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A Proposal for the Quantitative Assessment of Heterogeneous Photocatalytic Processes

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A critical assessment of the parameters needed for the correct comparison of activity and efficiency of various heterogeneous photocatalytic systems is presented in the present paper. Two parameters are to be evaluated in order to compare different photocatalytic systems. The first parameter, the "intrinsic reaction rate" (ri), allows one to have information on the specific catalytic reactivity, while the second one, the "rate of photon absorption" (rpa), allows the evaluation of the capacity of absorbing photons. From the knowledge of these two parameters 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 (anatase) TiO_2, has been used as a test reaction in order to determine the ri, rpa, and qy values of powdered specimens from different preparation methods and sources. © 1993 Academic Press, Inc.

INTRODUCTION

Heterogeneous photocatalysis by semiconductors is becoming a field of extensive basic and applied research (*1–6*). Several experimental quantities need to be accurately determined in order to acquire sufficient knowledge of the photocatalytic processes to allow a correct determination of their efficiency. The literature reports abundant and useful information for homogeneous systems, while for heterogeneous ones the information is to-date lacking. For heterogeneous systems, so far, the performances of the photocatalysts are difficult to assess because of the lack of a general agreement on which experimental parameters should be determined. In principle, two pieces of information are needed: one is related to the catalytic efficiency and the other to the photon efficiency.

The performance of homogeneous photochemical and photocatalytic processes is generally evaluated by the quantum yield (qy); this parameter informs one about the chemical events induced by the photons absorbed by the homogeneous system. The determination of the quantum yield implies the experimental measurement of the specific rates of reaction and of photon absorption.

In thermal catalysis the reaction rate is expressed by the turnover number (or, more strictly, the turnover frequency) (*7*); in the absence of diffusional limitations on the process, this quantity allows one to correctly compare the activity of different catalysts.

The situation of heterogeneous photocatalysis stands between thermal catalysis and homogeneous photocatalysis. In our opinion, two experimental parameters must be determined: a first one, giving information on the reaction rate as in thermal catalysis, and a second parameter giving information on the photons absorbed by the solid photocatalyst. This latter parameter, which is suggested in the present paper, is

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the "rate of photon absorption" (rpa). As in homogeneous photocatalysis, knowledge of these parameters allows one to determine the quantum yield of the process.

In the present work the values of the reaction rate and of the rate of photon absorption have been determined for a test reaction, namely, the photodegradation of phenol carried out by using an aqueous dispersion containing polycrystalline TiO_2 (anatase) of various origins and preparations. The phenol degradation process, already much studied (*8*, *9*), was performed in a batch photoreactor. An experimental method permitting determination of the amount of absorbed photons, already reported elsewhere (*10*, *11*), has been applied.

Before presenting and discussing the results, an account of the reasoning behind the proposal is reported.

METHOD

Intrinsic Reaction Rate, Rate of Photon Absorption, and Quantum Yield

In thermal heterogeneous catalysis, *a single quantity*, the turnover number, defined as

$$\text{turnover number} = \frac{\text{reacted molecules}}{\text{(time unit)(active sites)}} \left[\frac{\text{moles}}{\text{s}}\right], \quad (1)$$

measures the efficiency of the catalysts, giving the essential information on the reaction rate. The turnover number is calculated by experimentally determining two quantities: (i) the molecules reacting per unit of time and (ii) the number of active sites of the catalyst. Since in most cases neither the density nor even the exact nature of the active sites are known, the BET surface area (*7*) is often used instead of the number of active sites. The resulting rate, called the "intrinsic reaction rate" (ri) (*12*), is therefore defined as

$$\text{ri} = \text{intrinsic reaction rate} = \frac{\text{reacted molecules}}{\text{(time unit)(surface area)}} \left[\frac{\text{moles}}{\text{s} \cdot \text{m}^2}\right]. \quad (2)$$

In heterogeneous photocatalysis, owing to the fact that the active sites for the occurrence of the photoreaction are generally difficult to specify and hence to determine quantitatively, the intrinsic reaction rate, instead of the turnover number gives the essential information on the rate of catalytic reaction and, consequently, should be used following the definition given by Eq. (2).

The ri obviously does not give complete information on the photocatalytic process, since it is defined without taking into account the photons involved in the process.

For the occurrence of a heterogeneous photocatalytic process photons must be supplied to the system. The photons impinging on the surface of a polycrystalline semiconductor are absorbed and scattered in a ratio which can be experimentally determined (*10*, *11*). Only absorbed photons, whose energy is equal to or greater than the semiconductor band gap energy, can generate electron–hole pairs; these latter, once separated, can induce chemical transformations with the species adsorbed onto the surface (*13*). Indeed, the photons are absorbed at the fluid–solid interface which is affected by the nature of the medium. As a consequence, the absorbing (and reflecting) properties of solids strongly depend on the nature of the medium surrounding the particles (*10*, *11*), so that different rates of photon absorption may be observed when the same solid is dispersed in different media, even though the same photoprocess is occurring.

On this basis, in our opinion, it is necessary to determine a second parameter which gives information on the rate of photon absorption. This parameter, rpa, is defined as follows:

$$\text{rpa} = \text{rate of photon absorption} = \frac{\text{absorbed photons}}{\text{(time unit)(surface area)}} \left[\frac{\text{einstein}}{\text{s} \cdot \text{m}^2}\right]. \quad (3)$$

The quantum yield, qy, defined as

$$\text{qy} = \text{quantum yield} = \frac{\text{reacted molecules}}{\text{absorbed photons}}, \quad (4)$$

represents the number of reaction events which occur per photon absorbed by the system. The qy is a derived parameter as for its determination the previous independent quantities, the ri and rpa, must be experimentally measured at equal conditions of the system. The ratio of Eqs. (2) and (3) gives Eq. (4), i.e., the quantum yield. It must be noted that the qy has dynamic characteristics, i.e., it is the ratio of two rates, the rate of reaction and the rate of photon absorption. Moreover, whatever the definition of the reaction rate and of the rate of photon absorption, the qy must be the ratio of reacted molecules to absorbed photons. In the case that the turnover number of the photocatalytic reaction would be used in the definition of the reaction rate, i.e., the active sites are known, for the determination of qy it would be necessary to know the number of active sites per unit of surface area in order to have a qy independent of active sites and surface area, as it results from Eq. (4).

In the case of heterogeneous photocatalytic processes, the majority of qy values reported in the literature have been evaluated by measuring the photons leaving the lamp and impinging on the system. These qy values are meaningless since the photons leaving the lamp and impinging on the system are much dependent on the particular lamp–photoreactor setup, on the particular medium used, and so on. Moreover, the photons impinging on the system are partially absorbed and partially scattered in a ratio which cannot be theoretically evaluated. With the aim of obtaining a more significant value of qy, some authors (*14*, *15*) determine the number of absorbed photons with the equation

$$\text{absorbed photons} = n_f \cdot P_o \cdot \delta \cdot (1 - R), \quad (5)$$

where n_f is the number of photons absorbable by the photocatalyst per unit radiant flow, P_o is the incident photon flow, and R is the photocatalyst reflectivity. $\delta = (P_o - P_t)/P_o$ is the correction coefficient which must be introduced into Eq. (5) when the amount of the photocatalyst is not sufficient to completely absorb the incident light flow; P_t is the nonabsorbed radiant flow passing through the reaction system. This procedure gives a rough estimate of the absorbed photons as the determination of R is carried out by using bare solids instead of solids in the presence of their reaction ambient.

In order to correctly compare the photocatalyst effectiveness, the quantum yield must be computed by considering *the photons absorbed by the solids in the particular reacting system.*

Finally, it must be observed that, by reporting only the qy parameter, information is given about the possibility for each absorbed photon (by a molecule or by a semiconductor) to induce chemical events but not about the total amount of absorbed photons and of reacted molecules. For evaluating the overall reactivity of a photocatalytic system (homogeneous or heterogeneous) and for correctly comparing the behaviour of the photocatalysts, the ri and the rpa must be reported.

EXPERIMENTAL

A stirred batch photoreactor of cylindrical shape (internal diameter of 5.64 cm and height of 8 cm) was used for all the experiments. The photodegradation runs lasted 30 min and samples of 3 ml of the dispersion were withdrawn at 5-min intervals for the standard colorimetric analysis of phenol (*16*). The dispersion was magnetically stirred and oxygen was bubbled for 10 min before the run. The volume of the aqueous dispersion was 50 ml, and the initial pH was adjusted at 3 or 11.3 using H_2SO_4 or NaOH. The phenol and the catalyst concentrations were 0.1 g · liter^{-1} and 1 g · liter^{-1}, respectively. Several TiO_2 (anatase) polycrystalline specimens of different preparation and source were used. Home-prepared specimens were obtained by two different methods, one (TD3) from $TiCl_3$ solutions and the other (TD4) from $TiCl_4$ solutions. TD3 was prepared by precipitation by adding aqueous NH_3; after it was washed, the amorphous precipitate was dried at 393 K for 24 h and then calcined at 773 K for 24 h. TD4 was prepared by hydrolysing $TiCl_4$ in water (final adjusted pH of 4.5). The precipitate underwent the same thermal treatments as TD3. Details of the preparation can be found elsewhere (*17*). The particle sizes ranged from 50 to 450 μm. These dimensions, far greater than the wavelengths of the used radiation, allow one to consider the light scattering phenomena as geometrical reflection (*10, 11*). Grade reagents (Carlo Erba, RPE) were always used. The photoreactor setup was kept in a Solarbox (CO.FO.ME.GRA., Milan, Italy) equipped with a 1500-W Xe lamp and was irradiated only from the circular top surface. The temperature inside the Solarbox was 313 K throughout the duration of the runs.

The actinometer runs were performed with the technique described in Refs. (*10*) and (*11*) by using a standard ferrioxalate solution (*18*). Details of both the experimental setup and the procedures can be found in those papers (*10, 11*).

The rate of impinging photons, Φ_i, had the value of 1.554×10^{-7} einstein · s^{-1}.[2] It was experimentally checked that the phenolic solution does not absorb in our experimental conditions. The rate of transmitted photons, Φ_o, was measured having the photoreactor filled with the dispersion and the rate of backward reflected photons, Φ_r, was determined by the extrapolation method reported and discussed in detail in Refs. (*10*) and (*11*). The method mainly consists in measuring the rate of transmitted photons as a function of the mass of catalyst present in the photoreactor. The following relationship was found to hold (*11*):

$$\Phi_o = \Phi' \cdot \exp(-Km). \qquad (6)$$

Φ' is the rate of photons able to penetrate the dispersion, K is the extinction coefficient of dispersion, and m is the mass of the catalyst. By applying a macroscopic photon balance on the photoreactor at the limiting condition of $m = 0$, it is found that

$$\Phi_r = \Phi_i - \Phi'. \qquad (7)$$

The value of the rate of photon absorption, Φ_a, for a phenol photodegradation run was obtained by the following macroscopic photon balance:

$$\Phi_a = \Phi_i - \Phi_o - \Phi_r. \qquad (8)$$

Φ_o was measured for a dispersion of 50 ml, and Φ_r and Φ_i were constant for a given powder and setup and did not depend on the volume of dispersion.

The phenol photodegradation reaction follows pseudo-first-order kinetics (*8, 9, 19*). For each photocatalyst the experimental determination of the rate constant, k_{Phenol}, was used for calculating the number of photodegraded molecules of phenol needed to evaluate the turnover number (tn) values.

RESULTS AND DISCUSSION

The results are presented in Table 1, which reports several items of information: the name, the source and the surface area (SA) of the photocatalysts, the values of reflected photons (Φ_r), of absorbed photons (Φ_a), and of rpa, the values of k_{Phenol}, qy,

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[2] In Ref. (*10*), the value of Φ_i was erroneously reported as 1.55×10^{-4} einstein · s^{-1} instead of 1.55×10^{-7} einstein · s^{-1}. As a consequence, the values of Φ_r and Φ_a in Tables 1 and 2 of that paper, reported as $\Phi_r \times 10^6$ and $\Phi_a \times 10^6$, must be read as $\Phi_r \times 10^9$ and $\Phi_a \times 10^9$. The values of qy reported as qy × 10^4 must be read as qy × 10. The mistake originated from the use of a formula, given in the book by Murov (*18*) on p. 122, for the determination of the light intensity. In this formula the value of the extinction coefficient of ferrous phenanthroline complex at 510 nm is given as 1.11×10^4 without dimensions. As its dimensions are $M^{-1} \cdot cm^{-1}$, i.e., liter · $mol^{-1} \cdot cm^{-1} = 10^3 \cdot cm^3 \cdot mol^{-1} \cdot cm^{-1}$, and the centimeter is used as length unit for all the terms in the formula, the correct value to be used for the extinction coefficient is 1.11×10^7 $cm^2 \cdot mol^{-1}$.

TABLE 1

Actinometer and Reactivity Results for Commercial and Home Prepared TiO_2 (Anatase) Specimens (Particle Size Distribution Between 40 and 500 μm, Incident Photon Flow: $\Phi_i = 1.55 \times 10^{-7}$ einstein · s^{-1})

Catalyst	SA (m^2/g)	pH	$\Phi_r \times 10^9$ (einstein/s)	$\Phi_a \times 10^9$ (einstein/s)	rpa $\times 10^8$ (einstein/s · m^2)	$k_{Phenol} \times 10^4$ (1/s)	ri $\times 10^8$ (mol/s · m^2)	qy $\times 10^2$ (mol/einstein)	qy' $\times 10^2$ (mol/einstein)
TiO_2 (BDH)	10.5	3	115	38	7.2	1.7	1.8	25	6.2
TiO_2 (Tioxide)	14	3	7	134	19.1	1.8	1.3	7	6.6
TiO_2 (Merck)	10.5	3	13	120	22.9	1.2	1.2	5	3.5
TiO_2 (Merck)	10.5	11.3	120	29	5.5	1.1	1.2	21	4.0
TiO_2 (TD4)	26	3	5	132	10.1	2.6	1.0	10	9.6
TiO_2 (TD3)	45	3	7	55	2.4	1.3	0.33	14	11.5

Note. SA, surface area; k_{Phenol}, pseudo-first-order rate constant. The rpa, qy, qy', and ri values have been calculated for 50 ml of dispersion with a powder concentration of 1 g · $liter^{-1}$.

and ri. In addition, the values of qy', calculated by considering both the reflected photons, Φ_r, and the absorbed photons, Φ_a, i.e., the traditional values of quantum yield, are reported.

Several considerations can now be given and conclusions drawn:

(i) The parameter which gives information on the capacity of absorbing photons is the rpa, i.e., it informs one about the number of photons absorbed per second and per square meter by a solid. As can be seen, the rpa values are widely distributed and they are pH dependent. This latter observation is a clear indication that the optical features (reflected and absorbed photons) are due to the interfaces, i.e., the layer between the photocatalyst surfaces and reacting medium. This point explains also why a great variety of rpa values is found. Indeed, the interfaces are different because the features of each surface are different due to their preparation methods and to several other causes, such as, for instance, different species adsorbed on the surface and/or present in the solution. Also worthy of note is the fact that there is no apparent correlation between the amounts of absorbed and reflected photons. Turning to the capacity of absorbing photons the results suggest that the specimen TiO_2 (Merck) is the best one (rpa = 22.9×10^{-8} einstein · s^{-1} · m^{-2}).

(ii) The ri values give information about the catalytic efficiency of the specimens. The ri values tell us that the moles of reacted molecules per second and per square meter on our photocatalysts are of the order of 10^{-8}. The order of activity, taking into account only the ri parameter, is that reported in Table 1 from TiO_2 (BDH) to TiO_2 (TD3). An order of magnitude of the turnover number can be estimated from the ri value of 10^{-8}. By considering that the active sites are OH groups which can constitute simultaneously the adsorption site for phenol and the precursor for the oxidizing $OH^\cdot$ radical and that the OH density is ca. 5×10^{18} m^{-2} (*20, 21*), then the turnover number is about 1.2×10^{-3} s^{-1}. This value is compatible with the values found in heterogeneous thermoactivated catalysis according to Ref. (*12*). The turnover number is close to 1 s^{-1} for fast catalytic reactions and can decrease to 10^{-3} s^{-1} for slower reactions. In the present case, since the concentration of phenol is small, the coverage and consequently the reaction rate are also small.

(iii) Since the photocatalytic process must take into account the "transformation" of the absorbed photons into reacted molecules, then the qy parameters should be considered. The order of activity, therefore, is that described by the values of qy reported in Table 1, i.e., TiO_2 (BDH), TiO_2 (Merck) pH = 11.3, TiO_2 (TD3), and so on, an order of activity different from those based on rpa and ri values.

(iv) It must next be pointed out that, if the values of qy′ were considered, an order of activity completely different from that based on qy, i.e., based on the true absorbed photons, would have been established. This is a clear indication of the fact that the impinging photons are reflected and absorbed in a ratio which cannot be established a priori.

(v) Furthermore, knowledge of the rpa and ri values is also essential, since the order of activity based on the qy values may be misleading. Indeed, the qy parameter is linked to the ratio (reacted moles)/einsteins, but the values of "reacted moles" and "einsteins" are given by the knowledge of rpa and ri.

(vi) A direct correlation, however, between Φ_r, Φ_a, rpa, and the parameters related to the photocatalytic reactivity unfortunately cannot be made as the photoreactivity is affected by several electronic and physicochemical parameters (*22*) such as, for instance, the amount of amorphous material and/or the degree of crystallization, the amount and nature of the surface hydroxyls, the morphology, the lifetime of the photoproduced pairs (*23–25*), and the impurities due to different preparation methods. The level of photoreactivity is an interplay of these parameters, most of which are not known. The knowledge of rpa and ri, however, is useful to evaluate the photonic and catalytic efficiency.

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