Glossary of Terms in Photocatalysis and Radiation Catalysis

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Synopsis

This document presents a glossary of terms to be used for phenomena generalized under the very wide terms “photocatalysis” and "radiation catalysis". A clear distinction has been made between phenomena of different nature related to either both photochemistry and photocatalysis or both radiation chemistry and radiation catalysis. Consistent definitions of terms in these areas are given, as well as definitions of the most important parameters used for the quantitative description of “photocatalysis” and “radiation catalysis” phenomena.

Introduction

Photocatalysis and related phenomena are now well known and well recognized. Biogenic photocatalytic phenomena, such as those occurring along the cycle of natural photosynthesis, have been known since prehistoric times (indeed, without realizing the intrinsic chemical mechanisms of growing plants). The term “photocatalysis” has introduced during the early 1930s. Since that time, this term has been used in the scientific literature, and for years there was no need to define it more clearly. Usually the term represented a division of chemistry studying catalytic reactions proceeding under the action of light. The totality of phenomena connected with both photochemistry and catalysis was referred to as belonging to the field of photocatalysis. For a long period of time, such phenomena seemed to be mainly “exotic”, and of interest to a narrow group of specialists only. However, recent interest in natural photosynthesis and chemical methods for solar energy transformation greatly developed our knowledge in this direction and revealed a variety of phenomena related to both photochemistry and catalysis. Many of the phenomena noted differ qualitatively by their nature and, generally speaking, are to be placed in different areas of chemistry.

In our opinion, the semantic analysis of the terms becomes most fruitful and definitions less ambiguous, if one starts from the notion "photocatalyst" and not from the notion "photocatalysis". The usefulness of this approach has been demonstrated in the past when defining the classical notions of "catalysis" and "catalyst" on the basis of the primacy of the definition of the notion "catalyst":

"*Catalysis is a change in the rate of chemical reactions in the presence of substances (catalysts) that come into intermediate chemical interactions with the reactants, but restore their chemical composition after each cycle of the intermediate interactions. Reactions with the participation of catalysts are called catalytic*".[1]

Note that the given definition is universal in the sense that it allows one gradually, as the mechanism of the particular catalytic process becomes more clear, to refine step by step the content of the notion "catalyst" for this process. Following this approach, we put forward the following starting definition:

A photocatalyst is a substance that is able to produce, by absorption of light quanta, chemical transformations of the reaction participants, repeatedly coming with them into the intermediate chemical interactions and regenerating its chemical composition after each cycle of such interactions.

Such a definition, along with the above definition of the concept "catalyst", enables one to refine the sense of the term photocatalyst when the object comes to be better understood.

[1] *The Glod Book of IUPAC gives also a simpler definition: Catalysis is the action of a catalyst. A catalyst is a substance that increases the rate of reaction without modifying the overall standard Gibbs energy change in the reaction.*

Thus, we can propose the following definition of the phenomenon of photocatalysis:

Photocatalysis* *is a change in the rate of chemical reactions or their generation under the action of light in the presence of substances — called photocatalysts (already defined) – that absorb light quanta and are involved in the chemical transformations of the reaction participants.

The glossary of terms presented below is based on these principal definitions. As a result, the glossary is totally consistent with the earlier "Glossary of Terms used in Photochemistry" suggested by IUPAC.

References

- S.E. Braslavsky, K.N. Houk, *Pure Appl. Chem*., 60 (1988) 1055.
- J.W. Verhoven, *Pure Appl. Chem*., 68 (1996) 2223

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Main part of Glossary of terms

Catalyzed photolysis (photoreaction) **— see *catalysis of photochemical reaction***

Catalysis (promotion) of photochemical reactions **(*catalyzed photolysis, catalyzed photoreaction*) is the raising (alteration) of efficiency of the photochemical reactions after direct excitation of photochemically active (and thus light-absorbing) reactants, via an intermediate interaction of these reactants with certain compounds that act as "catalysts" (promoters) of the appropriate chemical transformations of the reactants. Sometimes this process can be identical with true *photocatalysis***

Catalyst photoactivation (photomodification) **is the generation or alteration of the catalytic activity (selectivity) of a substance after its interaction with light quanta.**

Photoadsorption (photoinduced adsorption) **is adsorption (typically chemisorption, i.e., a stoichiometric reaction of adsorbate molecules with a solid surface) initiated by light absorbed either by the adsorbate or by the adsorbent.**

Areal (apparent) photoadsorption capacity **of an adsorbent is the number of *moles* of molecules (atoms, ions) photoadsorbed *per unit area* at the uniformly irradiating surface of a given adsorbent (see also *ultimate* photoadsorption capacity).**

Photoadsorption center **(see also *active state of a surface photoadsorption center)* is a surface site or a surface defect capable of attracting photoadsorbed species via chemical interaction with adsorbate molecules (atoms, ions) in its active state after photoexcitation.**

Apparent photoadsorption efficiency (apparent quantum yield of photoadsorption) **is the *ratio* of the maximal (typically initial) rate of photoadsorption to the *incident* photon flux at a given wave length. Both rates should be measured under exactly the same conditions and be expressed in the same units, in order to avoid concentration and/or surface area effects.**

Apparent photoadsorption quantum yield **is the number of photoadsorbed molecules atoms, ions, radicals, *or photoadsorbed species* formed at the surface per photon of light (at a given wavelength), that is absorbed by the system (typically by an adsorbent) during the initial time of irradiation.**

Photoassisted catalysis **is the phenomenon of catalytic transformations taking place under the action of light quanta. The use of this term is recommended only for situations when it is still not known whether the light absorbing substance is a reactant molecule or a photocatalyst particle.**

Photocatalysis **is a change in the rate of chemical reactions or their generation under the action of light in the presence of substances — *photocatalysts* that absorb light quanta and are involved in chemical transformations of the reaction participants.**

Photocatalyst **is a substance that is able to produce, by absorption of light quanta, chemical transformations of the reaction participants, repeatedly coming with them into intermediate chemical interactions and regenerating its chemical composition after each cycle of such interactions.**

Photocatalytic active center (photocatalytic active site) **is a surface center (a defect or a regular surface site) where chemical transformations take place after transition of the photocatalytic active center into *the active state of photocatalytic center* via any photophysical process (e.g., via photoexcitation).**

Apparent photocatalytic activity (apparent photocatalytic efficiency) of a system **is the number of molecules (product) of a given photocatalytic process formed (alternatively, the number of molecules of a given reactant disappearing) per one quantum of light with the given energy, that is impinging on the photocatalytic system.**

True photocatalytic activity (true photocatalytic efficiency) of a system **is the number of molecules (product) of a given photocatalytic process formed (alternatively, the number of molecules of a given reactant disappearing) per one quantum of light that is being absorbed by the photocatalytic system. It must be noted that this quantity has a well-defined meaning only when the reaction-operating conditions are also stated and the results are reported in terms of the initial conditions.**

Photochemical capacity **of a heterogeneous photocatalyst (the capacity of a photocatalyst to absorb photons) is usually defined as the ratio:**

photochemical capacity = (number of absorbed photons)/(time·surface area)

However, one should note that absorption of radiation is a phenomenon occurring in a volume. Consequently, the magnitude to be used is the number of absorbed photons per unit volume and unit time. Thus, the more strictly defined photochemical capacity must be defined as:

photochemical capacity = (photocatalyst absorption coefficient) $\times$ (photonic irradiance) [=]

Photodesorption **is desorption induced by the absorption of light quanta either by the adsorbate or by the adsorbent.**

Photoelectrocatalysis **— see *photoelectrochemical transformations***

Photoelectrochemical transformations (photoelectrocatalysis) **usually have the same physico-chemical nature as photocatalysis. The role of the photocatalyst in photochemical transformations is played by a photoelectrode, which is often a semiconductor.**

Photoelectrode **is an electrode capable of initiating electrochemical transformations after absorbing light quanta.**

Photogenerated (photoinduced, photoinitiated) catalysis **is the initiation of chemical transformations through the photochemical formation of substances that are catalytically active even without the action of light.**

Photoinitiator **is an agent that initiates, under the action of light, certain chemical transformations and is consumed therewith.**

Apparent photonic efficiency **(*apparent quantum yield for monochromatic radiation*) is the ratio of the photogenerated reaction rate measured at a specified time span (usually the initial conditions) to the rate of incident photons. It must be noted that this quantity has a well-defined interpretation only when the reaction-operating conditions are fully stated. Nevertheless, this concept has no photochemical meaning and, moreover, it is very difficult to repeat the experiments by another group of researchers when the fraction of light absorbed by the photochemically active component on the system is not known. However, this type of parameter attracts the most attention for any practical application of photocatalysis.**

True photonic efficiency **(*true quantum yield for monochromatic radiation*) is the ratio of the reaction rate measured at a specified time to the volumetric rate of photon absorption. It must be noted that this quantity has a well-defined interpretation only when the reaction-operating conditions are fully stated.**

Photosensitizer **(*sensitizer*) is an agent that absorbs light and subsequently initiates a photochemical or photophysical alteration in the system, the agent being not consumed therewith. In case of chemical alteration, the photosensitizer is usually identical to a *photocatalyst.***

Quantum efficiency **is the *photonic efficiency* resulting from polychromatic measurements.**

Quantum yield of a photocatalytic process **is exactly equal to the quantum yield of a photochemical process; that is, the number of molecules of a given product formed (alternatively, of a given reactant consumed) per photon of light at a given wavelength, that is absorbed by the photocatalyst:**

quantum yield = (quantity of reacted molecules)/(quantity of absorbed photons)

Both terms appearing in the ratio must be evaluated at the same time; therefore, in reality, the terms defining the quantum yield are “rates”. The numerator represents the reaction rate and the denominator represents the rate of the photon absorption:

quantum yield = (volumetric reaction rate corresponding to a given reactant or product)/ (volumetric rate of photon absorption by the reactant or by the catalyst)

Apparent quantum yield — see *photonic efficiency*

Relative photonic efficiency is the ratio of the photonic efficiency of a chemical process under study and the photonic efficiency of a standard process under the same conditions. It is also possible to specify the relative *apparent* photonic efficiency on the basis of incident rates.

Turnover frequency (turnover rate) in heterogeneous photocatalysis, TOF_{het}, is the number of photocatalytic turnovers, n (see *turnover number*), per catalytic site and per unit time:

$$TOF_{het} = \frac{1}{N} \cdot \frac{dn}{dt} [=] \frac{1}{s\ (active\ site)},$$ where (=) N is the number of the catalyst active site. This definition of the turnover rate should be used whenever possible. However, when the number of active sites is not known, the surface area should be used to normalize the number of turnovers and an apparent quantity results:

$$TOF_{het,app} = \frac{1}{S} \cdot \frac{dn}{dt} [=] \frac{1}{m^2 s},$$ where S is the [BET(N_2)] area

Areal (apparent) turnover frequency (apparent turnover rate) in heterogeneous photocatalysis, $TOF_{het,app}$ is the number of photocatalytic turnovers, n (see *turnover number*), per unit area and per unit time:

Turnover frequency (turnover rate) in homogeneous photocatalysis, TOF_{hom}, is the number of photocatalytic turnovers, n (see *turnover number*), per unit concentration of the photocatalyst molecules and per unit time:

$$TOF_{hom} = \frac{1}{C} \cdot \frac{dn}{dt} [=] \frac{m^3}{s\ molecule},$$ where C is the concentration of the photocatalyst

Turnover number **in photocatalysis, n, is the number of events that the overall reaction (the photochemical transformation) includes during a photocatalytic cycle.**

Turnover number of a heterogeneous photocatalyst **is the number of photogenerated transformations with respect to the number of active sites of the heterogeneous photocatalyst that is known. When the number of active sites is known, the turnover number can be expressed per unit area.**

Areal turnover number of a heterogeneous photocatalyst **is the number of photogenerated transformations per unit area [BET(N_2)] of the photocatalyst.**

Turnover number of a homogeneous photocatalyst **is the number of photogenerated transformations (per unit volume) divided by the number of the photocatalyst species per unit volume.**

Turnover rate in heterogeneous photocatalysis **is the number of the photocatalytic turnovers, n, per active site and per unit time:**

$$\text{turnover rate} = \frac{1}{N}\cdot\frac{dN}{dt}[=]\frac{1}{(\text{active sites})\ s},$$ **where N is the number of active sites of the photocatalyst**

Areal turnover rate in heterogeneous photocatalysis **is the number of photocatalytic turnovers, n, per the photocatalyst unit area and per unit time:**

$$\text{Areal rate} = \frac{1}{S}\cdot\frac{dn}{dt}[=]\frac{1}{m^2 s},$$ **where S is the surface area (e.g. [BET(N_2)]) of the photocatalyst**

It is evident that the areal turnover rate of a heterogeneous photocatalytic process is equivalent also to the rate of photogenerated transformations per unit surface area of the photocatalyst (see also comments to *turnover number*)

Turnover rate in homogeneous photocatalysis **is the number of the photocatalytic turnovers, n, per unit reaction volume and per unit time:**

$$\text{turnover rate} = \frac{1}{V}\cdot\frac{dn}{dt}[=]\frac{1}{m^3 s},$$ **where V is the total reaction volume**