JOURNAL OF CATALYSIS **127**, 332–341 (1991)

An Experimental Method for the Determination of the Photon Flow Reflected and Absorbed by Aqueous Dispersions Containing Polycrystalline Solids in Heterogeneous Photocatalysis

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Received June 23, 1989; revised July 2, 1990

An experimental method for the evaluation of the photon flow reflected and absorbed by aqueous dispersions containing polycrystalline solids is proposed. The method is based on actinometric measurements. It is shown that the values obtained are independent of the particle sizes and of the concentration of the solids at least in the experimental conditions and in the range used in the present study (particle size range: 40–500 μm; solids concentration: 0.1–2 g liter^{-1}). The results suggest that the values obtained should be attributed to the interfaces formed between the surface of the solids and the medium. The method is applied to a photocatalytic reaction, namely to the photodegradation of phenol carried out in a batch system using aqueous dispersions containing TiO_2 or other semiconductors and insulators for comparison. It is also proposed to use separately two parameters for evaluating the photocatalytic efficiency: the "apparent quantum yield" and the "turnover number." © 1991 Academic Press, Inc.

INTRODUCTION

The aim of the present investigation is that of proposing a simple experimental method for the determination of the quantity of photons absorbed by aqueous dispersions containing a polycrystalline semiconductor. The knowledge of such a parameter is of much interest due to the fact that the efficiency of a photocatalytic process must be evaluated on the basis of the absorbed photons, and not, as to-date done, on the basis of the total photon flow entering the photoreactor.

So far the information available in the literature for evaluating this efficiency concerns the type of the lamp, seldom the global photon flow, and the photoreactivity results are reported in various manners as: (reacted molecules)/(unit time · unit mass) or (reacted molecules)/(unit time · unit surface area). The choice of the parameter to which the reactivity is referred is not trivial. In fact the choice of the surface area instead of the mass of the powder may completely change a reactivity order among various catalysts (*1*).

Recently Childs and Ollis (*2*) proposed a parameter called the "photocatalytic turnover number," defined as: (reacted molecules)/(unit time · active sites · absorbed photons), combining the quantum yield as used in photochemistry, and the turnover number as used in thermal catalysis. Due to the difficulty of determining the active sites parameter, it was suggested that the BET surface area, SA, be used instead (*3*), as in thermal catalysis. To our knowledge, the photocatalytic turnover number was never used on account of at least two reasons: (a) the difficulty of determining the amount of absorbed photons and (b) the consideration that this last term has a meaning consistent with the other ones only if it is considered per unit surface area and per unit time and thus the photocatalytic turnover number would reduce to the quantum yield.

The present study proposes a simple experimental method for the evaluation of the number of photons absorbed per unit time

0021-9517/91 $3.00

by a dispersion and recommends the reporting of the essential information on photocatalytic processes by using separately the "turnover number," tn, defined as:

(reacted molecules)/
(unit time · active sites [≡surface area])

and the "apparent quantum yield," qy, defined as:

(reacted molecules)/(absorbed photons).

For the qy, the "reacted molecules" and the "absorbed photons" terms were calculated per unit time.

The use of the turnover number, as above defined, follows the IUPAC proposal (*3*), which suggests the use of the BET surface area instead of the active sites, a parameter which is difficult to determine experimentally. In the present study two values of turnover numbers are used: (a) the value tn_1, calculated according to the above definition; (b) the value tn_2, calculated using, instead of the BET surface area, the number of surface OH^-, likely to be present on the surface of the various photocatalysts and certainly involved in the reaction mechanism (*1–10*).

For the quantum yield, it must be observed that the definition is meaningful to the efficiency of the absorbed quanta only for homogeneous systems, for which the photons are directly absorbed by the reacting molecules themselves.

For heterogeneous systems, as is the case for the present study, the emitted photons are in part scattered, in part absorbed by the solid particles, producing or not a photocatalytic reaction, and in part are transmitted through the dispersion. On this account, in the recent past it was suggested by Teichner and co-workers (*11*) to use the term apparent quantum yield: in their definition, the parameter absorbed photons was substituted by the parameter "photons entering the reactor during a given time."

In the present study, it is demonstrated that, because of the particle sizes used, the scattered photons can be considered reflected and an experimental method for its evaluation is proposed. Since the emitted and transmitted photons are directly measured, the photons absorbed by the dispersions can be easily calculated. Moreover, an unknown fraction of the absorbed photons does not produce photocatalytic reaction; therefore the meaning of the apparent quantum yield used in this study is: "molecules reacted/absorbed photons," both parameters calculated for the same time, it being clear that only a portion of the absorbed photons by the dispersions is photoactive.

The proposed method has been applied to the photocatalytic degradation of phenol, carried out in a batch reactor using an aqueous dispersion of TiO_2 or other semiconductors and insulators irradiated by an Xe lamp, since many features of this reaction have already been investigated (*1, 8–10*).

METHODS

Method for the Determination of Absorbed Photons

The method is essentially based on the actinometric measurements of the photon flow at the entrance and at the exit of the photoreactor. The arrangement of the experimental apparatus is reported in Fig. 1. In a cylindrical frame, the walls of which are covered by mirror-finished aluminum foil, a Pyrex Petri plate containing distilled water (a), a Pyrex beaker containing the reacting dispersion (the photoreactor) (b), and a Pyrex Petri plate containing the actinometric solution (c), were positioned in direct contact. The distance between the lamp and the upper Petri plate was 12 cm. This set-up and the lamp were contained in a box.

The balance of the photon flow on the photoreactor, expressed as einsteins · s^{-1}, can be set as follows:

$$\phi_i = \phi_a + \phi_r + \phi_o, \qquad (1)$$

where ϕ_i are moles of photons per second entering the photoreactor, ϕ_a moles of photons per second absorbed by the dispersion, ϕ_r moles of photons per second reflected,

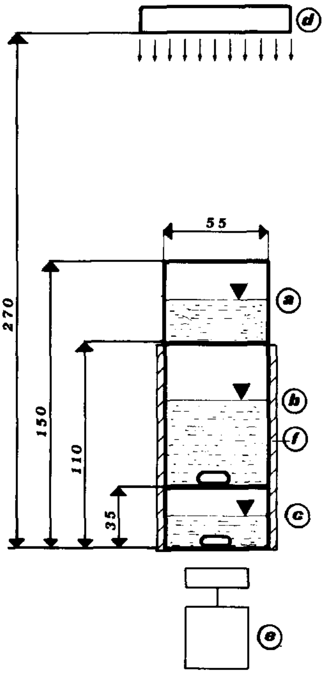

FIG. 1. Experimental setup: (a) Petri plate containing distilled water; (b) Pyrex beaker containing the reacting dispersion; (c) Petri plate containing the actinometer solution; (d) lamp; (e) magnetic stirrer; (f) aluminum foil. Numbers indicate distances in millimeters.

and ϕ_o moles of photons per second transmitted by the photoreactor. It must be reported that the particle sizes used in the present investigation ranged from 40 to 500 μm and the radiation available for the photoprocess, as shown later, had a wavelength range from 300 to 400 nm. In this situation, the scattering effects can be chiefly considered as specular and diffuse reflection processes (*12*). Thus in Eq. (1) the Rayleigh and Mie scattering, due to small and intermediate particles, have been neglected (*12, 13*). Therefore the term ϕ_r is designated as flow of reflected photons in the following discussion.

Equation (1) holds strictly only for monochromatic radiation. In our case, since the range of radiation used is short, its validity can be assumed.

For the evaluation of the ϕ_r term, the following procedure was employed. A series of different values of ϕ_o were measured at different volumes of the dispersion by maintaining constant the TiO_2 concentration, and all of the other conditions. By plotting the ϕ_o values versus the thickness of the dispersion layer, an exponential curve fitted the data very well. The value of the ordinate at height equal to zero is considered proportional to ϕ_r.

Indeed, for the limiting condition of zero thickness of the dispersion layer, it can be assumed that $\phi_a = 0$, and therefore ϕ_r can be calculated from Eq. (1) as

$$\phi_r = \phi_i - \phi_{o,(s=0)}, \qquad (2)$$

where ϕ_r is the flow of photons reflected by a given dispersion for the given set-up and $\phi_{o,(s=0)}$ is the flow of photons transmitted by the dispersion with height equal to zero.

For testing if the values of ϕ_r determined with the aforementioned method were dependent, or not, on the powder concentration, another procedure for determining ϕ_r was used. It consisted in measuring ϕ_o for dispersions having the same thickness, but containing increasing amounts of the catalyst (from 0.1 to 2 $g \cdot liter^{-1}$) while maintaining constant all the other operative conditions of the dispersions. By plotting ϕ_o versus the powder mass, an exponential relationship between ϕ_o and the mass was best fitted through the data. The extrapolation of this relationship to zero mass gave a similar value of ϕ_r, as for the first method. This aspect was checked for various powders and was found to hold in all cases; therefore the determination of ϕ_r for all of the specimens was carried out with the first method, i.e., by measuring ϕ_o vs thickness of the dispersion at a constant powder concentration. From the knowledge of ϕ_r the values of ϕ_a are easily computed by Eq. (1). In this equation it must be considered that: (a) ϕ_i, directly measured, is a constant parameter for the given lamp configuration and cell arrangements; (b) ϕ_r represents the photon flow reflected by the dispersion contained in the defined photoreactor, and thus in this situation it is also a constant parameter; and

(c) ϕ_o, directly measured, is the photon flow transmitted through the dispersion contained in the defined photoreactor. If we recall that the photoreactor used (see below in the photodegradation experiments section) for all the photodegradation experiments was a 50-ml Pyrex beaker, and that the concentration of TiO_2 in the dispersion was always 1 g liter^{-1}, then ϕ_a is the photon flow absorbed by that dispersion contained in that photoreactor. While further considerations on the meaning of ϕ_a and ϕ_r are made in the discussion, it is useful to point out that the methods used for determining ϕ_r (ϕ_o vs height or ϕ_o vs mass of the catalyst) allow measurement of ϕ_a and ϕ_o for any concentration of TiO_2 varying from 0.1 to 2 g liter^{-1}.

Photodegradation Experiments

The photoreactor, (b), in Fig. 1, was filled with 50 ml of dispersion always having the following features: pH 3, phenol concentration 0.1 g liter^{-1}, catalyst concentration 1 g liter^{-1}. The dispersion was magnetically stirred and oxygen was bubbled for 10 min before the run. It was checked experimentally that the stirring speed did not affect the results provided that precaution was taken to avoid vortex formation. This dispersion is indicated as "standard dispersion" later in the text.

The duration of each run was 30 minutes, samples of 3 ml of the dispersion being withdrawn for analysis of the phenol at each 5 min interval (1). The dispersion was irradiated by a 1500 W Xe lamp: the entire system was kept in a Solarbox (CO.FO.ME.GRA., Milan) where the temperature was 313 K.

Actinometry Experiments

The actinometric solution was of the standard ferrioxalate type, prepared as described in the literature (*14*). The concentrations of the various reactants were selected to obtain an absorption spectrum of the solution such as to overlap as much as possible the $(1 - R'_\infty)$ spectrum of TiO_2. The actinometric runs lasted 2 min. The volume of the actinometric solution was 20 ml and was contained in the Petri plate, (c), of Fig. 1.

ϕ_i was measured with the photoreactor filled with distilled water or with phenol solutions at pH 3 and pH 11.3: in all cases the ϕ_i values were the same (1.55×10^{-4} einsteins s^{-1}), indicating that the phenolic solution, at least at the low concentration used, does not behave as an absorbing medium in our experimental conditions. The ϕ_i value was also the same when the actinometer was kept just below the Petri plate, (a), of Fig. 1, containing water.

ϕ_o was measured having the photoreactor filled with the dispersion.

For the evaluation of ϕ_r of the standard dispersions, actinometric experiments were performed by gradually varying the volume of the dispersion from 10 to 100 ml in not less than 10 steps. A few experiments for determining ϕ_r for other semiconductor and insulator specimens were carried out at various pH values, maintaining constant all of the other parameters.

For calculating the number of photodegraded phenol molecules to be used in qy and tn, the following procedure was applied:

—the rate of photodegradation was calculated from the photocatalytic experiments which, as stated, lasted 30 min;

—from this rate, the number of phenol molecules photodegraded in 2 min was calculated and used for the evaluation of qy and tn, since ϕ_a is obtained by actinometric experiments which lasted 2 min.

UV-Vis Measurements

All absorption measurements for the actinometric experiments, and for the phenol determination, were performed on a Varian UV-Vis DMS 90 apparatus. Also the reflectance spectra were recorded on the same apparatus equipped with an integrating sphere and using $BaSO_4$ as reference.

Catalysts

Several commercial and home-prepared TiO_2 specimens, all of the anatase modification, were used. The home-prepared (hp) specimens were obtained by two different methods: one, from $TiCl_3$ solutions, designated as TD3, and the other from $TiCl_4$ solutions, designated as TD4. Details of the preparations can be found elsewhere (*1*). The dimensions of the particles were in the 40–500 μm range, as determined by sieving. In some selected experiments specimens with particles having a narrower range of dimensions were used.

For special experiments for the determination of ϕ_r, commercial semiconductors and insulators were used. They were ZnO (Höechst), $BaSO_4$ (Carlo Erba) fired for 48 h at 1073 K, SiO_2 (BDH) fired for 48 h at 973 K, SiO_2 (BDH) fired for 48 h at 973 and successively for 168 h at 1273 K, MgO (Merck) fired for 48 h at 1073 K, MgO (Merck) fired for 48 h at 1073 K and successively fired for 168 h at 1273 K, TiO_2 (Tioxide, rutile).

RESULTS

Assessment of the Radiation Wavelength Range

Due to the band-gap energy of TiO_2 (anatase), 3.2 eV, the upper limit of the radiation useful for the excitation is about 400 nm. Moreover, since a water Pyrex filter was kept between the lamp and the photoreactor, the infrared radiation and the radiation having wavelengths lower than 300 nm were removed. Therefore the radiation available for the photoprocess was in the range 300–400 nm.

The actinometric solution was prepared in such a way as to measure photons in the wavelength range 300–400 nm, as is clear from Fig. 2, where the $(1 - R'_\infty)$ spectrum of TiO_2 and the absorption spectrum of the actinometric solution are reported. It is notable that they match fairly well.

Influence of the Particle Size on the Light Transmission

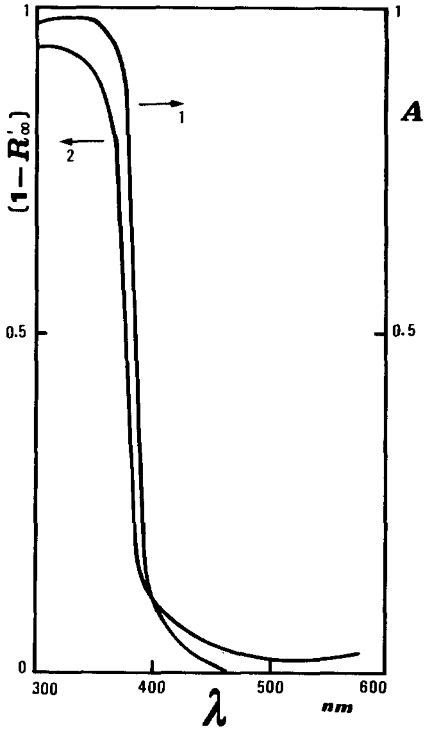

FIG. 2. Absorbance spectrum (1) of the actinometer solution, as A vs wavelength and diffuse reflectance spectrum (2) of TiO_2 (BDH) specimen, as $1 - R'_\infty$ vs wavelength.

The specimens used throughout this study had particle sizes ranging from 40 to 500 μm, determined by sieving. To study the influence of the particle sizes on the light transmission, two experiments were carried out in which ϕ_0 was measured as function of two selected size ranges while maintaining constant the mass of the catalyst, the thickness of the dispersion, and all of the other operating conditions. The selected sizes were in the 40–60 μm and 400–500 μm ranges and ϕ_0 was found to be the same for both experiments, showing that the particle size of our specimens, in the experimental conditions used, does not affect the light transmission. Thus most experiments were carried out with powders not having selected particle sizes.

Determination of ϕ_r and ϕ_a

Two sets of experiments were carried out:

(a) using several specimens of anatase, not

TABLE 1

Actinometer and Photocatalytic Results for Some Commercial and Home-Prepared TiO_2 (Anatase) Specimens (Size of Particles: 40–500 μm) at pH 3

Anatase catalysts	SA ($m^2\ g^{-1}$)	$\phi_r \times 10^6$ (einsteins s^{-1})	$\phi_a \times 10^6$ (einsteins s^{-1})	$k_{C_6H_5OH} \times 10^4$ (s^{-1})	qy $\times 10^4$ (moles · einsteins^{-1})	$tn_1 \times 10^{-15}$ (molecules · $s^{-1}\ m^{-2}$)	$tn_2 \times 10^4$ (molecules · $s^{-1}\ OH^{-1}$)
Tioxide	14	7 (4.5%)	134 (87%)	1.8	0.7	8	16
TD4	26	5.4 (3.5%)	132 (85%)	2.6	1	6	13
Merck	10	13 (8.5%)	120 (77%)	1.2	0.5	7	13
Carlo Erba	5	36 (23%)	107 (69%)	0.8	0.4	10	19
B5 Montedison	22	15 (10%)	71 (46%)	1.0	0.6	3	5
TD3	45	7 (4.5%)	55 (35%)	1.3	1.3	2	4
BDH	10	115 (74%)	38 (24%)	1.7	2.4	11	21

Note. SA, surface area; ϕ_r, moles of photons per second reflected by the dispersion; ϕ_a, moles of photons per second absorbed by the dispersion; $k_{C_6H_5OH}$, rate constant. The qy and tn values have been calculated for a dispersion with a powder concentration of 1 g · liter^{-1}.

having selected sizes, with the aim of determining ϕ_r for the standard dispersions;

(b) using several semiconductor and insulator oxides with selected sizes (90–106 μm) at various pH values with the aim of checking the sensitivity of the method and of better understanding the meaning of ϕ_r.

The results for the two series of experiments are reported in Tables 1 and 2, respectively. Tables 1 and 2 also report, in parentheses together with the ϕ_r and ϕ_a data, the values of the percentages of reflection and absorption by the dispersion, i.e., the ϕ_r/ϕ_i and ϕ_a/ϕ_i ratios. The observations in Table 1 provide information of a large variation of ϕ_r and ϕ_a: the percentage of absorption varies from 24% for the BDH specimen to 87% for the Tioxide specimen.

From the observations in Table 2 various considerations can be drawn: (a) for the semiconductors, the ϕ_r and ϕ_a values are somewhat sensitive to pH values; note the very low ϕ_a value at pH 11.3 for TiO_2 (Merck) specimen. For the other two semiconductor specimens, the decrease of ϕ_a at pH 11.3 is less pronounced; (b) the ϕ_r and ϕ_a values obtained for the insulator oxides are insensitive to the pH variation. Two specimens (SiO_2 and $BaSO_4$) do not exhibit reflection at all, while the third insulator investigated (MgO) shows small reflecting properties which are unaffected by the pH variation. Note also that the ϕ_a values, except for the $BaSO_4$ specimen, for the other two insulators are of the order of magnitude similar to those obtained for some semiconductors.

Photocatalytic Degradation of Phenol

The photodegradation results are reported in Tables 1 and 2 as the values of the rate constant, $k_{C_6H_5OH}$, of this photoreaction. The photodegradation reaction showed always pseudo-first-order kinetics with respect to phenol concentration. The discussion on this aspect and on the validity of $k_{C_6H_5OH}$ for expressing the photoreactivity of specimens tested in the same experimental conditions can be found elsewhere (*7–10*).

The qy values represent the light efficiency; the tn_1 values indicate the number of molecules photodegraded per second and per unit square meter, while the tn_2 values indicate the number of molecules photodegraded per second and per OH^- group. The OH^- groups were considered to be 5×10^{18} per square meter (*15*).

The results of Table 1 show that there is not a simple correlation within ϕ_r, ϕ_a, $k_{C_6H_5OH}$, qy, and tn. It can be noted that the light efficiency, i.e., the molecules photodegraded per photon absorbed by the dispersion, is of the order of about 1 molecule photodegraded per 10^4 photons. It is worth reporting that there is no direct correlation between ϕ_a and qy; in fact the least absorb-

TABLE 2

Actinometer and Photocatalytic Results for Commercial Semiconductor and Insulator Specimens

Catalysts	pH	SA ($m^2 \cdot g^{-1}$)	$\phi_r \times 10^6$ (einsteins s^{-1})	$\phi_a \times 10^6$ (einsteins s^{-1})	$k_{C_6H_5OH} \times 10^4$ (s^{-1})
TiO_2 Merck	3	10	14 (9%)	114 (73.5%)	1.2
	7	10	14 (9%)	114 (73.5%)	1.1
	8	10	18 (12%)	118 (76%)	1.1
	11.3	10	120 (77%)	29 (19%)	1.1
ZnO Höechst	3	4	0 (0%)	128 (83%)	4.1
	8	4	0 (0%)	136 (88%)	4.6
	11.3	4	20 (13%)	113 (73%)	2.9
TiO_2 Tioxide, rutile	3	20	31 (20%)	124 (80%)	0
	8	20	40 (25%)	115 (75%)	0
	11.3	20	39 (25%)	116 (75%)	0
$BaSO_4$ C.E.	3	1	0 (0%)	15 (10%)	0
1073 K, 48 h	7	1	0 (0%)	15 (10%)	0
	11.3	1	0 (0%)	15 (10%)	0
SiO_2 BDH	3	127	0 (0%)	57 (37%)	0
973 K, 48 h	11.3	127	0 (0%)	59 (38%)	0
MgO Merck	3	16	23 (15%)	77 (50%)	0
1073 K, 48 h	11.3	16	21 (14%)	78 (50%)	0
SiO_2 BDH	3	85	0 (0%)	41 (27%)	0
973 K, 48 h and 1273 K, 168 h	11.3	85	0 (0%)	56 (36%)	0
MgO Merck	3	15	13 (8.6%)	75 (48%)	0
1073 K, 48 h and 1273 K, 168 h	11.3	15	12 (7.7%)	69 (45%)	0

Note. SA, surface area; ϕ_r, moles of photons per second reflected by the dispersion; ϕ_a, moles of photons per second absorbed by the dispersion; $k_{C_6H_5OH}$, rate constant at various pH for the same solids (particle size 90–106 μm).

ing specimen, BDH, has the highest qy value.

Similarly the catalytic efficiency can be expressed as varying from about 2×10^{15} to 10^{16} molecules photodegraded per second and per m^2 or varying from 4×10^{-4} to 20×10^{-4} molecules photodegraded per one OH^- group per second. The results reported in Table 2 confirm that the insulators are photoinactive, that ZnO is more photoactive than TiO_2 (*8*), and that the photoactivity of the semiconductors are pH sensitive (*1, 8*).

DISCUSSION

Determination of ϕ_r and ϕ_a

The key point of the present study is the method used for the determination of ϕ_r, and consequently of ϕ_a, and the meaning to be given to both parameters. The determination of ϕ_r is based on the assumption that, when the mass of the catalyst is reduced to the limit value of zero, the rate of photons absorption is also zero and that the rate of photons leaving the upper boundary plane of the dispersion is largely determined by the reflection occurring on the top layers of particles of the dispersion. The assumption that ϕ_a is zero in the limit conditions of mass zero is quite likely, while the assumption that ϕ_r can be evaluated by this method and that it is not (or little) affected by the photons reflected backward from the internal layers requires some consideration. The variation of ϕ_o vs the thickness or ϕ_o vs the mass of the catalyst is expressed by an equation similar to the Lambert–Beer law:

$$\phi_o = \phi_{o,(s=0)} \exp(-km), \qquad (3)$$

where $\phi_{o,(s=0)}$ is the photon flow transmitted when the mass (m) has the limit value of zero.

Note that $\phi_{o,(s=0)}$ in this limiting condition, should be equal to ϕ_i, but in most cases it was found that $\phi_{o,(s=0)}$ is less than ϕ_i. In such cases the balance, in our view, is due to the reflected photons and Eq. (2) can be applied.

For the few cases in which $\phi_{o,(s=0)}$ was found to be almost the same as ϕ_i, ϕ_r is negligible (see in Table 2 the specimens ZnO at pH 3, 8 and $BaSO_4$, SiO_2 at any pH).

As for the contribution to ϕ_r of the photons reflected from the internal layers, when the diameter of the particles is large compared with the wavelength of the incident radiation, as in the present case, the scattering in the forward direction (downward) is more important than that in the backward direction, and more precisely the most relevant effect in the backward direction occurs for a scattering angle θ equal to 180° (*12, 13*).

Therefore ϕ_r, evaluated with the proposed method, represents, to a good approximation, the photon flow reflected, as a first event, by the very top layers of the dispersions.

As for the meaning of ϕ_a, as stated in the Introduction, a portion of the absorbed photons is wasted and does not produce any photocatalytic reaction. This is due to the fact that the electron-hole pairs produced by the photoexcited semiconductor can: (a) recombine producing thermal energy; (b) react with the components of the oxidic semiconductor causing photocorrosion; (c) react with suitable adsorbed species, thus producing the photocatalytic reaction.

Moreover it is worth noting that the ϕ_a value includes directly absorbed photons and photons which, as a first event, are not absorbed, but are reflected in multiple ways before final absorption.

As for the chemical meaning of ϕ_a and ϕ_r, the results suggest that these parameters represent the moles of photons per second absorbed and reflected by the interface formed between the surface of the particles and the medium, and not by the bare surfaces. If the ϕ_a and ϕ_r values were due to the bare surfaces, at least the anatase specimens should give similar values of ϕ_a and ϕ_r. The great variability of ϕ_a and ϕ_r observed for these specimens is due to interfaces which have different absorbing and reflecting properties, thus stressing the point that the interface is mainly responsible for the absorbing and reflecting features. Indeed, by changing the properties of the medium, a more or less sensible change of ϕ_a and ϕ_r is observed for the semiconductors, while for the insulators this variation is not observed as their values are fairly constant. The behavior of ϕ_r for the insulators underlines even more the hypothesis that the reflecting and absorbing properties, as measured by this method, are due to the interfaces. Indeed, for instance, it is well known that "dry" $BaSO_4$ is often used as reference material in the integrating sphere of the reflectance spectrophotometer for its very high reflecting properties. The likely explanation of the experimental results that ϕ_r is almost zero for this material is that the actual interface formed between its surface and the medium no longer exhibits the reflecting properties of the "dry" $BaSO_4$.

It is not easy to describe the nature of the interfaces for each specimen and their role in the absorbing and reflecting mechanisms: both problems are outside the aim of this study. However, by considering that the medium is formed by an aqueous solution containing a variety of species (H^+, OH^-, phenol, phenate, etc.) whose ratio varies with the pH, the results seem to indicate that for the semiconductors the increase of pH improves the reflecting properties and consequently depresses the absorbing properties. The results obtained with the insulators seem to suggest that the properties of the interfaces are not influenced by changing the pH of the medium. Note also that if the values of the surface area (Table 2, specimens SiO_2 and MgO) are changed, the features of the formed interfaces are not very affected; i.e., similar ϕ_a values are obtained for specimens having different surface areas. The difference in behavior of semiconductors and insulators probably reflects their different chemical and electronic natures.

Photocatalytic Reactivity

A clear indication of the efficiency of the light for the photocatalytic reactivity is given by the values of ϕ_a and qy reported in Table 1. The least absorbing specimen, BDH anatase, exhibits the highest qy value. The obvious consideration is that the recombination rate of the hole-electron pairs is different for each specimen, showing a very low value for the BDH specimen, so that its absorbed photons behave very efficiently.

The TD3 and TD4 specimens, prepared by different methods, exhibit very different ϕ_a values, while the qy values are similar. The indication is therefore that the preparation methods affect not only the absorbing properties but also the rate of recombination of the photoproduced pairs. It was reported (*1*) that different physicochemical properties of the surfaces induced by preparation methods may determine different photocatalytic behaviors for this same reaction carried out over several catalysts prepared in different ways.

The present study shows that, among other reasons, the absorbing capacity and the efficiency of the pairs are also dependent on the preparation methods.

As for the catalytic behavior exhibited by the various solids for the photodegradation process, the $k_{C_6H_5OH}$, the tn_1, and tn_2 values give several kinds of information. As already observed and reported, TiO_2 rutile and all the insulator compounds were found to be inactive: the reason for this behavior as well as the high activity shown by the ZnO specimen (*1, 8–10*), has been discussed. For the anatase specimens, a large spread of values is found suggesting that the properties of the surfaces and the nature of OH groups are very different. A thorough discussion on these aspects can be found elsewhere (*1*). Here it is useful to note that the BDH specimen, which has the lowest ϕ_a value, has not only the highest qy value, but also the highest tn_1 and tn_2 values, exhibiting the best light and catalytic efficiencies among the studied solids.

The set of two specimens (B5 and TD3), which have also a low value of ϕ_a exhibited very low tn_1 and tn_2 values, in contrast to the BDH specimens.

The set of four specimens (Tioxide, TD4, Merck, Carlo Erba), which have the highest ϕ_a value, exhibited also high tn_1 and tn_2 values.

Therefore, it seems that, apart for the peculiar behavior of the BDH specimen, a direct correlation exists between absorbed photons and catalytic behavior. It is not an aim of this study to go deeper in this direction.

CONCLUSION

The proposed method allows one to measure experimentally ϕ_i and ϕ_o and to evaluate ϕ_r and ϕ_a. These latter parameters can be used to evaluate the light and catalytic efficiencies for a given photocatalytic process, determining the apparent quantum yield and the turnover number.

The point must be stressed that ϕ_r and ϕ_a values are attributed to the actual interfaces formed between the surfaces of the solids and the medium.

While the method can be of widespread use for aqueous dispersions, the values ϕ_i, ϕ_o, ϕ_r, and ϕ_a can be applied to a particular dispersion used in a particular set-up. Standardization of the apparatus should therefore allow one to obtain values to be used on a comparable scale.

ACKNOWLEDGMENT

The authors thank Ministero della Pubblica Istruzione (Roma) for financial support.

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