an increase in the rate of a thermodynamically allowed ($\Delta G < 0$) reaction in the presence of an irradiated solid with the increase originating from the creation of some new reaction pathways involving photocreated species and a decrease of the activation energy. In this sense, one might argue that many of the reactions involving irradiated semiconductors belong to the class of photogenerated catalysis (see below). Yet reaction (2) was labeled [12] a photocatalytic oxidation.

$$CH_3CHOHCH_3 + \tfrac{1}{2}O_2 \xrightarrow[\text{TiO}_2]{h\nu} CH_3COCH_3 + H_2O \qquad (2)$$
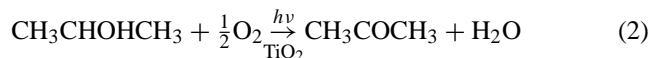
It was also suggested that if $\Phi > 1$ (as in reactions involving radical species) the process is catalytic in photons, but if $\Phi \leq 1$ then the process is non-catalytic in photons. The latter suggestion is somewhat artificial to the extent that if $\Phi > 1$ then either the process is a photoinduced catalysis (see below) or the process is a photoinitiated chain reaction which is not necessarily catalytic. Typically, the quantum yield of a primary reaction step is less than 1.

Salomon [13] proposed that the broad description of photocatalysis can be subdivided into two main classes: (i) photogenerated catalysis which is catalytic in photons, and (ii) catalyzed photolysis which is non-catalytic in photons (Table 1). In the former, ground states of the catalyst and the substrate are involved in the thermodynamically spontaneous (exoergic) catalytic step, whereas in the latter either the nominal catalyst T (Fig. 1) or the substrate, or both, are in an excited state during the catalytic step (note: C is the catalytic entity). Kutal [8,14] clarified Salomon's formal schemes and Hennig et al. [15] proposed consistent labels that applied to experimental observations. A quagmire of mechanism-specific labels appeared (see Chanon and Chanon [11] for an elaborate account of this topic). This calls attention to usage of the more broad description of photocatalysis suggested by Chanon and Chanon [11] and later emphasized by Serpone and coworkers [6,7,16] (see
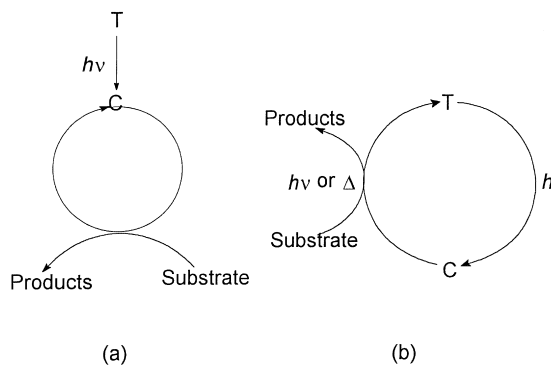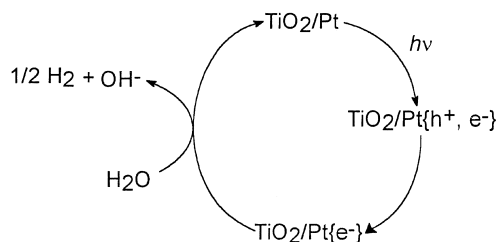
Fig. 1. Proposed scheme of an example of photogenerated catalysis (a) which is catalytic in photons, and of catalyzed photolysis (b) which is non-catalytic in photons. Note that T refers to a nominal catalyst and C denotes the catalytic entity. (Adapted after [8,11]).

Scheme 1.

above). Fig. 1a illustrates a simple scheme of photogenerated catalysis, whereas Fig. 1b depicts an example of catalyzed photolysis.

The distinction between an assisted photoreaction (TON < 1) and a catalyzed photoreaction (TON ≫ 1) generally poses no difficulty in homogeneous (photo)catalysis since TONs can be described. This is not the case in heterogeneous (photo)catalysis where a solid catalyst semiconductor, for example TiO_2, fulfills the dual role of light harvester and catalytic entity. An example is provided of the photocatalyzed reduction of water by the bifunctional catalyst TiO_2/Pt in the presence of some electron donor D (Scheme 1). Several photoreactions that take place in the presence of semiconductor particles and that have been claimed to be photocatalytic may be described more appropriately as semiconductor-assisted photoreactions [20].

1.2. Turnover quantities

The quantitative measure of (photo)catalytic activity of a solid (photo)catalyst is an essential quantity in heterogeneous (photo)catalytic gas/solid or solution/solid chemistry, particularly in industrial processes where catalytic activities bear on process economics and thus on acceptance of a given process. Such measures are characteristically derived from process kinetics to express a rate referenced to the number of (photo)catalytic sites to infer how many times a catalytic cycle turnsover. Traditionally, this parameter is the TON. Two other related parameters are sometimes used and

described [21–23]: (a) TOR which designates the number of reagent molecules consumed or product molecules formed per surface active site per unit time, and (b) TOF which denotes the number of reactant molecules consumed, or product molecules formed, per active site per unit time (note the similarity with TOR). Laidler [21] noted that because TONs (and by extension, TORs and turnover frequencies) vary with temperature, concentration and other experimental conditions, they are not a useful quantity in kinetic work.

The expression sought to signify activity should serve two basic functions: (i) establish whether a given process is *catalytic* or *stoichiometric*, and (ii) provide a quantity to compare activities (unrelated to photons) of various catalysts for a given process under a set of conditions. An IUPAC article [24] pointed out that:

"...the *turnover frequency*, N, (commonly called the *turnover number*) *defined*, as in enzyme catalysis, *as molecules reacting per active site in unit time* can be a useful concept if employed with care. In view of the problems in measuring the number of active sites discussed in..., it is important to specify exactly the means to express... in terms of active sites. A realistic measure of such sites may be the number of surface metal atoms on a supported catalyst but in other cases estimation on the basis of a BET surface area may be the only readily available method. Of course, *turnover numbers* (like rates) must be reported at specified conditions of temperature, initial concentration (or initial pressure) and extent of reaction..."

It is not surprising then that some workers (see e.g. [21–24,26]) have taken TON, TOR and TOF to refer to a singular description, viz., that they describe the number of molecules reacted (or produced) per active site per unit time. Boudart [25,26] makes no distinction between TOR and TOF.

Conceptually, we view the three quantities: (1) TON, (2) TOR and (3) TOF as being distinct from one another. The problem originates from common usage in which TOR and TOF are often used interchangeably by catalycists just as photochemists often make no distinction between quantum yield and quantum efficiency and chemical kineticists often use the rate constant to mean the rate of a reaction.

Recently, Boudart [26] deplored usage of the quantity TON because it has become to be not a dimensionless number but a number expressed in per unit time, i.e. a number which expresses a frequency. Thus, the equivalence often made by many workers between TON and TOF. For some (see e.g. [27]), TON is understood to be a quantity that does not involve the element of time (see below).

Only in a very specific case will the TOR and the TON be identical. Just as a unique quantum yield is described for a zero-order process, equivalence of TOR and TON may occur solely for zero-order processes and for small conversion of reactants (initial rates).

For a semiconductor-based heterogeneous photocatalytic process, a description of the number of photocatalytic active

sites and thus of the measure of activity of a photocatalyst is rendered difficult as photons can easily generate new active sites on the semiconductor particle, not to mention the possible changes in the surface adsorption/desorption characteristics. Added to this, there is a likely possibility that active and inactive sites switch identities during a photocatalytic sequence and that activity during a photocatalytic process may then have a different meaning for different steps of the process [28]. For example, in a photocatalyzed oxidation of an organic substrate involving TiO_2 nanoparticles, oxidation may be mediated by an $\bullet OH$ radical at some surface site on the particle. Once oxidation has occurred, this particular surface site becomes extinct and is no longer active until such time as the site has been reconstructed and another $\bullet OH$ radical formed on that very same site.

Despite the above issues, it will nonetheless be useful to report a turnover quantity (to paraphrase from Boudart [26]) in heterogeneous solid/liquid or solid/gas (photo)catalysis (a) that can be reproduced in various laboratories, (b) that can disclose whether a given process is truly (photo)catalytic, (c) that can ascertain the absence of artifacts in rate measurements, (d) that can indicate the importance or the irrelevance of anisotropy in crystalline (photo)catalysts, and (e) that can prove useful in assessing new materials as (photo)catalysts.

Although much has been written on catalysis (see in [26]), it is worthwhile to briefly revisit some of the major steps of the photocatalytic process in a heterogeneous phase.

Where the (photo)catalyst is a solid material, the following events typically take place [29]: (i) the molecule is adsorbed on the particle surface; (ii) the molecule undergoes chemical transformation while visiting several reaction surface sites by surface diffusion; and (iii) the intermediate or product molecule is subsequently desorbed to the gas phase or to the condensed phase.

A closer scrutiny of the adsorption step reveals that if the reactant molecule or any subsequent intermediate product is strongly chemisorbed, i.e., has formed strong chemical bonds with the surface atoms at the site, no (photo)catalysis will be possible. The process is stoichiometric because one molecule of product has formed per surface active site (TON =1), signifying that the reaction has turned only once on that site. Moreover, if during the (photo)catalytic process the reactant molecule is strongly (chemically) bonded to surface atoms, the (photo)catalytic site becomes inactive and is said to be poisoned. By contrast, if (chemical) bonding interactions are too weak, the substrate is poorly adsorbed and there will be no opportunity for chemical bond rupture, an integral part of any catalytic process [29]. Thus, interactions between the reactant molecule and the (photo)catalyst's surface site must be such that bond breaking and bond making can take place within the residence time of the intermediate(s), and that desorption/adsorption can occur.

In heterogeneous (photo)catalysis a primary difficulty with describing the TON or the TOR is how to specify the *number of surface active sites*. It has become a common practice to substitute this quantity by the total surface area (m^2) or by the specific surface area ($m^2 g^{-1}$) of the catalyst particles, as determined by physical adsorption of nitrogen or argon at low temperatures. The use of the usual 'Brunauer–Emmett–Teller (BET) surface area' in lieu of the number of active sites is tenuous, since the latter is seldom known in catalysis and much less known (if at all) in heterogeneous photocatalysis. In some cases, however, the number of active sites may be determined by kinetic measurements of gas photoadsorption (stoichiometric process) when the conditions of uniform irradiation of the catalyst surface and maximum surface coverage are satisfied; such sites may be taken to reflect the concentration of surface centers. The number of active sites is known for electron and hole centers on ZnO, TiO_2, BeO, $MgAl_2O_4$ and SiO_2/TiO_2 (and some others); they range between 10^{10} and 10^{12} centers cm^{-2} [30–32]. It must be emphasized that the BET surface areas reflect the number of adsorption sites and *not necessarily the number of catalytically active sites*. On this point, it was noted [29] that about 10% *or less* of the surface sites may be active in any given catalytic reaction/process, and that the specific TON is only a conservative estimate of the real turnover. In other cases, the surface density of OH^- groups (10^{14}–10^{15} cm^{-2} for TiO_2) has been used in lieu of the surface area to express catalytic activity [33,34]. However, this usage also does not address the real issue. The TON estimated in this manner also represents a lower limit.

Contrary to the other two turnover quantities, TOF requires no knowledge of the surface area [29], nor the number of surface photocatalytically active sites, a number impossible to assess in heterogeneous photocatalysis. TOF increases with increasing active surface area and thus may be different from one batch of a catalyst to another and between various catalysts for the same reaction/process. Note that both TOR and TOF may be less than one. When the turnover quantity depends on the surface characteristics (e.g., number of active sites) it represents only a conservative estimate. It must be emphasized that an active site (or (photo)catalyst) will have a finite lifetime for various reasons, one being inactivation through poisoning by impurities.

We now consider these turnovers on a more quantitative basis to determine the parameters or factors that may influence the assessment of these quantities and thereby the extent of (photo)catalytic activity.

2. Mathematical formulation of turnover quantities

2.1. Description of photocatalysis

For a chemical reaction described by Eq. (3) there may be a corresponding catalytic process, Eq. (4):

$$A \rightleftarrows B \tag{3}$$

$$A + Cat \rightleftarrows B + Cat \tag{4}$$

The simplest description of a catalytic process is that catalysis occurs when addition of a catalyst (Cat) changes the rate of establishing an equilibrium state in reaction (4), compared to the equilibrium state of reaction (3). After a single act of the reaction (or completion of reaction), the catalyst can be separated in the same original state as before the reaction. This description requires no prior knowledge of the mechanism of any particular catalytic process. The more complex and more precise description of catalysis says that the catalyst is intimately involved in the chemical steps (the reaction pathway in the catalytic process is different from that of reaction (3). After completion of the reaction cycle that yields products, the catalyst is regenerated into its original state. Note that there is no need to know the mechanistic details of the process except for the existence of interactions (e.g., adsorption in heterogeneous (photo)catalysis) between reagents and catalyst. This notion is valid for acid–basic catalysis, redox catalysis and biocatalysis (and other types). The reaction rate increases if the total activation energy in the catalytic process (Eq. (4)) is less than the corresponding energy in reaction (3). In thermal (catalytic) reactions, changes in the electronic configuration of the system occur following the regrouping of nuclei/fragments without transitions to electronic excited states.

As emphasized earlier a definition of photocatalysis should also be general just as in the case of catalysis, and must not depend on any particular mechanism of the process.

Transformation of chemistry to photochemistry occurs when a chemical reaction is induced by absorption of photons by some reagent A, Eq. (5):

$$A + h\nu \rightarrow B \tag{5}$$

and the corresponding photocatalytic process is:

$$A + h\nu + Cat \rightarrow B + Cat \tag{6}$$

Unlike thermal reaction (3), photoreaction (5) occurs through an excited electronic state of the reagents followed by regrouping of the various nuclei/fragments. Typically, the photochemical reaction (5) is irreversible. If light is taken as a quasi-reagent in reaction (5) (as used in kinetic mechanisms), the back reaction must follow the pathway $B \rightarrow A + h\nu$, where $h\nu$ denotes photons of identical energy as those used in the forward reaction (5). Clearly, such back reaction is unlikely, and the process $B \rightarrow A$ must proceed by a different pathway.

For discussion, we consider two different approaches to photocatalysis. The first approach sees the sequence $3 \rightarrow 4 \rightarrow 6$, that is from chemistry (Eq. (3)) to catalysis (Eq. (4)) to photocatalysis (Eq. (6)). The second approach is $3 \rightarrow 5 \rightarrow 6$ (chemistry $\rightarrow$ photochemistry $\rightarrow$ photocatalysis). From this point of view, the problem of defining photocatalysis is associated with our approach(es) to photocatalysis. Indeed, using the approach $3 \rightarrow 4 \rightarrow 6$ we consider photocatalysis as catalysis of a thermal reaction (Eq. (3)) by an excited state of the catalyst produced as a result of light absorption by the catalyst. Thus, the role of light is to form the active (excited) state of the catalyst or to produce more active sites on its surface during photoexcitation. An example of such a process is the photoinduced isotope exchange of oxygen and hydrogen on photogenerated surface hole centers (O_s^-) on metal oxides. Oxidation of organic compounds over TiO_2 particles is another example if absorption of photons by TiO_2 generates the active state.

In the second approach ($3 \rightarrow 5 \rightarrow 6$), photocatalysis can be treated as catalysis of a photoreaction. Photoexcitation of molecules adsorbed on a photochemically inactive surface is an example of this approach if the adsorbed state of the molecule leads to a decrease of the total activation energy, and thus to an increase of the reaction rate. Note also that changes in the structure of adsorbed molecules compared to their original state as free molecules can increase the absorption probability, stabilize the excited state of such adsorbed molecules (decrease the rate of decay) and increase the reaction rate. In addition, the different structures of adsorbed molecules can lead to spectral (red) shifts of photoexcitation, in which case the photoreaction may be initiated by photons of lesser energy that otherwise would not be active for the original photoreaction (Eq. (5)). The latter can be taken as the analog of decreasing the total activation energy in thermal catalysis.

Subsequent to light absorption by the catalyst, surface photochemical processes may be treated as catalysis of a photoreaction if light is considered as one of the reagents. In this case, there is catalysis of photochemical reaction (5) with changes of the reaction pathway, in which the first step is interaction of the catalyst with the reagent (light) to form an intermediate species (e.g. an excited state of the catalyst), which subsequently reacts with another reagent (molecules A) to form the final reaction product (B).

Clearly, a definition of photocatalysis must be quite general to cover all particular processes (considered above and others) when there is an acceleration of reactions equivalent to reaction (4) with the participation of light, or of reactions analogous to reaction (5). In the final reaction step, the photocatalyst is regenerated into its original state. In catalysis, the kinetic parameters (TOR, TOF and TON) are used to determine whether a given surface reaction is catalytic. We consider below some particular but quite common processes to determine the corresponding kinetic parameters to demonstrate whether photocatalysis is catalytic.

2.2. Catalyzed photolysis

We first consider a simple photochemical process, summarized by mechanism I, that takes place on an inactive surface of a photocatalyst when light is absorbed by an adsorbed substrate.

2.2.1. Mechanism I

1. $M + S \rightarrow M_{ads}$
2. $M_{ads} \rightarrow M + S$
3. $M_{ads} + h\nu \rightarrow M_{ads}^*$
4. $M_{ads}^* \rightarrow M_{ads}$
5. $M_{ads}^* \rightarrow S + \text{products}$

Stage 1 describes adsorption of reagent M on the surface site S of the catalyst while stage 2 reflects the desorption of adsorbed molecules M_{ads}. Both processes lead to the establishment of an adsorption/desorption Langmuir equilibrium whose constant is $K = k_1/k_2$. Stage 3 is photoexcitation of adsorbed molecules to form some appropriate excited state M_{ads}^* followed by the spontaneous decay of excitation (stage 4) and chemical reaction (stage 5) to regenerate the original state of the catalyst surface S, as required by the definition of catalysis (otherwise mechanism I would simply describe a surface stoichiometric photoreaction). All the kinetic parameters (TOR, TOF, TON) are determined under steady-state conditions in all mechanisms considered I–III, i.e. when the concentrations [M] and [S], and photon flow ρ are constant. In the general case, the reaction rate is given by,

$$\frac{dC}{dt} = \frac{d[M]}{dt} = \frac{k_3 k_5 \rho [M][S_0]}{((K + (k_3\rho/k_2))[M] + 1)(k_4 + k_5)} \quad (7)$$

where C denotes a generic concentration of some species. According to the definitions given earlier, TOF is proportional to dC/dt and TOR is proportional to $(dC/dt)/[S_0]$, i.e.

$$\text{TOF} \propto \frac{dC}{dt}s \quad (8)$$

where s is the total surface area of the catalyst participating in the process. By contrast,

$$\text{TOR} \propto \frac{k_3 k_5 \rho [M]}{((K + (k_3\rho/k_2))[M] + 1)(k_4 + k_5)} \quad (9)$$

and TON is proportional to $\int (dC/dt)\, dt/[S_0]$, Eq. (10). (Note that dC/dt is a constant because of the steady-state conditions),

$$\text{TON} \propto t \frac{k_3 k_5 \rho [M]}{((K + (k_3\rho/k_2))[M] + 1)(k_4 + k_5)} \quad (10)$$

where t is the time at which TON is determined. Obviously, if there are no side processes to block the surface sites (ideal situation) one can always choose the time period t' when TON $\gg 1$; in other words, the process is photocatalytic provided that this period $t' < \tau$, where τ is the lifetime of the catalytic site S (catalyst). Other additional steps, such as energy transfer to any acceptor molecules or other decay pathways of the excited state of adsorbed molecules, have no effect on the general conclusions and can be included in the effective (apparent) constant k_4.

The turnover quantities TOF, TOR and TON depend on the concentration of reagent M (because of the dependence of the concentration of M_{ads} on M) and on photon flow ρ (since we deal with a photoprocess and ρ is taken as

the concentration of another reagent, light). If the rate of achieving adsorption/desorption equilibrium is much greater than the rate of photoexcitation (i.e. if $k_3\rho \ll k_1$ or $k_3\rho \ll k_2$ then,

$$\frac{dC}{dt} = \frac{k_3 k_5 \rho K [M][S_0]}{(K[M] + 1)(k_4 + k_5)} = \frac{k_3 k_5 \rho [M'_{ads}]}{k_4 + k_5} \quad (11)$$

where M'_{ads} is an equilibrium concentration of the adsorbed molecules in the dark.

$$\text{TOF} \propto \frac{dC}{dt}s$$

and

$$\text{TOR} \propto \frac{k_3 k_5 \rho \theta}{k_4 + k_5} \quad (12)$$

where θ is the equilibrium coverage of the surface by adsorbed molecules $\theta = [M'_{ads}]/[S_0]$ in the dark at concentration [M]. TON is then given by Eq. (13),

$$\text{TON} \propto t \frac{k_3 k_5 \rho \theta}{k_4 + k_5} \quad (13)$$

Introducing the photochemical parameter, Φ, i.e. the quantum yield of product formation we have

$$\Phi = \frac{k_5}{k_4 + k_5}\phi \quad (14)$$

where ϕ is the quantum yield of absorption of light ($\phi = 1$), and

$$\text{TOF} \propto \Phi k_3 \rho [M_{ads}] \quad (15)$$

$$\text{TOR} \propto \Phi k_3 \rho \theta \quad (16)$$

$$\text{TON} \propto \Phi t k_3 \rho \theta \quad (17)$$

To the extent that TON yields information about 'photo-catalysis' being catalytic, the efficiency and activity of the photocatalytic process are better characterized by the quantum yield. The greater the quantum yield is, the greater are the three turnovers. Note that the same expression for the quantum yield is obtained for the photochemical reaction if in stages 3–5 we substitute M_{ads} with M and M_{ads}^* with M*. The rate of such a photochemical process at the same concentration [M] is given by:

$$\frac{dC}{dt} = \frac{k_3' k_5' \rho [M]}{k_4' + k_5'} \quad (18)$$

(The primed parameters are for a homogeneous process). Thus, acceleration of the photoreaction in a heterogeneous system (over a homogeneous one) is observed provided that changes in the structure of the adsorbed molecule cause an increase in photon absorption cross-sections $k_3 > k_3'$, stabilization of the excited state of the molecule $k_4 < k_4'$, and a decrease of the reaction activation energy $k_5 > k_5'$ (see above). Of course, the rate depends on the concentration of

adsorption sites on the surface of the catalyst. The overall condition to observe acceleration is given by:

$$\left(\frac{k_3 k_5}{k_3' k_5'}\right)\left(\frac{k_4' + k_5'}{k_4 + k_5}\right)\left(\frac{[M_{ads}]}{K[M]}\right) > 1 \qquad (19)$$

that is,

$$\frac{k_3 \Phi}{k_3' \Phi'}\left(\frac{[M_{ads}]}{K[M]}\right) > 1 \qquad (20)$$

Consequently, if the absorption spectra of adsorbed and free molecules are similar (i.e. if $k_3 \sim k_3'$), then in order to observe photocatalytic acceleration the quantum yield of the heterogeneous photoreaction must be greater than the corresponding quantum yield of the homogeneous process, that is $\Phi > \Phi'$ (see Eq. (20)).

2.3. Langmuir–Hinshelwood photocatalytic process

We now consider the case of a Langmuir–Hinshelwood photocatalytic reaction that occurs at a photochemically active surface when light is absorbed by the catalyst leading to the generation of surface electrons (e^-) and holes, (h^+), as described in mechanism II:

2.3.1. Mechanism II
6. $M + S \rightarrow M_{ads}$
7. $M_{ads} \rightarrow M + S$
8. $Cat + h\nu \rightarrow e^- + h^+$
9. $M_{ads} + h^+ \rightarrow M_{ads}^+$
10. $M_{ads}^+ + e^- \rightarrow M_{ads}$
11. $M_{ads}^+ \rightarrow product + S$

Stages 6 and 7 are identical to stages 1 and 2 above, and both processes lead to the establishment of an adsorption/desorption Langmuir equilibrium with constant $K = k_6/k_7$. Stage 8 reflects the photoexcitation of the catalyst producing electrons and holes. Stage 9 describes carrier (hole) trapping by the adsorbed molecule to form a reactive radical state, whose decay occurs through recombination with an electron described by stage 10. Stage 11 is the chemical reaction that yields products and regenerates the original state of the catalyst surface, S. The surface concentrations of holes and electrons in the kinetic approach are given by:

$$[h^+] = \alpha_h \rho \tau_h \qquad (21)$$

and

$$[e^-] = \alpha_e \rho \tau_e \qquad (22)$$

where α_h and α_e are the absorption coefficients of holes and electrons absorption bands (note that in the intrinsic absorption region $\alpha_h = \alpha_e$), and τ_h and τ_e are the lifetimes of holes and electrons, respectively. The disadvantage of the kinetic approach is that it considers the spatially uniform carrier generation in the bulk of the catalyst (i.e. $\alpha\rho = const.$) and

there is no diffusion limitation for carrier motion. For a more detailed description one should use the expression for the concentration of surface carriers reported earlier [4].

The rate of the (photo)catalytic reaction at steady-state is given by Eq. (23):

$$\frac{dC}{dt} = \frac{k_6 k_9 k_{11}[S_0][h^+][M]}{(k_{10}[e^-] + k_{11})(K[M] + (k_9[h^+]/k_7) + 1)} \qquad (23)$$

If establishment of the adsorption/desorption equilibrium is faster than the rate of hole trapping, that is if $k_9[h^+] \ll k_7$ or if $k_9[h^+] \ll k_6[M]$, then

$$\frac{dC}{dt} = \frac{k_6 k_9 k_{11}[S_0][h^+][M]}{(k_{10}[e^-] + k_{11})(K[M] + 1)} \qquad (24)$$

or

$$\frac{dC}{dt} = \frac{k_6 k_9 k_{11}[h^+][M_{ads}]}{k_{10}[e^-] + k_{11}} \qquad (25)$$

and

$$TOF \propto \frac{dC}{dt} s$$

$$TOR \propto \frac{dC/dt}{[S_0]} = \frac{k_6 k_9 k_{11}[h^+]\theta}{k_{10}[e^-] + k_{11}} \qquad (26)$$

$$TON \propto t\frac{dC/dt}{[S_0]} = t\frac{k_6 k_9 k_{11}[h^+]\theta}{k_{10}[e^-] + k_{11}} \qquad (27)$$

As in the previous case, all the parameters depend on concentration and light intensity (photon flow). In the present instance, the time period t can also be chosen to obtain TONs for TON greater than unity.

The similarity between Eqs. (8) and (24)–(27) and Eqs. (8) and (11)–(13) (for mechanism I) is evident. In fact, the process described by mechanism II can be treated as a photochemical reaction on the surface of a solid whose role is to absorb light. Subsequent charge carrier transfer to the adsorbed molecule produces an ionized state of the adsorbed molecule as might also occur by direct interaction between the adsorbed molecule and light (not shown in mechanism II). The excitation rate in mechanism II, $k_9[h^+] = k_9\alpha_h\rho\tau_h$, is analogous to the rate $k_3\rho$ in mechanism I. In mechanism II, the photocatalyst also takes part in the deactivation process, such that $k_{10}[e^-]$ (or k_{10} for thermal ionization of the adsorbed molecule) corresponds to k_4 in mechanism I. The 'inert' catalyst in mechanism I also plays a role in the decay step (stage 4) changing the probability of deactivation.

If $\alpha_h = \alpha_e = \alpha$, the rate of photon absorption is given by $\int_V \alpha\rho \, dV$, where V is the volume of the catalyst, and in the case of spatially uniform photoexcitation this rate is $\alpha\rho V$. The quantum yield of the photocatalytic process is then given by:

$$\Phi = \frac{TOF}{\alpha\rho V} = \frac{s}{V}\frac{k_6 k_9 k_{11}\tau_h[M_{ads}]}{k_{10}[e^-] + k_{11}}$$
$$= \frac{s}{V}\frac{k_6 k_9 k_{11}\tau_h[M_{ads}]}{k_{10}\alpha\rho\tau_e + k_{11}} \qquad (28)$$

consequently,

$$\text{TOF} = V\alpha\rho\Phi \tag{29}$$

$$\text{TOR} = \frac{\alpha\rho\Phi}{[S_0]}\frac{V}{s} \tag{30}$$

$$\text{TON} = t\frac{\alpha\rho\Phi}{[S_0]}\frac{V}{s} \tag{31}$$

Hence just as in mechanism I, all the turnover quantities are associated with the quantum yield of the photoprocess. Once again the activity and efficiency of the (photo)catalyst are determined by Φ.

In a previous consideration, we assumed that the surface adsorption centers S are the active centers of (photo)catalysis, so that photoelectrons and photoholes are the intermediates produced from the interaction between the catalyst with one of the reagents: light. In the electronic theory of catalysis, however, Volkenstein [35] proposed that the free surface electrons and holes are the reactive centers. In such instance, TOR and TON are given by,

$$\text{TOR} \propto \frac{k_6 k_9 k_{11}[M_{ads}]}{k_{10}[e^-] + k_{11}} = \left(\frac{V}{s}\tau_h\right)\Phi \tag{32}$$

$$\text{TON} \propto t\left(\frac{V}{s}\tau_h\right)\Phi \tag{33}$$

In this case, catalysis occurs from the excited state of the catalyst and neither TOR nor TON depend on light intensity, unless the decay of the ionized state of the adsorbed molecule is caused by recombination or photoionization, and $k_{10}[e^-] \sim k_{11}$.

2.4. Catalytic activity

According to the electronic theory of catalysis, the activity of the catalyst is related to the concentrations of electrons and holes on the surface which are determined by the position of the Fermi level (or by the electrochemical potential of the electron) in the catalyst. The concentration of free carriers is:

$$[e^-] = \int_E N_C(E) f(E, T)\,dE \tag{34}$$

and

$$[h^+] = \int_E N_V(E)(1 - f(E, T))\,dE \tag{35}$$

where

$$f(E, T) = \frac{1}{1 + e^{(E-F)/\kappa T}} \tag{36}$$

E refers to an energy scale and F is the Fermi level; N_C and N_V are the density of states in the conduction and valence bands, respectively. If the catalyst is not a degenerate semiconductor (typical of photocatalysts), then

$$[e^-] = N_C\, e^{(F-E_C)/\kappa T} \tag{37}$$

and

$$[h^-] = N_V\, e^{(E_V - F)/\kappa T} \tag{38}$$

where E_C is the lowest energy level in the conduction band and E_V is the highest energy level in the valence band. On the one hand, the number of reaction centers (electrons and holes) depends on the position of the Fermi level. On the other hand, the different positions of the Fermi level correspond to different states of the catalyst, i.e. to different catalysts. Indeed, for different concentrations of reactive centers (e.g. metal ions doped on the surface) we can distinguish different types of catalysts with corresponding positions of the Fermi level. Under irradiation, the Fermi level of the catalyst splits into two quasi-Fermi levels: one for electrons and the other for holes, provided that the relaxation time of momentum and energy is much less than the lifetime of the carriers in the corresponding bands.

In the dark, the next expression is true (E_G is the band gap energy):

$$[e^-][h^+] = n_i^2 = N_C N_V\, e^{-E_G/\kappa T} \tag{39}$$

and under irradiation this expression can be written as

$$[e^-][h^+] = n_i^2\, e^{(F_e - F_h)/\kappa T} = N_C N_V\, e^{-(E_G - \Delta F)/\kappa T} \tag{40}$$

where $\Delta F = F_e - F_h$

Thus, a catalyst under irradiation behaves differently with an apparent band gap given by $E_G - \Delta F$. The energy difference between the two quasi-Fermi levels, ΔF, depends on the intensity of irradiation. Consequently, we have different states which behave as different catalysts at different light intensities. In fact, at the higher light intensities we have higher concentrations of electrons and holes, i.e. of the reactive centers.

2.5. Eley–Rideal photocatalytic process

Another family of heterogeneous photochemical processes is observed when the catalysts are photoexcited. Below we consider some common cases for such processes from the kinetics point of view.

2.5.1. Mechanism III

8. $\text{Cat} + h\nu \rightarrow e^- + h^+$
12. $S + h^+ \rightarrow S^+$
13. $S^+ + e^- \rightarrow S^+$
      (13a. $S^+ \rightarrow S + h^+$;   13b. $S^+ + h\nu \rightarrow S + h^+$)
14. $S^+ + M \rightarrow (S–M)^+$
15. $(S–M)^+ \rightarrow S + \text{products}$
      (or 15a. $(S–M)^+ \rightarrow S^+ + \text{product}$)

As in the previous mechanism II, stage 8 corresponds to the photogeneration of free carriers. Stage 12 describes the trapping of carriers (in this particular case, holes) by surface defects (i.e. 'potential' surface active centers) S to produce surface active centers S^+; stage 13 represents the 'physical'

decay pathway of surface active centers through recombination with charge carriers of opposite sign, viz. electrons; it may also be a first-order thermal deactivation process (stage 13a) or a second-order photoionization process (stage 13b). Stage 14 is a chemical reaction (chemisorption) which yields the intermediate species (S–M)$^+$ followed by secondary reactions to produce the photoreaction products (stage 15). Note the difference between stages 15 and 15a. In stage 15 the original (ground) state S of the photocatalyst is restored (the quantum yield $\Phi < 1$, so-called non-catalytic in photons process), whereas in stage 15a the ionized state S$^+$ remains at the end of the reaction cycle (the quantum yield Φ may be greater than 1, the so-called catalytic in photons process). Parmon [36] refers to the latter process as photoinduced (photoinitiated) catalysis, whereas the former is denoted photocatalysis. It is instructive to compare the kinetic parameters for both of these types of catalysis.

2.5.1.1. Photocatalysis. For the photocatalytic process with stage 15 the steady-state reaction rate is given by

$$\frac{dC}{dt} = \frac{k_{12}k_{14}k_{15}[S_0][h^+][M]}{k_{15}(k_{13}[e^-] + k_{14}[M]) + k_{12}[h^+](k_{15} + k_{14}[M])} \quad (41)$$

and with stage 15a the rate is

$$\frac{dC}{dt} = \frac{k_{12}k_{14}k_{15}[S_0][h^+][M]}{k_{15}k_{13}[e^-] + k_{12}[h^+](k_{15} + k_{14}[M])} \quad (42)$$

where $[h^+] = \alpha_h \rho \tau_h$ and $[e^-] = \alpha_e \rho \tau_e$ are the (surface) concentrations of holes and electrons, respectively. These equations reflect the fact that in the process described with stage 15a the only pathway for deactivation of the excited state of the catalyst is the 'physical' decay path (recombination $k_{13}[e^-]$), whereas in the catalytic process with stage 15 deactivation occurs as much by the 'physical' decay pathway as through the chemical reaction ($k_{13}[e^-] + k_{14}[M]$). In the latter case, the reaction rate is smaller provided that all the kinetic constants in both processes are the same. Note also, that both dependencies of the rates on concentration of reagent M resemble the Langmuir–Hinshelwood kinetics, although both are of the Eley–Rideal type. Maximal rates would be observed when $k_{14}[M] \gg k_{15}$ and $k_{14}[M] \gg k_{13}[e^-]$. Then,

$$\frac{dC}{dt} = \frac{k_{12}k_{15}[S_0][h^+]}{k_{15} + k_{12}[h^+]} \quad (43)$$

which for $k_{12}[h^+] \gg k_{15}$, yields

$$\frac{dC}{dt} = k_{15}[S_0] \quad (44)$$

that is, under the given conditions the rate of the process equals the rate of regeneration of the surface reaction centers S after completion of the reaction cycle, and for $k_{12}[h^+] \ll k_{15}$, yields

$$\frac{dC}{dt} = k_{12}[S_0][h^+] \quad (45)$$

that is, the reaction rate is determined by the production of excited (ionized) states of the surface reactive centers.

Since the rate of the photocatalytic reaction is known, the only problem remaining to determine the turnover quantities is to decide on the nature of the surface active centers in photo-catalysis. The simplest way is to suggest that the ionized states S$^+$ are such centers. In such a case,

$$TOF \propto \frac{dC}{dt}s$$

$$TOR \propto \frac{dC/dt}{[S^+]} = k_{14}[M] \quad (46)$$

$$TON \propto tk_{14}[M] \quad (47)$$

As in the case of surface photochemical reactions (mechanisms I and II), TON is greater than unity if turnover is determined for time $t < \tau$, where τ is the lifetime of the catalytic site. Hence the process can be said to be catalytic. It should be emphasized that TOR and TON are independent of light intensity. They depend solely on reagent concentration, whereas the reaction rate and TOF behave differently. The latter two depend on light intensity and (perhaps) on temperature for constant concentration of M. Indeed, as $k_{13}[e^-]$ (or $k_{13}) \to \infty$, then $dC/dt \to 0$ and $TOF \to 0$, whereas, according to Eqs. (34) and (35), TOR and TON are constant. The physical sense of this behavior is that at high rate of 'physical' decay, i.e. when $k_{13} \to \infty$, the concentration of the active centers $[S^+] \to 0$, and so do the reaction rate and TOF. However, since TOR and TON are determined relative to a single center, as soon as this center becomes available the reaction cycle occurs and TOR and TON remain constant. Thus, TOR and TON reflect the activity of a given active center (ionized state) S$^+$ but say nothing about the efficiency and activity of the catalyst. Moreover, for an effective physical decay (e.g. at sufficiently high light intensity), the rates of both processes (photoinduced catalysis (stage 15a) and photocatalysis (stage 15)) become equal since they are determined only by the rate of photogeneration and (photo)decay of the ionized state; only one (or less) reaction cycle can occur during the lifetime of the active center.

In another approach, when we consider catalysis of a photochemical reaction and assume that light is one of the reagents, all the excited states of the catalyst (electrons, holes, and S$^+$ states) may be taken as intermediates of the catalytic photoreaction. The latter takes place by a different reaction pathway in contrast to the original photochemical reaction. Hence, the original state of the catalyst is S which is restored at the end of the reaction and the number of active centers is given by S_0. This is analogous to thermal catalysis. For example, the oxidation reaction can follow the path:

$$O_s + M \to MO \uparrow + V_{Os} \quad (48)$$

$$V_{Os} + \tfrac{1}{2}O_2 \to O_s \quad (49)$$

The reactive center in such a process is neither surface oxygen O_s nor the oxygen vacancy V_{Os}, but is some cluster

corresponding to oxygen vacancies either with or without oxygen in the cluster. By analogy, in photocatalysis there are surface centers (defects) which can be in a state with trapped carriers (i.e. an intermediate, just like surface oxygen in the previous example) or without trapped carriers. These centers are then the centers of (photo)catalysis).

TOF is identical to that given by Eq. (8), whereas TOR and TON are given by Eqs. (50) and (51), respectively:

$$\text{TOR} \propto \frac{\mathrm{d}C/\mathrm{d}t}{[\text{S}_0]} = \frac{k_{12}k_{14}k_{15}[\text{h}^+][\text{M}]}{\substack{k_{15}(k_{13}[\text{e}^-] + k_{14}[\text{M}]) \\ + k_{12}[\text{h}^+](k_{15} + k_{14}[\text{M}])}} \tag{50}$$

and

$$\text{TON} \propto t \frac{k_{12}k_{14}k_{15}[\text{h}^+][\text{M}]}{\substack{k_{15}(k_{13}[\text{e}^-] + k_{14}[\text{M}]) \\ + k_{12}[\text{h}^+](k_{15} + k_{14}[\text{M}])}} \tag{51}$$

In this case TOR and TON depend on light intensity and on the concentration of reagent M. The rate of decay of the active state S^+ (i.e. $k_{13}[\text{e}^-]$) affects both TOR and TON parameters which now characterize the activity of the (photo)catalyst.

Note that the quantum yield of the photocatalytic process in the kinetic approach used in this article can be described by Eq. (52):

$$\Phi = \frac{(\text{const.})(\mathrm{d}C/\mathrm{d}t)s}{\alpha\rho V} = \frac{\text{TOF}}{\alpha\rho V} \tag{52}$$

where s is the total surface area of the catalyst, V is the volume of the catalyst, α is the absorption coefficient of the catalyst and ρ is the photon flow. Then, Eqs. (29)–(31) can be used to describe the relationships between TOF, TOR and TON with the quantum yield of the photocatalytic process.

2.5.1.2. Photoinduced catalysis. To complete the consideration of the previous examples, it is relevant to note that photoinduced catalysis (stage 15a) does not require continuous irradiation since the excited state is reproducible. In this case, the excited state is created during pre-irradiation and there is no 'physical' decay during the course of the reaction. Consequently, stages 12 and 13 must be excluded from this consideration and the rate of the photoinduced catalytic process is then given by,

$$\frac{\mathrm{d}C}{\mathrm{d}t} = \frac{k_{14}k_{15}[\text{S}_0^+][\text{M}]}{k_{15} + k_{14}[\text{M}]} \tag{53}$$

so that

$$\text{TOF} \propto \frac{\mathrm{d}C}{\mathrm{d}t}s$$

$$\text{TOR} \propto \frac{k_{14}k_{15}[\text{M}]}{k_{15} + k_{14}[\text{M}]} \tag{54}$$

and

$$\text{TON} \propto t \frac{k_{14}k_{15}[\text{M}]}{k_{15} + k_{14}[\text{M}]} \tag{55}$$

Thus, even though in both cases the active (excited) state of the catalyst is restored, the kinetic parameters of photoinduced catalysis (Section 2.5.1.1) and photocatalysis (Section 2.5.1.2) are different, since we deal with a different excited state of the catalyst, i.e. we deal effectively with different catalysts. Indeed, under irradiation the state of the catalyst may be characterized by the splitting of the Fermi level into two quasi-Fermi levels (see above), whereas in photoinduced catalysis (in the dark) the state of the catalyst is characterized by a unique Fermi level. This level may be shifted compared to the original state of the catalyst because of the possibility of having different excited states after pre-excitation of the catalyst.

2.6. Further considerations

It must be noted that there is nothing special about photocatalysis. It is simply another type of catalysis joining, as it were, redox catalysis, acid–base catalysis, enzyme catalysis, thermal catalysis, and others. Consequently, any description of photocatalysis must correspond to the general definition of catalysis. This said, we might then argue that *photocatalysis* simply describes *catalysis of a photochemical reaction*. To ascertain this proposition we consider the following.

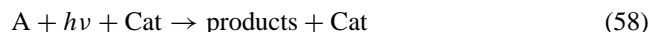If reaction (56) describes the catalyzed reaction between reagent A and reagent B,

$$\text{A} + \text{B} + \text{Cat} \rightleftarrows \text{products} + \text{Cat} \tag{56}$$
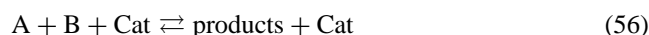
then in the absence of the catalyst (Cat) one is left with the chemical reaction:

$$\text{A} + \text{B} \rightleftarrows \text{products} \tag{57}$$

which is no longer catalyzed by Cat as in reaction (56).

If we carry this argument further to the photocatalyzed reaction (58),

$$\text{A} + h\nu + \text{Cat} \rightarrow \text{products} + \text{Cat} \tag{58}$$

removal of the catalyst (Cat) leads to the photochemical reaction described by Eq. (59).

$$\text{A} + h\nu \rightarrow \text{products} \tag{59}$$

By analogy, then, we deal with catalysis of a photochemical reaction by the catalyst (Cat) in its ground state. This notion is very important for determining the kinetic turnovers TOR and TON since their evaluation requires knowledge of which state of the catalyst (i.e. the state of the surface reactive centers) must be considered.

Some additional points are worth noting:

1. The photochemical reaction (59) takes place through the excited electronic state of the reagent, A^*, produced by the primary act of light absorption by reagent A, unlike the chemical reaction (57) which occurs through the ground states of the reagents A and B. In the photocatalytic process (58), the reaction also takes place after

electronic photoexcitation of either the catalyst (Cat) or the adsorbed molecules (A_{ads}), unlike catalysis which involves only the ground electronic states (but thermally excited vibrational states).

2. The photocatalyzed reaction (Eq. (58)) and the photochemical reaction (Eq. (59)) are irreversible processes, unlike thermal catalysis (Eq. (56)) and the thermal chemical reaction (57).

Thus, photocatalysis is a photochemical process and the photocatalyst accelerates this process as any catalyst must do according to the definition of catalysis.

Photoexcitation of the catalyst can be considered as changing the photochemical reaction pathway that is typical of a catalytic process. It can also lead to possible changes in the spectral range of photoexcitation relative to the non-catalytic photochemical reaction (Eq. (59)) which, by analogy, can be considered as a change of the total activation energy because of the different reaction pathway in the catalytic process (Eq. (56)). Indeed, photoexcitation of the catalyst to form its excited state (Eq. (60)) in reaction (58) is analogous to the formation of the intermediate adsorption complex (Eq. (61)) in

$$Cat + h\nu \rightarrow Cat^* \qquad (60)$$

$$B + Cat \rightarrow (Cat–B) \qquad (61)$$

thermal catalysis (Eq. (56)), both of which are followed by secondary interaction steps with another reagent A.

Hence, just as in thermal catalysis (Eq. (56)) in which such an adsorption complex is not considered as the reactive center, the excited state of the (photo)catalyst in the photocatalytic process (58) is not a reactive center but an intermediate. Consequently, to determine TOR and TON in the proposed earlier mechanisms I–III (see above) we need to consider as reaction centers the corresponding surface centers S in the *original state* of the (photo)catalyst and not S^+ nor M^*_{ads}. As an example, we note the photocatalytic oxidation of organic compounds over TiO_2 in aqueous media. In this case, the ground state of S centers corresponds to the surface OH^- groups. It is these OH^- groups that should be taken as the catalytic centers, whereas the $^\bullet OH$ radicals formed by hole trapping represent intermediate species. Note also that the original S state of surface active centers is restored after reaction is completed. In the example of TiO_2, this restoration or reconstruction of the original state of the catalyst is achieved by dissociative adsorption of water on the particle surface. Thus, photocatalysis is catalysis of a photochemical reaction by the original ground state of the catalyst prior to photoexcitation. Catalyzed photolysis (mechanism I) is also a case of photocatalysis, unlike photoinduced catalysis which is not photocatalysis (i.e., it is not catalysis of a photochemical reaction).

In photoinduced catalysis, pre-irradiation of the original state of the catalyst is the only means for the physical development of a new catalyst to create new centers; the corresponding catalytic process completely follows reaction (56). The similar changes to the state of the catalyst can be achieved by chemical doping, irradiation with ions or electrons, and additive coloration process, among others. Thus photoinduced catalysis is thermal catalysis by a catalyst produced by pre-irradiation (Fig. 1a). The principal difference between photoinduced catalysis and photocatalysis can best be described as follows.

Any photochemical reaction (Eq. (59)) starts from light absorption by the reagent to form an excited state of the molecule A:

$$A + h\nu \rightarrow A^* \qquad (62)$$

and there always exists a physical pathway (radiative and nonradiative) for relaxation of this state back to the ground state:

$$A^* \rightarrow A \qquad (63)$$

Thus there is always a competition between chemical and physical pathways for decay of excited states. If the chemical pathway is inefficient, then the physical path will lead to relaxation of A^* to its ground electronic state.

The same is true for photocatalysis. Indeed, since photocatalysis is catalysis of a photochemical reaction there is a physical pathway for decay of the system back to its ground state. If the photocatalytic process occurs through photoexcitation of the catalyst, physical decay may occur through recombination, and/or through thermal and photo ionization of the excited state of the surface centers which ultimately lead to regeneration of the original state of the catalyst. Obviously, there is no such process in the case of photoinduced catalysis. In the latter case, the state of the catalyst does not have a physical decay pathway and is the same before and after reaction as in any thermal catalytic reaction. Note also that the catalytic process in photoinduced catalysis is reversible unlike in photocatalysis.

3. Conclusions

One of the major conclusions of this article is that determination of the turnover quantities TOR and TON in photocatalysis necessitates that the concentration of the surface centers (S) in the original state of the (photo)catalyst be taken into account and not the concentration of one of its excited states (e.g. S^+). This simplifies the experimental determination of turnover quantities. However in most cases, assessment of the concentration of surface reactive centers remains a big challenge, except in some particular cases (see [30–32]). Another problem connected with turnover parameters is that all are likely to depend on light irradiance (or photon flow), an effect yet to be determined and verified experimentally. Indeed, although light irradiance incident on the reactor can easily be measured by actinometry, scattering and absorption keep changing from particle to particle and are different at different points of the reactor, not least of

which is the dependence on reactor geometry. This requires complex calculations of the light irradiance distribution in a given reactor. Also, it is worth noting that the irradiated surface area is not necessarily equal to the total surface area of the catalyst, *s*. Thus, the practical determination of turnover quantities remains a very complex problem.

On the basis of the above discussion then, we propose that the TOR be taken simply as the number of molecules reacted or produced per unit time per active site [2] (unit: molecules per site per unit time); TOF as the number of molecules reacted or produced per unit time (unit: molecules per unit time); and, in accord with others [29], TON as a quantity that describes how many times a reaction or process turnsover at some active site (or at some catalyst molecule in homogeneous catalysis) integrated over time (unit: molecules per site).

Acknowledgements

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[2] Somorjai [29] referred to this as a specific TOR.