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Photoreactions occurring on metal-oxide surfaces are not all photocatalytic
Description of criteria and conditions for processes to be photocatalytic

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Abstract

Studies involving the TiO_2-assisted photodegradation of organic substances report that the processes are photocatalytic in nature. Yet, no evidence exists confirming such assertions. Previously, we examined the usage of relative photonic efficiencies [N. Serpone, G. Sauve, 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. Terzian, D. Lawless, P. Kennepohl, G. Sauve, J. Photochem. Photobiol. A: Chem. 73 (1993) 11] to systematize discrepant claims about process efficiencies. An experimental protocol is now available [N. Serpone, A. Salinaro, Pure Appl. Chem. 71 (1999) 303] to measure true Φ in heterogeneous media. Photoinduced reduction of O_2 and photooxidation of H_2 occurring on *oxidized* and *reduced* surfaces of ZrO_2 were recently examined [A.V. Emeline, G.N. Kuzmin, L.L. Basov, N. Serpone, J. Photochem. Photobiol. A: Chem. 174 (2005) 214] to probe the spectral variations of the photoactivity and photo-selectivity of ZrO_2 by determining Φ for the two redox reactions at various wavelengths of photoexcitation ($200 < \lambda < 400$ nm). Irradiation of ZrO_2 in the *intrinsic* absorption region ($\lambda < 260$ nm) led predominantly to photoreduction of O_2, whereas photooxidation of H_2 predominated on irradiation in the *extrinsic* spectral region ($260 < \lambda < 360$ nm). A difficult task in heterogeneous catalysis and photocatalysis is determination of the actual number of active sites, an issue that has heretofore been elusive to assess the (photo)catalytic activity of a given material in heterogeneous solid–liquid and solid–gas (photo)catalysis. A kinetic description of the three turnover quantities, *viz.*, turnover number (TON), turnover rate (TOR) and turnover frequency (TOF) has been described [N. Serpone, A. Salinaro, A.V. Emeline, V.K. Ryabchuk, J. Photochem. Photobiol. A: Chem. 130 (2000) 83], concluding that turnover quantities are conceptually distinct, with TON and TOR requiring knowledge of the number of active sites on the (photo)catalyst's surface. Apparently, turnovers depend on the nature of the active state of the catalyst and how it is described. The number of surface-active sites on the ZrO_2 particle surface have been determined quantitatively ($\sim 10^{16}$ active centers) through thermoprogrammed desorption spectroscopy, affording an estimate of TONs for the photooxidation of H_2 (TON > 14.5) and photoreduction of O_2 (TON > 6.6) on ZrO_2 and demonstrating for the first time that a photoreaction occurring on the surface of a metal oxide is *truly* photocatalytic [A.V. Emeline, A.V. Panasuk, N. Sheremetyeva, N. Serpone, J. Phys. Chem. B 109 (2005) 2785]. Photocoloration of a metal oxide such as ZrO_2 (process of photoinduced formation of Zr^{3+}, F- and V-type color centers) during a surface photochemical reaction was also used to assess whether a reaction is photocatalytic. Our study on the influence of simple photoreactions involving the photoreduction of O_2, photooxidation of H_2, photooxidation of H_2 by adsorbed O_2, and photoinduced transformation of NH_3 and CO_2 on the photocoloration of ZrO_2 concluded that photoreactions involving NH_3 and CO_2 are *non-photocatalytic* processes, in contrast to the photooxidation of H_2 which is *photocatalytic* [A.V. Emeline, G.V. Kataeva, A.V. Panasuk, V.K. Ryabchuk, N.V. Sheremetyeva, N. Serpone, J. Phys. Chem. B 109 (2005) 5175]. In this article, we describe the criteria and conditions by which a photoreaction taking place on the surface of a solid can be said to be photocatalytic by considering both a chemical approach and a physical approach.

Keywords: Photoreactions on metal-oxide surfaces; Photocatalytic processes; Criteria and conditions for photocatalysis; Zirconium dioxide; Titanium dioxide; Photocoloration of metal oxides

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1. Introduction

Photophysical and photochemical processes taking place in heterogeneous systems have been studied (see e.g. refs [1–8]) both intensively and extensively for several decades since the pioneering studies of De Boer [9] and Terenin [10] in the 1930s. The reason for such interest is rather simple: our world is a world of interfaces that are highly affected by the action of Sunlight. Consequently, numerous photostimulated processes in various natural and artificial heterogeneous systems play important roles in our daily lives starting from the origin of life [11] and production of biomass from natural photosynthesis to problems of photosensitivity and photoresistance of modern materials, to formation of self-cleaning surfaces and environmental protection, among others.

As a fundamental and applied (technological) field of science, heterogeneous photochemistry and its analog, heterogeneous photocatalysis, continue to be an important component of modern chemistry in the 21st century. Research in this area has evolved significantly during the last two decades and has enriched the knowledge base with regard to mechanisms, development of new technologies for storage and conversion of solar energy, environmental detoxification of liquid and gaseous ecosystems, and the photochemical production of new materials, to mention but a few.

To date, most research in heterogeneous photocatalysis has been directed at increasing the activity of metal-oxide photocatalysts [12–24] (mostly TiO_2) through optimization of experimental conditions, synthesis of new types of photocatalysts, and through chemical and physical modifications of photocatalysts that includes their sensitivity to visible light through doping the metal oxides with foreign atoms (e.g., N) [25–29]. However, the question as to if and to what extent the photochemical surface reactions reported in hundreds of earlier studies of heterogeneous systems are truly photocatalytic remains a significant unknown in the photocatalytic landscape. Possible approaches to answer this question require first of all a description of what heterogeneous photocatalysis is all about, followed by a definition of major features of a true photocatalytic process. In this regard, in a recently proposed glossary of terms in photocatalysis and radiation catalysis [30], photocatalysis was described as *a change in the rate of chemical reactions or their generation under the action of light in the presence of substances* (*the photocatalysts*) *that absorb light quanta and are involved in chemical transformations of the reaction participants*, and heterogeneous photocatalysis is *photocatalysis taking place at the interfacial boundary between two phases*. Evidently, the meaning of photocatalysis is strongly determined by how one views a photocatalyst, which was taken [30] as the *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*. In this description, the major focus was directed at the chemical features of the process.

In an otherwise alternative approach [6], photocatalysis was considered as a combination of the term *photo*, representing both photophysical and photochemical processes, and *catalysis* that brings the phenomenon of photocatalysis into the wide class of catalytic processes. From this viewpoint, details of the role of physical multi-step processes of photoexcitation and decay of the excited state of the photocatalyst must be considered as is generally done in photochemistry, in addition to chemical reactions typical of catalytic processes.

It must be recognized that separation of a complex process, such as the photocatalytic process, into physical and chemical steps is a rather conditional decision depending, as it were, on one's past experience. This is a productive approach for a better understanding of truly photocatalytic processes from both a chemist's and a physicist's points of view.

2. The chemical approach

As in general catalysis, a complete photocatalytic cycle necessitates some essential criteria and crucial conditions that need to be fulfilled:

(1) In the Langmuir–Hinshelwood (L–H) model of surface photoreactions [31,32] the reagent molecules must be chemisorbed on the photocatalyst surface long enough for adsorbate molecules to undergo the chemical transformation. This condition provides the lifetime of the adsorbed state of such molecules. In the Eley–Rideal (E–R) model, the condition concerns interaction of reagent molecules with the active state(s) of photoinduced surface center(s); this is the fundamental step of photostimulated adsorption (i.e., photoadsorption). In both mechanistic models, however, the energy of adsorption must not be too high, otherwise the adsorbate molecules will be bound to the surface too strongly that might prevent their consequent transformation.

(2) The activation energy barrier for a surface photoreaction must be lower than the corresponding energy barrier of the thermal dark process. This requirement for a photocatalytic process is typically fulfilled by formation of highly active species; for instance, such active species as radicals photogenerated upon photoexcitation of the system leading initially to generation of free electrons and free holes in the conduction and valence bands of the solid, respectively, and to formation of surface excited states that subsequently react with adsorbed molecules of the reagents.

(3) The binding energy of reaction products on the surface formed in the process must be low so that they can easily desorb under ambient conditions, thereby releasing the surface sites occupied during the chemical transformation. This is critical in completing the catalytic cycle and in fulfilling the requirement of chemical restoration of the initial state of the photocatalyst. In some cases, desorption of reaction products can be a photostimulated process, that is a photostimulated desorption (or photodesorption).

Clearly, the third criterion of a photoinduced process is the most crucial for the conclusion of the reaction cycle, if the heterogeneous photoreaction is to be photocatalytic. The first 2 requirements can also be fulfilled for stoichiometric photochemical reactions in heterogeneous systems. The result of such reactions is that, in being involved in chemical interactions with reagent molecules, the solid changes its surface chemical composition. As an example, consider the dissociative photoadsorption of methane on surface-active hole centers to produce methyl radicals and surface OH_S^- groups as the primary products (reactions (1)–(3)). Subsequent recombination of ${}^\bullet CH_3$ radicals results in the formation of higher hydrocarbons (reaction (4); ethane, propane, and others) that subsequently desorb into the gas phase, while the OH^- groups remain on the surface. As a consequence, the surface composition is different after the reaction cycle from the one that existed before the reaction:

$$O_S{}^{2-} + h^+ \rightarrow O_S{}^{\bullet -} \quad (1)$$

$$O_S{}^{\bullet -} + CH_4 \rightarrow \{O_S{}^{\bullet -}{-}CH_4\} \quad (2)$$

$$\{O_S{}^{\bullet -}{-}CH_4\} \rightarrow OH_S{}^- + {}^\bullet CH_3 \quad (3)$$

$${}^\bullet CH_3 + {}^\bullet CH_3 \rightarrow C_2H_6 \quad (4)$$

The surface of the solid becomes hydroxylated. Moreover, active centers are blocked by these hydroxyl groups and cannot be reactivated for the second reaction cycle. Accordingly, such processes cannot be considered as photocatalytic. Note that the first 2 requirements are fulfilled in such heterogeneous photochemical reactions, whereas the third requirement is not since the reaction products, $OH_S{}^-$, remain on the surface and block the active sites. Thus, we conclude that the first 2 criteria are necessary but not sufficient conditions for a photocatalytic process.

Only the realization of all three requirements makes the heterogeneous photoreaction a photocatalytic process. This can be demonstrated by consideration of the well-known classic photolysis of water taking place on the surface of a metal-oxide photocatalyst. Water molecules are easily adsorbed on the surface of most potential (metal-oxide) solid photocatalysts to form hydroxylated surfaces. And because of this adsorptive perturbation, which leads to a stronger polarization of the adsorbed water molecules, such molecules exist in a more reactive state than in the liquid or gas phase. Trapping of photogenerated charge carriers in the solid that results from the absorption of light leads to both reduction (electron trapping) and oxidation (hole trapping) of adsorbed water molecules, provided that the energy levels of the bottom of the conduction band and the top of the valence band lie higher and lower, respectively, than the potentials of reduction and oxidation of water. Thus, photoexcitation of the solid provides the necessary excess energy to initiate the chemical transformations on the solid surface. Finally, the gaseous products of the surface photochemical reaction, namely molecular hydrogen and oxygen, easily desorb with the consequence that the surface sites return to their hydroxylated state, thus completing the reaction cycle and allowing the cycle to be repeated. In such a process, all three criteria described above are fulfilled and the process can then be described as being a photocatalytic process.

In summary, the most important requirement that distinguishes a photocatalytic process from a stoichiometric heterogeneous photoreaction is desorption of the reaction products in order to restore the initial state of the photocatalyst.

Recognition of the fulfillment and role of each criterion in a given photochemical heterogeneous process to assess whether the surface process is photocatalytic requires some very complex and detailed experiments that too often are difficult to perform in typical laboratories concerned mainly with kinetic measurements. Consequently, other means must be found to distinguish between a photocatalytic and a stoichiometric process. Unfortunately, in too many studies photoreactions taking place in heterogeneous systems that involve metal oxides (especially TiO_2) are *a priori* claimed to be photocatalytic without any experimental evidence.

One simple way to characterize a photochemical process as being photocatalytic is measurement of a stationary rate. Indeed, if all three conditions above for a photocatalytic process are satisfied and the corresponding process is shown to be quite effective, the reaction rate should then reach the value corresponding to the stationary state of the system, provided that other experimental conditions (especially, the concentration of reagents) are kept constant. In practice, however, most photocatalytic measurements occur in closed photoreactors in which the concentration of reagent decreases during the photoreaction and thus causes a decrease of the reaction rate in a manner that parallels the L–H dependence on concentration [31–34]. Note that even if the reaction cycle were repeated several times (usually three to five times in most cases) in such closed photoreactor to demonstrate that the reaction kinetics remain the same, this evidence cannot be accepted as proof that the photoprocess is photocatalytic because of reasons described in some detail below (see Section 3). As well, because of secondary reactions the total rate of photoprocesses (typically measured in experiments) can vary during the photoreaction even if the major reaction pathway is photocatalytic and all other experimental conditions are kept constant. Accordingly, demonstration of the time invariance of the reaction rate of photochemical heterogeneous processes cannot always be taken as proof and as a sufficient condition that the reaction is photocatalytic.

The accepted parameter to determine whether a thermal (dark) reaction is catalytic and a photochemical reaction is photocatalytic is the turnover number (TON) of the thermal and photochemical process. In the proposed glossary referred to earlier [30], the turnover number was described to be *the ratio of the number of photoinduced transformations for a given period of time to the number of photocatalytic sites* (*or centers in heterogeneous photocatalysis*). TON is a dimensionless quantity. In photocatalysis TON is attributed to the overall system including the photocatalyst, even if a part of the photocatalyst active centers appear not to be illuminated by the light source. Note that when TON > 1, the (photo)catalytic character of the reaction or process is confirmed, even if one uses the lower limit of TON. That TON is greater than unity indicates that once a molecule has undergone the chemical transformation on a given active center (giving TON = 1), the active center then returns to its original state to initiate the chemical transformation of another fresh molecule ultimately leading to $\mathrm{TON} > 1$, and rendering such a process photocatalytic. In practice, estimation of TON necessitates measurement of the total number of reagent molecules that undergo chemical transformation and the number of active centers on the surface of the solid photocatalyst. In other words, to determine the turnover number TON for a heterogeneous photoreaction, the number of *photocatalytic surface-active centers* (or sites) must be known. This begs the following question: what is an active center in heterogeneous photocatalysis?

Some researchers have suggested that surface-active centers are photogenerated during the heterogeneous photocatalytic reaction and that once the reaction cycle has been completed they switch into inactive surface sites. Clearly, such suggestion is contraproductive, since TON will always be equal to or less than unity with the consequence that there is no such thing as photocatalysis. We cannot over-emphasize that it is the number of *photocatalytic centers* (sites) in the *ground state* (not in the active state) that must be used to determine TON in heterogeneous photocatalysis, just as is done to determine TON in homogeneous photocatalysis in which one considers the total number of photocatalyst molecules and *not* the number of excited molecules. Unfortunately, the number of such catalytic centers often remains elusive in a heterogeneous system that involves particles of solid photocatalysts. Nonetheless, in spite of obvious experimental difficulties, it is possible to assess the number of potential photocatalytic centers for any given heterogeneous system. For instance, if the first step of a photocatalytic reaction is photoadsorption, then the surface concentration of surface-active centers can be taken as equal to the photoadsorption capacity of the photocatalyst, which *can* be measured experimentally [35–37]. Other methods to measure the number of surface-active sites, when photoadsorption is the first step of the photocatalytic cycle, have been reported in a recent article by Emeline et al. [8].

Another approach to determine TON for photochemical reactions is based on the total number of regular surface sites (i.e., surface lattice ions or atoms L). For example, suppose that L is determined to be ca. $10^{19}\ \mathrm{m}^{-2}$ and S (in m^2 units) is the total surface area of the solid photocatalyst, then $L \times S = L_\mathrm{T}$ gives the total number of such potential active sites L_T. Thus, it is possible to define a lower limit of the turnover number TON knowing the magnitude of L_T. This turnover quantity is sometimes referred to by some workers as the *areal turnover number*; however, it is more appropriate to refer to it as the *lower limiting value of TON* [30]. The surface area S can be found, for example, through the specific surface area of the photocatalyst using the well-known BET adsorption isotherm for N_2 or other suitable gases. Thus, the photoreaction can be considered as being photocatalytic as long as the lower limit of TON is greater than unity.

Indirectly, TON also characterizes the activity of photocatalysts. As shown earlier [6], the turnover number TON can be described mathematically by Eq. (5), or when the steady-state in the heterogeneous system has been achieved (that is the quantum yield, Φ, does not change with time) by Eq. (6),

$$\mathrm{TON} = \frac{V\int_{t_1}^{t_2}(\mathrm{d}C/\mathrm{d}t)\,\mathrm{d}t}{s[S_0]} = \mathrm{const}\frac{A\rho\int_{t_1}^{t_2}\Phi\,\mathrm{d}t}{[S_0]} \tag{5}$$

$$\mathrm{TON} = \mathrm{const}\frac{A\rho\Phi t}{[S_0]} \tag{6}$$

where V is the reactor volume; C the concentration of reagent in molecules per unit volume; t the time; s the total surface area of the photocatalyst; S_0 the concentration of surface-active sites in the ground state expressed as the number of sites per unit surface area; A the fraction of light absorbed by the system; ρ is the light irradiance. Since TON is proportional to the quantum yield Φ of the photoreaction, it also reflects the activity of the photocatalyst. In other words, the higher the TON determined for the same time period and under otherwise identical experimental conditions (same light irradiance, ρ) is, the higher is the activity of the photocatalyst.

Unfortunately, as mentioned above, many researchers pay no attention on the verification of the photocatalytic behavior of the heterogeneous system being examined and continue to refer to surface photochemical processes in heterogeneous systems as being photocatalytic. Only a few studies have been devoted to the determination of TON: for liquid–solid heterogeneous systems involving ruthenium complexes [38,39], and for gas–solid heterogeneous systems with deposited transition metal-oxide clusters where the number of active sites is known [40].

In our recent study [8] we explored relatively simple reactions involving the photooxidation of hydrogen by photoadsorbed oxygen and the photoreduction of molecular oxygen. Results of these studies provide a good illustration of the importance of all three conditions for a photocatalytic process (see above) and a demonstration of the photocatalytic behavior of the gas–solid heterogeneous system by determining the corresponding TONs of the photoinduced processes.

We demonstrated that the first step of the heterogeneous reaction was photoadsorption of oxygen on photoinduced electron surface-active centers such as Zr^{3+}, F^{+}, and F centers. Photoadsorbed oxygen exists in at least three different stable forms distinguished by the energy of adsorption (see curve 1, Fig. 1) under the conditions used. All forms are active in the photooxidation of hydrogen. However, their activity toward hydrogen photooxidation is significantly different. The most active form of oxygen, corresponding to the thermodesorption maximum at 120 °C, was formed as a result of adsorption of molecular oxygen on Zr^{3+} surface-active centers, whereas the least active form of oxygen desorbed only at higher temperatures (maximum at 370 °C). This is in accord with the first condition of a photocatalytic process that requires formation of adsorbate complexes on the surface, with chemical transformation taking place more easily with those adsorbed forms of oxygen that possess lower energies of adsorption. Obviously, adsorbed forms of oxygen that desorb at the higher temperature are formed with higher energies of adsorption, and thus manifest a lower activity in the photoreaction, whereas the lower temperature (low energy)

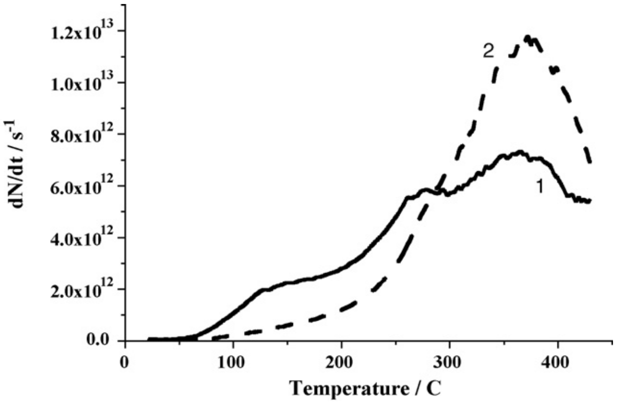

Fig. 1. Thermo-programmed desorption (TPD) spectra of oxygen accumulated at the surface of zirconia during photostimulated adsorption (1) and hydrogen photooxidation (2) after 6000 s of irradiation. Reproduced with permission from Ref. [7] {Copyright 2005 by the American Chemical Society}.

forms demonstrate very high activity. The latter forms of oxygen do not accumulate on the surface during the photoreaction (see curve 2, Fig. 1). The activation energy barrier is greater due to secondary photoexcitation as is typical of photochemical processes. In the dark, all forms of adsorbed oxygen are inactive; additional photoexcitation is required to initiate the photooxidation of hydrogen. As a result of secondary photoexcitations, highly reactive species are formed on the surface of the photocatalyst, namely hydrogen atoms that subsequently attack adsorbed oxygen (reactions (7)–(9)), or by

$$h^+ + O_S{}^{2-} \rightarrow O_S{}^{\bullet -} \qquad (7)$$

$$O_S{}^{\bullet -} + H_2 \rightarrow OH_S{}^- + H^\bullet \qquad (8)$$

$$H^\bullet + O_2{}^-{}_{(ads)} \rightarrow \text{products} \qquad (9)$$

formation of reactive forms of oxygen (e.g., singlet oxygen [40]) as might occur through reaction (10), which then leads to the photooxidation of hydrogen (reaction (11)).

$$O_2{}^-{}_{(ads)} + h^+ \rightarrow O_2{*}_{(ads)} \qquad (10)$$

$$O_2{*}_{(ads)} + H_2 \rightarrow \text{products} \qquad (11)$$

Reaction products (water was the final product detected during thermodesorption [8]) release the surface-active centers and diffuse to other inactive surface sites, so that the active centers become available for further reaction cycles. The release of surface-active centers was confirmed by diffuse reflectance spectroscopy and by determination of $TON > 1$ [7,8]. Thus, the third criterion is also satisfied, albeit only partially. Therefore, on the one hand, the photooxidation of hydrogen is said to be a photocatalytic process since the surface-active centers repeatedly participate in the reaction by restoration of their initial state after completion of the reaction cycle over and over again. And yet as a result of the photooxidation of hydrogen, the surface of the photocatalyst becomes hydroxylated due to a vanishingly small efficiency of desorption of reaction products. This causes changes in the chemical composition of the photocatalyst surface, so that according to the earlier description of photocatalysis such reaction cannot be considered as being photocatalytic. This paradox necessitates a reconsideration of what photocatalysis is, and certain choices need to be made. For instance, when referring to heterogeneous photoreactions as being photocatalytic, what is more important: (a) the chemical restoration of all surface sites of the photocatalyst, or (b) the restoration of surface-active centers only?

Desorption of reaction products is often a major problem in completing the reaction cycle in heterogeneous photocatalysis, particularly in gas–solid heterogeneous systems. Indeed, desorption of products requires the correspondingly suitable energy. In classical thermal (dark) heterogeneous catalysis, desorption is facilitated by carrying out the process at higher temperatures, which are also a necessary condition to activate the catalyst and to overcome the activation energy barrier(s) of the chemical reaction. At the same time, the ability to initiate a chemical transformation under ambient conditions is often considered a major advantage of photocatalysis because an increase in temperature can decrease the photocatalytic activity of photocatalysts as a result of the thermodesorption of pre-adsorbed reagent molecules (note, that in our example of the photooxidation of hydrogen the most active form of oxygen desorbed at 120 °C) and thermodestruction (i.e., thermobleaching) of photoinduced surface-active centers caused by thermoionization. In liquid–solid heterogeneous systems, desorption of reaction products is facilitated by solvation effects.

Hägglund et al. [41] recently reported that hydroxylation of the photocatalyst surface up to one to two monolayers significantly improved the photocatalytic behavior of the photooxidation of propane over TiO_2 by facilitating desorption of the reaction products. However, we should emphasize that such alteration of the photocatalyst's surface state can cause a significant change in product distribution; that is, in the selectivity of photocatalysts that sometimes can prove undesirable. At the same time, we should also note that a heterogeneous system reaches steady-state conditions only after a certain time period (see Fig. 2) when some surface hydroxylation has already happened.

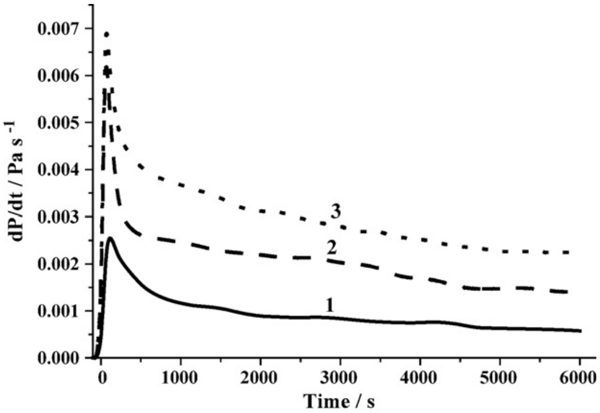

Fig. 2. Time evolution of the rates of changes of partial pressure of oxygen (1), hydrogen (2) and total pressure of gas mixture (3) during the photooxidation of hydrogen over zirconia. Reproduced with permission from Ref [7] {Copyright 2005 by the American Chemical Society}.

Therefore, we should consider the hydroxylated state of the photocatalyst, achieved at a stationary reaction rate, to be restored rather than the initial dehydroxylated state. This is also typical of classical thermal (dark) catalysis when during the initial period of the reaction the surface of the catalyst undergoes some structural changes from relaxation and reconstruction before it reaches the stationary state restored after each catalytic cycle. We will see below that this point of view has some additional supporting evidences from a physical sense as well (Section 3). On the basis of the above considerations, we concluded [8] that the photooxidation of hydrogen occurring over ZrO_2 was indeed a photocatalytic process.

3. The physical approach

To start the discussion about what photochemical process in a heterogeneous photosystem can be considered as being photocatalytic from a physical point of view, we should first recall the description of major pathways of photoexcitation and relaxation taking place in the solid [8,42]. In an ideal solid, the photoexcited state of the solid is produced by absorption of light quanta with energy corresponding to the formation of excitonic states and to band-to-band electron transitions that yield free electrons and free holes in conduction and valence bands, respectively. The relaxation process may involve band-to-band recombination and decay of the excitonic states. Thus, while the thermodynamic state in a non-irradiated ideal solid can be characterized by the position of a unique Fermi level (Fig. 3a), in a photoexcited ideal solid this state is split into two quasi-Fermi levels for electrons and holes, respectively. Therefore, from a thermodynamic point of view (unlike a simple chemical point of view) the photocatalyst in the dark (i.e., in the ground state) and under irradiation (in the excited state) are characterized by different thermodynamic functions that require reconsideration of the following issue: what is the initial state of the photocatalyst that should be restored after completion of the reaction cycle: the ground state or the excited state? According to the description of photocatalysis above, the photocatalyst absorbs light and initiates an interfacial chemical transformation subsequently returning to its initial state.

Obviously, the initial state before light absorption is the ground state of the photocatalyst. The result of an ideal photocatalytic reaction is the return of the photocatalyst to the ground state through external charge transfer processes. Therefore, in the ideal case, the ground state of the photocatalyst must be considered as the initial state and *not* its excited state. This corresponds to the statement made in Section 2 that it is the ground state (not the excited state) of the photocatalyst that must be considered as the initial state to be restored at the completion of the photocatalytic cycle. However, this issue becomes more complex in real solids. A major reason that raises this issue is the photoinduced formation of defects in solids [8,42–47] caused by trapping of photogenerated charge carriers and excitons by intrinsic and extrinsic defects in solids [8,42,46,47], and by the self-trapping of excitons in regular lattice sites of photosensitive solids [44,45]. The corresponding processes are considered photochemical redox reactions in solids that create new defects with higher reduced and/or oxidized states. Examples of such processes are the photoinduced formation of $O^{\bullet -}$ and Ti^{3+} or Zr^{3+} states in titanium and zirconium oxides, respectively [46,47]. Such processes take place regardless of the advent of surface photochemical reactions [8,42,46,47]. Accordingly, a solid photocatalyst typically changes its state (chemical composition) during photoexcitation. Thermodynamically, this corresponds to the creation of quasi-Fermi levels for the photoinduced defects that generally differ from the quasi-Fermi levels of photogenerated free charge carriers (electrons and holes) or from the Fermi level characterizing the ground state. The importance of these processes is dictated by the fact that, after irradiation of wide bandgap photocatalysts, a fraction of photoinduced defects can be preserved for a long, indeed often for an infinite time. Therefore, the solid does not return to its initial ground state and remains in a new metastable excited state. Thus, with photoinduced formation of new defects, the photocatalyst changes its thermodynamic and chemical states, and consequently does not possess the same state as the original state during or after irradiation. This is also a typical situation in heterogeneous catalysis when the stationary state of structure and composition of the catalyst surface during the catalytic process differs from the initial state. Rigorously stated, the photocatalyst retains its original state after photoexcitation *only* in the case of complete relaxation to its original ground state.

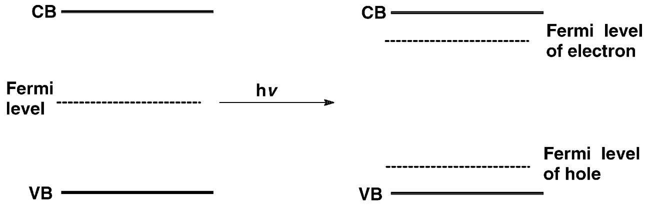

Fig. 3. Scheme illustrating the Fermi levels of a (metal-oxide) semiconductor photocatalyst in the dark and under irradiation.

An example of such relaxation is presented in Fig. 4a, which shows that photoexcitation of the solid specimen results in the generation of free charge carriers (electrons in the conduction band and holes in the valence band) as a result of band-to-band electron transition. Its relaxation occurs through *fast* recombination of charge carriers, either through band-to-band or through specific recombination centers (solid's defects; R). As a result of such a complete recombination relaxation, the photocatalyst restores its original state at the termination of photoexcitation.

However, when relaxation through a recombination pathway is incomplete, the original state of the photocatalyst is not regenerated (Fig. 4b). In this case, the first step of relaxation involves trapping of charge carriers by the solid's defects (e.g., anion and cation vacancies) in a manner otherwise identical to the first step of recombination through recombination centers (Fig. 4a) leading to formation of F- and V-type defects (i.e., the color centers). The subsequent step of recombination of a trapped charge carrier (e.g., electron) with its free counterpart (e.g., hole) is much less effective (dashed arrows, Fig. 4b). This leads to an accumulation of trapped charge carriers, to an incomplete relaxation of the solid, and to a new state of the photocatalyst that differs from the original state.

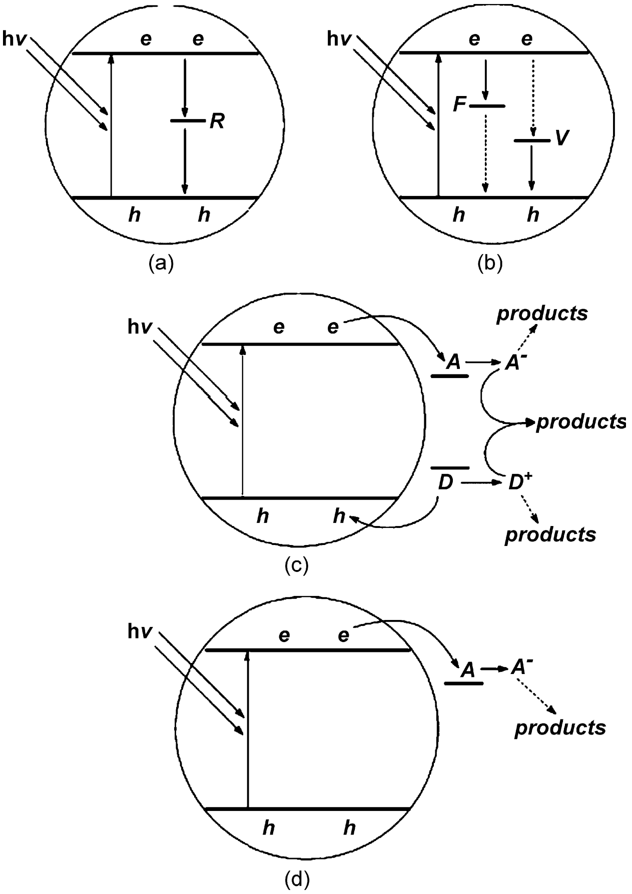

Fig. 4. Schemes illustrating the various possibilities of events that might occur on a (metal-oxide) semiconductor photocatalyst when exposed to suitable photon energies equal to or grater than the bandgap energy (see text for details). Reproduced with permission from Ref. [8] {Copyright 2005 by the American Chemical Society}.

The charge conservation law requires that in the case of complete relaxation there are no trapped charge carriers remaining after termination of irradiation; that is, $[F] = 0$ and $[V] = 0$ (F and V refer to trapped electrons and holes, respectively). For incomplete relaxation $[F] = [V] \neq 0$, and because pre-existing defects in the solid are limited the kinetics of accumulation of trapped carriers become saturated. The level of saturation is determined by the efficiencies of charge carrier trapping and by the decay of trapped carriers through different pathways including recombination with free charge carriers of the opposite sign. Saturation of photocoloration of the metal-oxide specimen is achieved when $\mathrm{d}[F]/\mathrm{d}t = 0$ and $\mathrm{d}[V]/\mathrm{d}t = 0$, where $[F]$ and $[V]$ are given by

$$[F] = \frac{k_{\mathrm{tr(e)}}[\mathrm{e}^-][\mathrm{V_a}]}{(k_{\mathrm{tr(e)}}[\mathrm{e}^-] + k_{\mathrm{r(h)}}[\mathrm{h}^+])} \tag{12}$$

$$[V] = \frac{k_{\mathrm{tr(h)}}[\mathrm{h}^+][\mathrm{V_c}]}{k_{\mathrm{tr(h)}}[\mathrm{h}^+] + k_{\mathrm{r(e)}}[\mathrm{e}^-]} \tag{13}$$

where $k_{\mathrm{tr(e)}}$ and $k_{\mathrm{tr(h)}}$ are the rate constants of trapping of electrons and holes by anion ($\mathrm{V_a}$) and cation ($\mathrm{V_c}$) vacancies, respectively, and $k_{\mathrm{r(h)}}$ and $k_{\mathrm{r(e)}}$ are the rate constants of recombination of free holes and electrons with F- and V-type color centers, respectively. Consequently, photocoloration of the solid specimen prevents the restoration of the original state of the photocatalyst even when no surface reaction occurs. As mentioned above, the rate of accumulation of electron and hole photoinduced defects is a sublinear dependence with saturation. Thus, while the saturation level is not reached, the thermodynamic state and the chemical composition of the photocatalyst undergo changes and reach the stationary state only when the corresponding levels of photocoloration become saturated. Consequently, only this stationary state can be considered as the *initial* state of the photocatalyst possessing the corresponding chemical and physical properties.

The ideal photocatalytic cycle is illustrated in Fig. 4c, which shows that the photocatalyst returns to its original ground state in the same manner as in the case of internal charge carrier recombination. This time, however, relaxation takes place through external surface chemical reaction cycles. In general, it is not necessary for the reaction cycle to be a closed-loop process. It is sufficient that the number of electrons consumed by the electron-acceptor, A, be equal to the number of electrons transferred to the catalyst by the electron-donor molecules, D, provided that the reaction products are not strongly bound to the surface of the catalyst so as not to change the chemical composition of the (metal-oxide) surface. The latter is also true for a photocatalytic process consisting of a closed-loop reaction cycle. In other words, the condition for true photocatalysis is then given by Eq. (14); that is, the rate of the surface reduction reaction must equal the rate of the oxidation reaction.

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{D}]}{\mathrm{d}t} \tag{14}$$

Otherwise, together with the occurrence of the catalytic process, there would also be a non-catalytic secondary surface chemical reaction determined by which half-reaction of the catalytic cycle is the more efficient. In addition, excess charge will accumulate in the solid creating attraction forces between the photocatalyst and intermediate products that often prevent further chemical transformation by blocking active sites. In the extreme case of Fig. 4d, when only one half-reaction takes place on the surface, the heterogeneous photochemical reaction is then stoichiometric and not photocatalytic. The simplest example of such a photochemical reaction is the photoinduced adsorption of molecules on the surface of metal-oxide specimens [8,42,46].

Typically, the fate of charge carriers in a heterogeneous system can be summarized by

$$[\mathrm{e}^-] + [\mathrm{e_R}^-] + [\mathrm{e_{V_a}}^-] + [\mathrm{e_V}^-] + [\mathrm{e_A}^-] = [\mathrm{h}^+] + [\mathrm{h_R}^+] + [\mathrm{h_{V_c}}^+] + [\mathrm{h_F}^+] + [\mathrm{h_D}^+] \tag{15}$$

where $[\mathrm{e}^-]$ and $[\mathrm{h}^+]$ refer to the number of photogenerated free electrons and holes, respectively. Under moderate levels of photoexcitation, these values rapidly become negligible relative to others in Eq. (15). The terms $[\mathrm{e_R}^-]$ and $[\mathrm{h_R}^+]$ represent the number of electrons and holes trapped by the recombination centers, R, and when fast recombination occurs these two quantities are equal and can thus be eliminated from Eq. (15).

By contrast, $[e_{V_a}{}^{-}]$ and $[h_{V_c}{}^{+}]$ denote the number of electrons and holes trapped by the corresponding defect centers (e.g., V_a and V_c) yielding F- and V-type color centers, whereas $[e_V{}^{-}]$ and $[h_F{}^{+}]$ refer to the number of electrons and holes trapped by the corresponding color centers through which complete recombination can occur; $[e_A{}^{-}]$ and $[h_D{}^{-}]$ are the number of electrons and holes involved in surface chemical reactions with acceptor and donor molecules, respectively. Eq. (15) then becomes

$$\{[e_{V_a}{}^{-}]-[h_F{}^{+}]\}+[e_A{}^{-}]=\{[h_{V_c}{}^{+}]-[e_V{}^{-}]\}+[h_D{}^{+}] \qquad (16)$$

or

$$[F]+[e_A{}^{-}]=[V]+[h_D{}^{+}] \qquad (17)$$

since $[e_{V_a}{}^{-}]-[h_F{}^{+}]=[F]$ is the number of photogenerated electron color centers, and $[h_{V_c}{}^{-}]-[e_V{}^{-}]=[V]$ is the number of photogenerated hole color centers. Eq. (17) establishes the correlation between the number of photoinduced color centers and the number of molecules involved in the surface chemical reaction. Clearly, for true photocatalysis (Fig. 4c) in which $[e_A{}^{-}]=[h_D{}^{+}]$, the condition for the photocoloration of the metal-oxide sample is the same with or without a surface reaction; i.e., $[F]=[V]$. However, if the surface photoreaction is not catalytic, that is if $[e_A{}^{-}]\neq[h_D{}^{+}]$, then $[F]\neq[V]$.

A non-photocatalytic surface reaction affects the formation of photoinduced color centers by altering the relationship between electron and hole color centers: i.e., the more pronounced the non-photocatalytic nature of the surface reaction is, the stronger is the deviation of Eq. (17) from equality. This is observed as the influence of photostimulated adsorption on photocoloration when photoadsorption of donor molecules increases the number of electron color centers, whereas photoadsorption of acceptor molecules increases the number of hole color centers [4,8,42]. Accordingly, monitoring the photocoloration of the solid during a surface photochemical reaction provides an opportunity to evaluate whether the surface process is truly photocatalytic and the extent to which it is photocatalytic. Similar conclusions can be made by monitoring the photoluminescence from the solid during an interfacial photoreaction.

Formation of photoinduced defects is caused by trapping of free charge carriers by pre-existing defects that can be accompanied by emission of photons, that is, by luminescence. Hence, the increase or decrease of the rate of formation of defects, caused by surface stoichiometric reactions, should lead to the growth or decay of photoluminescence, whereas during a stationary photocatalytic process the photoluminescence emission intensity will remain at a constant level. However, this level can differ from the one *in vacuo* depending on the extent to which the surface reaction affects the concentration of charge carriers. Also, an additional influence on the stationary level of the photoluminescence might originate from the chemiluminescence that accompanies the surface reaction; for example by the photoinduced chesorluminescence, PhICL, phenomenon [48,49].

To illustrate this discussion we revisit our recent data [42] concerning the formation of photoinduced defects in ZrO_2 during the photocatalytic oxidation of hydrogen and the stoichiometric photoreactions taking place on the surface of zirconia: for example the photoadsorption of oxygen and hydrogen. Both these photoadsorption events are necessary steps, as are the secondary reactions in the oxidation of hydrogen. The relevant data are illustrated in Fig. 5. The initial

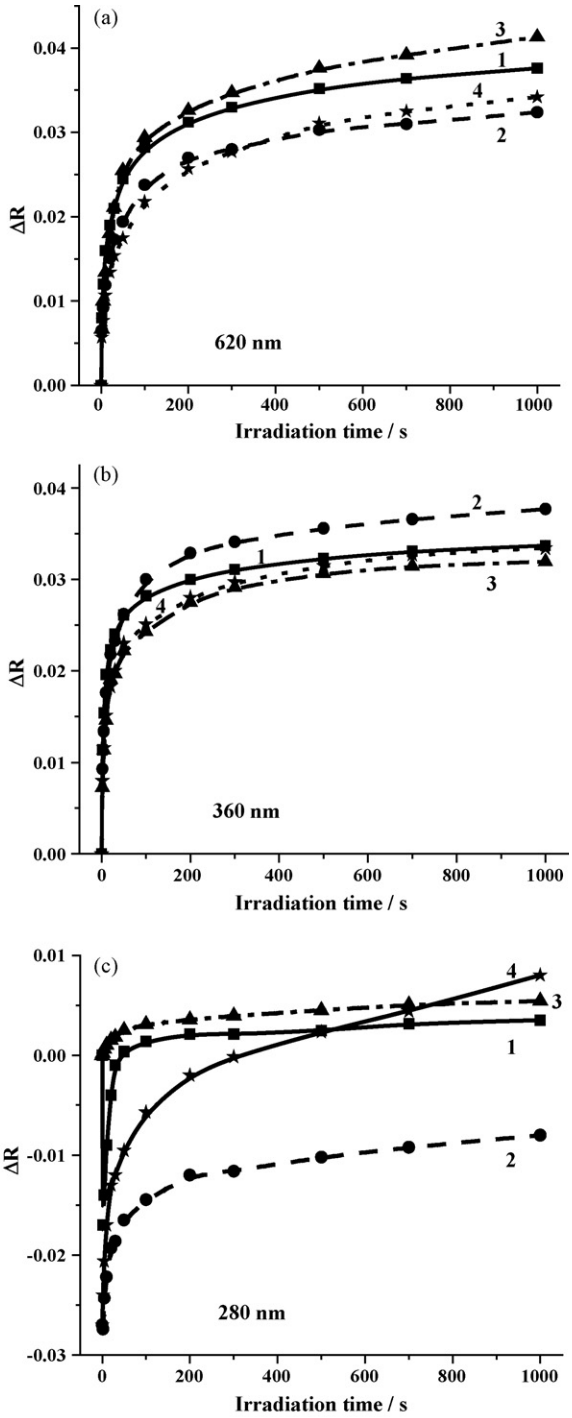

Fig. 5. Kinetics of accumulation of photoinduced (a) F-type color centers, (b) V-type color centers, and (c) Zr^{3+} color centers formed during irradiation of reduced zirconia *in vacuo* (1) and in the presence of oxygen (2) and hydrogen (3), and during the photooxidation of hydrogen (4) recorded at different wavelengths. Reproduced with permission from Ref. [8] {Copyright 2005 by the American Chemical Society}.

period of photocoloration of ZrO_2 *in vacuo* corresponds to the process of establishing the stationary metastable state of the metal-oxide photocatalyst, which is taken as the initial state that is restored upon completion of the photocatalytic cycle, rather than the ground state of the photocatalyst existing before irradiation.

Photoadsorptions of hydrogen and oxygen are typical stoichiometric surface processes, for which TON is unity (TON = 1). They bring about changes of the initial state of the photocatalyst. Indeed, in accordance with Eq. (17), photoadsorption of the electron-acceptor molecular oxygen causes an increase of the concentration of hole color centers and a decrease of electron color centers, whereas photoadsorption of electron-donor molecules of hydrogen leads to the opposite result. In other words, surface stoichiometric photoreactions cause a gradual increase of the mismatch in the photocatalyst between hole and electron color centers deflecting it from the stationary state. The opposite behavior is observed for the photocatalytic oxidation of hydrogen. Initially, when photoadsorption plays the major role, the kinetics of photocoloration are similar to those of photoadsorption. Over an extended period of time, however, when the photocatalytic reaction becomes the dominant process, the level of photocoloration approaches the stationary level of photocatalyst coloration *in vacuo*. In other words, unlike the stoichiometric reaction, the photocatalytic process leads to a decrease of the mismatch between electron and hole color centers in accordance with Eq. (17). It is remarkable that the decrease of such a mismatch during the photocatalytic reaction correlates with the establishment of the stationary rate of the photocatalytic process (Fig. 6).

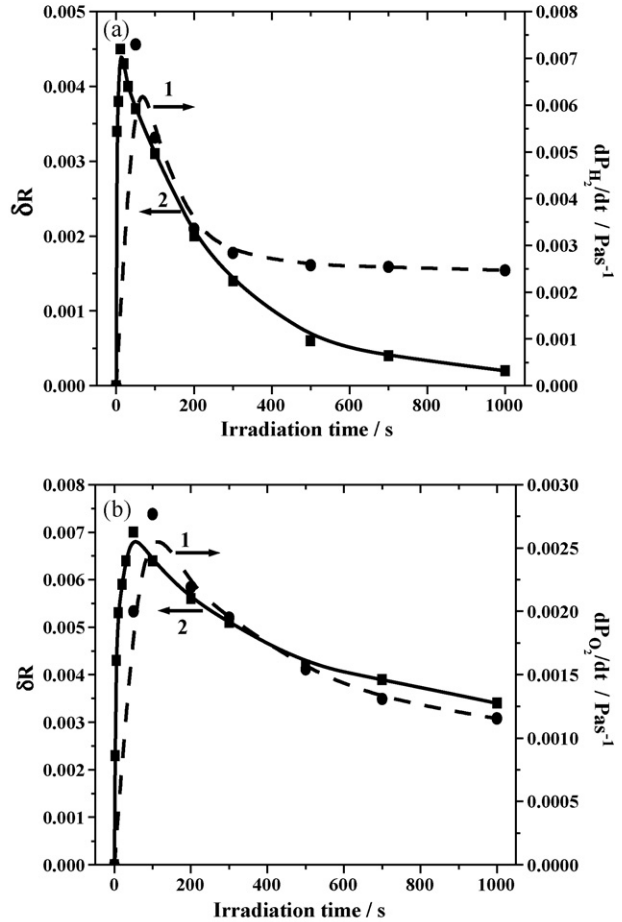

Fig. 6. (a) Time evolution of the rate of hydrogen consumption during the photooxidation of hydrogen (1) and kinetics of difference between accumulation of V-type hole color centers (2) during irradiation of ZrO_2 in hydrogen and in a mixture of oxygen and hydrogen recorded at 360 nm. (b) Time evolution of the rate of oxygen consumption during the photooxidation of hydrogen (1) and kinetics of difference between accumulation of F-type electron color centers (2) during irradiation of ZrO_2 in oxygen and in a mixture of oxygen and hydrogen recorded at 620 nm. Reproduced with permission from Ref. [8] {Copyright 2005 by the American Chemical Society}.

In summary, we conclude that in addition to the chemical composition of the photocatalyst surface, photophysical processes occurring in the photocatalyst must also be taken into consideration when one monitors the state of the photocatalyst. Accordingly, one should be certain that the stationary state of the photoinduced formation of defects has been reached and that it remains constant throughout the photocatalytic reaction. This stationary state can be monitored by a variety of (spectroscopic) methods, for example by diffuse reflectance spectroscopy, electron paramagnetic resonance spectroscopy, and photoluminescence, among others. Any deviation of the corresponding spectral signal from the stationary level points to a stoichiometric surface photochemical reaction playing (probably) a significant role in the overall chemical transformations that are taking place on the surface of the solid.

4. Concluding remarks

The above discussion has shown that the phenomenon referred to as photocatalysis still needs to be defined more precisely. It is also clear that any claim of a photochemical process in a heterogeneous system as being photocatalytic in nature requires strong experimental evidence. No such claims can be made *a priori* on the basis that some solids (e.g., TiO_2) involved in certain reactions behave as photocatalysts. The experimental determination of the turnover number TON (or its lower limit) is a necessary condition to define the heterogeneous photoreaction as being photocatalytic.

It is also important to note that since photoexcitation of solids can cause their transition to other excited metastable states (e.g., formation of photoinduced defects), the physical processes must also be taken into account so as to consider the restoration of the photocatalyst after completion of the reaction cycle. The essential feature of photoinduced defect formation is that the time to reach the stationary level of photocoloration be comparable (within an order of magnitude) to the time of establishing the stationary rate of the photocatalytic reaction. The reason for this is rather simple: so-formed photoinduced defects located on the surface often serve as active centers of surface photoreactions. At the same time, both formation of defects and surface reaction are closely connected to processes occurring in the electronic subsystem of the photocatalyst. Therefore, determination of the photocatalytic nature of an interfacial photochemical reaction in a heterogeneous system requires the monitoring of both the chemical and physical behavior of the photocatalyst. In turn, this means that the complete definition of the terms ''heterogeneous photocatalysis'' and ''photocatalyst'' needs to take into account both chemical and physical processes of photocatalyst transformation.

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