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Rate of photon absorption and turnover number: two parameters for the comparison of heterogeneous photocatalytic systems in a quantitative way

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Abstract

In order to correctly compare the performance of different photocatalytic systems using polycrystalline semiconductor oxides, two parameters are proposed: the rate of photon absorption (rpa) and the turnover number (tn). From these quantities the quantum yield (qy), which indicates the efficiency of the absorbed photons for promoting a reaction event, can be determined. The phenol photodegradation reaction, carried out in aqueous dispersions of polycrystalline TiO_2 (anatase) of different preparation methods and sources, has been used as "test reaction" in order to determine the tn, rpa and qy values.

1. INTRODUCTION

Heterogeneous photocatalysis by aqueous dispersions of particulate semiconductors for the case of pollutants abatement is becoming a field of industrial application [1-3]. Thus the need is felt to report the experimental photoreactivity results in a quantitative and comparable manner. In the present paper two parameters are proposed to be reported: one concerning the amount of absorbed photons and the other the amount of reacted molecules. These parameters are: "the rate of absorbed photons" (rpa) defined as (absorbed photons)/(time•surface area) and the "turnover number" (tn) defined as (reacted molecules/(time•surface area). The determination of the two above mentioned parameters allows one to evaluate the efficiency of a photocatalytic process, for which the knowledge of both the photonic and the catalytic efficiency is necessary.

For both parameters the active sites should be used, but since this parameter is difficult to be experimentally determined, the BET surface area, which is proportional to the active sites, can be used.

A difficult task, so far not generally solved, is the experi-

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mental determination of the absorbed photons by the polycrystalline solids. The intensity of the radiation has been, indeed, reported often as the quantity of the photons leaving the lamp or impinging on the system, without distinguishing the photons really absorbed from those scattered, reflected, or transmitted. For the case of the dispersions of polycrystalline solids directly irradiated, a method has been reported for the determination of the absorbed and reflected photons [4,5]. The method is suitable for application when the particles of the catalyst have dimension far greater than the wavelength of the incident radiation so that the laws of geometrical optics can be applied and the occurrence of Rayleigh and Mie scattering may be excluded [6].

The present paper reports and discuss rpa and tn data obtained for the photocatalytic degradation of phenol carried out in aqueous dispersions containing polycristalline titania anatase from various sources. The determination of rpa and tn was performed by measuring experimental quantities. A photoreactor allowing contemporarely the determination of the rate constant and of the optical parameters was used.

2. ASSESSMENT OF QUANTITATIVE PARAMETERS: RATE OF PHOTON ABSORPTION AND TURNOVER NUMBER

The determination of a reactivity level in heterogeneous photocatalytic systems using semiconductor oxides is to-date a very difficult task. The razionalization in this field is mainly hindered by the lacking of a general agreement on which quantities should be experimentally measured and on which parameters should be determined [4,5].

In thermal heterogeneous catalysis the specific reaction rate, well known as turnover number (tn) and defined as number of molecules reacting per unit time and per active site, is used as basic measure of level of catalytic activity [7]. The validity of this concept is limited by the difficulty of determining the number of the active sites. This difficulty is generally overcome by using the BET surface area instead of the active sites; the assumption of this simplification is that the number of active sites is proportional to the surface area.

The catalyst activity in thermal catalysis is, therefore, evaluated by a "single" parameter, the turnover number. The knowledge of the tn value only requires the experimental determination of molecules reacting per unit time and, for most cases, of the BET surface area.

In heterogeneous photocatalysis the tn quantity is not equally descriptive, however, because it strongly depends upon the irradiation conditions. For the occurrence of a reaction event it is necessary that photons of suitable energy are absorbed by the semiconductor, which usually is in the form of polycrystalline porous particles. A first quantity that must be measured is therefore the rate of photon absorption. Here a first question arises: as the absorption of radiation is a phenomenon occurring through a surface, which part of the particle surface is useful for the absorption of radiation ? Let us call this unknown surface as SAIVC, surface area of the irradiated volume of catalyst. The rpa, which strongly depends on the irradiation conditions as well, is the ratio:

$$\text{rpa} = \frac{\text{absorbed photons}}{\text{time} \cdot \text{SAIVC}}. \tag{1}$$

Once radiation is absorbed, electron-hole pairs are generated if the photon energy equals or exceeds the semiconductor bandgap energy. Three general possibilities exist for the pairs; they can: i) generate thermal energy (recombination); ii) determine a lattice conversion (photocorrosion); or iii) be trapped by suitable surface species, then separated and initiate a reaction sequence with adsorbed surface molecules (photocatalysis). It must be noted that "recombination" and "photocorrosion" are mainly bulk phenomena while "photocatalysis" is only a surface phenomenon. Here a second question arises: which surface is active for the occurrence of a reaction event, i.e. for the trapping of pairs ? Let us call this unknown surface as ASA, active surface area.

On this ground, a second quantity that must be measured is, therefore, the specific reaction rate, i.e. the turnover number, defined as:

$$\text{tn} = \frac{\text{reacted molecules}}{\text{time} \cdot \text{ASA}}. \tag{2}$$

Experimental determination of two quantities, the photon absorption rate (rpa) and the reaction rate (tn), is therefore needed for correctly evaluating the performance of heterogeneous photocatalytic systems. The knowledge of rpa and tn allows one to have also information on the photon efficiency, i.e. on the quantum yield. The quantum yield (qy), defined as:

$$\text{qy} = \frac{\text{reacted molecules}}{\text{absorbed photons}}, \tag{3}$$

gives the quantitative relationship between the number of molecules undergoing a particular process and the number of quanta absorbed by the system. The qy values may be determined by knowing the rpa, tn, SAIVC, and ASA parameters by the following equation:

$$\text{qy} = \frac{\text{tn}}{\text{rpa}} \, \frac{\text{ASA}}{\text{SAIVC}}. \tag{4}$$

Since independent measurements of the absorbed photon flow and of the molecules reacted per unit time may be experimentally performed for the same photoreacting system, it is possible to calculate the quantum yield of the photoreaction by directly applying Eqn. 3, without the knowledge of ASA and SAIVC parameters.

Let us now do some considerations on SAIVC and ASA. For most of the heterogeneous photocatalytic reactions [2] the particle diameters range between 40 and 500 µm. The useful wavelengths range between 200 and 600 nm though, when Pyrex photoreactors and titanium dioxide are used [2], between 300 and 400 nm. Consequently the light scattering phenomenon simplifies as in this circumstance all principles from geometric optics are valid [6]. The irradiated volume of the catalyst depends on the photoreactor features and on the intrinsic optical and geometrical features of the particle. Indeed, depending on the photoreactor type, the amount of irradiated catalyst may differ from the total amount of catalyst. In a fixed bed photoreactor only few layers of particles in the front of the light source can be reached by the radiation; on the contrary, for continuously stirred photoreactors all the particles may have equal probability of being irradiated [8].

Once the radiation reaches the suspended solid particles, the phenomena of reflection, refraction, absorption and transmission may occur. The catalyst particles [9] can be porous or nonporous solids and have different ratios of external and internal surface area. For non-porous materials only the external surface of the particle interacts with radiation. Porous particles of polycrystalline semiconductors present generally micropores (diameter < 2 nm), mesopores (diameter of 2÷50 nm), and macropores (diameter > 50 nm) [9] so that the wavelengths of useful radiation are greater than the average pore diameter. It may be assumed, therefore, that in such circumstance the pore presence does not substancially modify the patterns of the radiation-particle interaction and that photons may be absorbed and electron-hole pairs may be generated only in the external surface area of the particle.

The possibility that molecules adsorbed onto non-irradiated surface can trap the photogenerated pairs depends on the distance that pairs can cover before their recombination. By considering that the diffusivity length of pairs [10] is generally of the order of 1-2 µm, it may be assumed that the "photocatalytic" pairs partecipate to reaction events with molecules adsorbed on the external surface area and on the internal surface area of a spherical shell whose thickness is equal to the pair diffusivity length.

It must be noted that most of the porous photocatalysts, depending on their preparation method, have an external surface area far greater than the internal one. In this case the contribution of the internal surface area to ASA may be negligible and therefore ASA and SAIVC coincide with the external surface area, and thus equation 4 is equal to equation 3.

3. EXPERIMENTAL

3.1. Photodegradation apparatus and procedure

The photoreactor was a Pyrex beacker whose volume was 100 ml. The phenol content was 0.1 g/l and the TiO_2 concentration was 1 g/l. The dispersion was magnetically stirred and was illuminated from the top by a 1500 W Hg-Xe lamp (Hanovia L1573). A volume of 3 ml of dispersion was withdrawn time by time and centrifugated; the phenol concentration was determined by a standard colorimetric method [11]. The phenol photodegradation rate was found of first order with respect to phenol concentration [12-15]. The reactivity results are therefore reported as the first order rate constant, k. Details on the apparatus and procedure can be found elsewhere [4,5].

3.2. Catalysts

Various commercial and home prepared TiO_2 were tested. The commercial specimens (Merck) were used as received. Two different TiO_2 specimens were home prepared [16]. The first one was obtained by reacting an aqueous solution of $TiCl_3$ (15 wt %, Carlo Erba) with an aqueous solution of ammonia (25 wt %, Merck). After standing 24 hours at room temperature, the solid was filtered and washed repeatedly with bidistilled water to remove residual Cl^- ions. The resulting solid was dried in air at 393 K for 24 hours and subsequently underwent a thermal treatment for 3 hours at 873 K. This specimen is designated as TD3. The second specimen was obtained by reacting $TiCl_4$ (Carlo Erba) with pure water at about 278 K and adjusting by NaOH the initial very low pH value up to pH 4.5. The subsequent preparation procedure was the same as for TD3. This second specimen is designated as TD4. All the specimens were sieved and only the fraction with particle sizes in the 40-500 µm range was used.

3.3. Method for determining the absorbed and reflected photons

The measurement of the optical parameters was performed by the actinometer method using ferrioxalate solution [17]. Details on the procedure can be found elsewhere [4,5].

The macroscopic balance of the radiant energy on the dispersion can be set as follows:

$$\Phi_i = \Phi_a + \Phi_r + \Phi_o \tag{5}$$

where Φ_i is the flow of the incident photons, Φ_a is the flow of the absorbed photons, Φ_r is the flow of the reflected photons and Φ_o is the flow of the transmitted photons. This balance equation holds because anelastic light scattering is absent in our case due to the dimensions of the particles used [6,18].

The Φ_i and Φ_o quantities are directly measured. The quantity Φ_r is determined by an extrapolation method consisting either in measuring Φ_o as function of catalyst concentration, maintaining constant the dispersion thickness, or measuring Φ_o as function of the dispersion thickness, maintaining constant the catalyst concentration. Both extrapolation methods gave the same Φ_r value.

The Φ_a value can be easily determined as follows:

$$\Phi_a = \Phi_i - \Phi_o - \Phi_r. \tag{6}$$

4. RESULTS

For the sake of illustrating the proposal outlined in the Introduction, only few representative results, obtained for selected TiO_2 specimens, are reported in Table 1. Quantities concerning some features of the catalysts (origin and BET surface area), of the photocatalytic reaction (rate constant and turnover number), and of the optical properties (reflected and absorbed photons, rate of photon absorption, and the quantum yield) are reported.

Table 1
Some selected actinometer and reactivity results for TiO_2 anatase specimens (particle size distribution between 40-500 μm, incident photon flow, $\Phi_i = 1.55 \cdot 10^{-7}$ einstein/s).

	TiO_2 (Merck)	TiO_2 (Merck)	TiO_2 TD4	TiO_2 TD3
SA	10.5	10.5	26	45
pH	3.0	11.3	3.0	3.0
$\Phi_r \cdot 10^9$	13	120	5	7
$\Phi_a \cdot 10^9$	120	29	132	55
rpa$\cdot 10^8$	22.9	5.5	10.1	2.4
k $\cdot 10^4$	1.2	1.1	2.6	1.3
tn $\cdot 10^8$	1.2	1.2	1.0	0.33
qy $\cdot 10^2$	5	21	10	14

SA, surface area [$m^2 \cdot g^{-1}$]; Φ_r, reflected photon flow [einstein$\cdot s^{-1}$]; Φ_a, absorbed photon flow [einstein$\cdot s^{-1}$]; rpa, rate of photon absorption [einstein$\cdot s^{-1} \cdot m^{-2}$]; k, first order rate constant [s^{-1}]; tn, turnover number [moles$\cdot s^{-1} \cdot m^{-2}$]; qy, quantum yield [moles$\cdot$einstein^{-1}].

From the observation of the data reported in Table 1 it may be noted the strong influence of the interface on the values of the absorbed and reflected photon flow (see TiO_2 Merck at pH 3 and 11.3). It may also be noted the significant variation of all of the quantities reported in the Table 1, despite to the fact that the same TiO_2 phase (anatase) has been used.

5. DISCUSSION

The essential question addressed in this study is: which quantity or quantities are needed to correctly evaluate the efficiency of a heterogeneous photocatalytic process or, in other words, which parameters characterize the "best" photocatalyst ?

In homogeneous photochemistry the quantum yield (qy), defined as "transformed molecules/absorbed photons" is the parameter usually reported. In our opinion, however, the qy parameter alone is not sufficient to evaluate the efficiency of a photocatalytic process. Indeed to this aim the two terms needed to determine qy should be reported separately and, for the case of a dispersion containing polycrystalline particles, also as function of the specific surface area.

In our opinion, from the point of view of photoreactivity, the best photocatalyst is that for which both the specific reaction rate and the quantum yield are maximized. It should be said that the rate of utilization of the absorbed photons should be maximum for the best photocatalyst. Let us to hypothesize the following situation: two different photocatalyst (A and B) exhibit the same specific reaction rate at equal reaction conditions. By investigating the photon balance, it happens that A catalyst reflects photons in a great amount but the absorbed photons are able to promote a great number of reaction events so determining a high qy and a certain reaction rate. The opposite situation occurs for B catalyst which reflects photons in a little amount but the absorbed photons are able to promote a few reaction events so determining a low qy but the same reaction rate of that of A catalyst. Which is the best one ? In our opinion A catalyst should be preferred for its better intrinsic characteristics of photon utilization rate. It may be noted that the reflected photons do not play a role in this context. This is right as the reflected photons depend on external parameters such as the irradiation way and the photoreactor set up.

From similar considerations our proposal of using the term "moles transformed/time•SA", i.e. the tn and the term "moles of absorbed photons/time•SA" i.e. the rpa, steams out. From their ratio the qy can be obtained. Finally it may be observed that while the absorbed photons, in the case of photochemistry, excite directly the molecules which undergo the phototransformation, for the case of heterogeneous photocatalysis they excite the semiconductor particles generating electron-hole pairs. These photoproduced pairs can, upon separation, induce the beginning of the photocatalytic reactions or can recombinate with emission of thermal energy.

Having briefly assessed the principal reasons for proposing the two terms, the rpa and the tn parameters, let us try to apply these quantities to our results.

It was observed that there is a wide spread of the optical and photocatalytic parameters. Indeed this behaviour is partially understandable on the light of a previous study [16] concerning the correlation between the catalyst preparation methods and the photoreactivity for the same photodegradation reaction. In that study it was found also a great spreading of photoreactivity behaviours. Therefore the preparation method influences the physical and chemical properties of the photocatalysts and their interplay determine the final level of activity. The present study shows that also the optical properties are influenced by the preparation methods. Although it is not easy to explain all the reasons of this influence and the present study has not this aim, the knowledge of the optical and photoreactivity parameters allows one to do some interesting considerations.

For instance, if we take the qy parameter as criterion to evaluate the efficiency of the heterogeneous photocatalytic process, then the TiO_2 Merck specimen at pH 11.3 should be chosen as the best. It must be observed that the value of 0.21 comes out from the ratio tn/rpa, which have the numerical values of $1.2 \cdot 10^{-8}$ moles/s•m^2 and $5.5 \cdot 10^{-8}$ einstein/s•m^2, respectively. The same specimen, exhibits at pH 3 the same catalytic activity as that at pH 11.3 ($1.2 \cdot 10^{-8}$ moles/s•m^2) but the value of rpa is exceedingly more high ($22.9 \cdot 10^{-8}$ einstein/s•m^2) and thus the value of qy lowers to 0.05. If, instead of the rpa parameter, the Φ_i parameter (number of incident photons) would have been used, as it is usual, a similar value of qy would have been obtained and the conclusion about the efficiency of the process would have been different (the efficiency is the same at pH 3 and at pH 11.3).

Many other paradoxal conclusions could be reached by the lack of the knowledge of the rpa parameter and by the fact that there is not any apparent correlation between Φ_a and Φ_r. For instance the numerical value of rpa for TD4 is almost double than that of TiO_2 Merck at pH 11.3 and thus the numerical value of qy is half that of TiO_2 Merck at pH 11.3, being the two tn values almost the same (1.2 and $1 \cdot 10^{-8}$ moles/s•m^2). The value of qy for TD3, instead, is similar to that of TD4, but for this catalyst tn is $0.33 \cdot 10^{-8}$ moles/s•m^2 and rpa is almost 1/4 than that of TD4 ($10.1 \cdot 10^{-8}$ einstein/s•m^2). Therefore the choice of qy for evaluating the efficiency of a heterogeneous photocatalytic process is misleading, unless the experimental values of tn and rpa are known.

By concluding, the experimental quantities that must be measured for a photocatalytic system utilizing fine porous particles of a polycrystalline semiconductor oxide are: i) the photons absorbed per unit time; ii) the reacted molecules per unit time; iii) the diffusivity length of photoproduced pairs; iv) the external and internal surface area; and v) the macroscopic aliquot of irradiated catalyst. Information regarding points ii), iii), iv), and v) can be easily obtained by standard techniques reported in the pertinent literature. The knowledge of the diffusivity length is not necessary, obviously, for comparing semiconductor oxides with the same chemical and electronic properties and solids whose internal surface area is negligible.

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