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A quantitative method of photoadsorption determination for irradiated catalyst in liquid–solid system

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ABSTRACT

A method for determining the amount of substrate adsorbed onto the catalyst surface in liquid–solid photocatalytic system under reaction conditions (photoadsorption) is proposed. The method has been applied to the photocatalytic oxidation of benzyl alcohol carried out in aqueous suspensions of a home prepared TiO_2 catalyst. The influence of alcohol concentration, catalyst amount and irradiation power on photoadsorption was investigated. The photoadsorption per unit mass of catalyst increased by increasing concentration of benzyl alcohol and irradiation power but it decreased, increasing the catalyst amount. By taking into account the photoadsorption phenomena, the kinetic modeling of the photooxidation process has been carried out and the parameters of the model have been determined. The results indicate that all these parameters are favorably affected by an increase of the photon flow absorbed per unit mass of catalyst.

1. Introduction

The utilisation of irradiation to initiate chemical reactions is the principle on which heterogeneous photocatalysis is based. When a wide-band gap semiconductor like titanium dioxide [1] is irradiated with suitable light, excited electron–hole pairs result that can be applied in chemical processes to modify specific compounds. If recombination or lattice reaction does not involve all the photogenerated pairs, the conduction band electrons participate to reduction reactions on the catalyst surface while positive holes are involved in oxidation reactions. Suitable substrates must be adsorbed on the catalyst surface for the occurrence of a photoreaction process which always starts with the substrate(s) adsorption and eventually ends with the product(s) desorption.

The knowledge of heterogeneous photocatalytic systems has grown very much since the pioneering work of Fujishima and Honda [2]. The basic principles of heterogeneous photocatalysis are now well established [3,4] and also the applicative aspects of this technology are being investigated in the fields not only of environment remediation [5–7] but also of green chemistry [8–11]. There are, however, many aspects waiting to be investigated. One of these is the determination of the photoadsorption, i.e. of amount of substrate adsorbed on the surface of irradiated catalyst under reaction conditions.

Photoadsorption is defined [12] as adsorption initiated by light absorbed by the solid surface and it can be expressed by the following simple mechanism:

$$S + h\nu \rightarrow S* \tag{1}$$

$$S* \rightarrow S \tag{2}$$

$$S* + M \rightarrow M_{p\text{-}ads} \tag{3}$$

where S is the photoadsorption center, S^* the active state of photoadsorption center, M the substrate in the fluid phase and $M_{p\text{-}ads}$ the photoadsorbed substrate. The photoadsorption center is a surface site which reaches an active state after photoexcitation and then it is able to form photoadsorbed species by chemical interaction with substrate at solid/fluid interface [13].

For a batch catalytic reaction, carried out in liquid medium of known volume, the determination of the adsorbed amount of a species is carried out by measuring the concentration decrease determined in the starting solution by the added catalyst. This procedure is based on the correct assumption that the measured decrease of the species amount in the solution corresponds to the amount of species adsorbed on the catalyst. The same procedure can not be applied for the photoadsorption determination; in fact, once the semiconductor catalyst is irradiated, the photoreaction

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also starts so that the measured decrease of species in the solution is determined both by photoadsorption and reaction, these contributions being indistinguishable from the solution side.

This difficulty determines that investigations on heterogeneous photocatalytic processes sometimes report information only on dark adsorption and use this information for discussing the results obtained under irradiation. This extrapolation is scarcely justified as it is known that the characteristics of photocatalyst surface changes under irradiation. For example, the surface of TiO_2, the most used photocatalyst, shows hydrophobic features under dark conditions, while it gets hydrophilic under irradiation [1,6,14,15]. In general the surface characteristics of an irradiated suspended photocatalyst depend on many factors such as: (i) its crystal phase and crystallinity, (ii) kind of adsorbed molecules, (iii) radiation intensity, (iv) medium pH and (v) solvent features.

Nowadays, very effective methods allow a sound characterisation of bulk properties of catalysts and powerful spectroscopies to give valuable information on surface properties. Unfortunately information on the photoadsorption extent in real reaction conditions, i.e. at the same operative conditions at which the photoreactivity tests are performed, is not at disposal. Since photocatalysis is a surface phenomenon, a critical step to affect the effectiveness of the transformation of a given compound is to understand the adsorption process of this compound on the catalysing surface. The study of the adsorbability of the substrate allows one to predict the mechanism and kinetics that promote its photoreaction and also to correctly compare the performance of different photocatalytic systems.

This paper presents a quantitative method to evaluate the photoadsorption capacity of a polycrystalline semiconductor oxide irradiated in liquid–solid system. The determination is performed under reaction conditions so that it is really indicative of the photoadsorption capacity. The method is based on a macroscopic model of photoadsorption, whose assumptions are similar to those involved in the Langmuir model. In order to determine the amount of photoadsorbed species, the method uses the experimental results obtained in typical photoreactivity runs; on this ground it has been applied to the photocatalytic oxidation of benzyl alcohol carried out in aqueous suspensions of a home prepared TiO_2 catalyst. The influence on photoadsorption of alcohol concentration, catalyst amount and irradiation power was investigated. The kinetic modeling of the photooxidation process has been carried out by taking into account the photoadsorption phenomena. A least-squares best fitting procedure applied to all the photoreactivity data allowed to determine the values of the model parameters.

2. Experimental

Photoreactivity runs were carried out in aqueous suspensions of a home prepared nanostructured TiO_2 specimen. The preparation method of catalyst is here summarized; the details are elsewhere reported [16]. The precursor solution was obtained by slowly adding $TiCl_4$ to water under magnetic stirring that was prolonged for 12 h at room temperature, eventually obtaining a clear solution. This solution was heated at 373 K for 0.5 h, obtaining a white suspension at the end of the treatment. The suspension was then dried at 323 K in order to obtain the final powdered catalyst which consists of pure anatase.

A cylindrical batch photoreactor of Pyrex glass with immersed lamp was used for the photocatalytic runs of benzyl alcohol oxidation; details of the experimental set up are elsewhere reported [16]. The catalyst was used in aqueous suspension well mixed by means of a magnetic stirrer; the suspension was irradiated by medium-pressure Hg lamps (Helios Italquarz, Italy) of 125, 500 or 1000 W electric power. Average irradiances impinging onto and leaving the suspension were measured by using a radiometer (UVX, Digital) at $\lambda = 360$ nm, these measurements were carried out for each lamp and each catalyst concentration and they allowed to calculate the photon flow absorbed by the suspension. The benzyl alcohol initial concentration varied in the 0.1–3.6 mM range and the catalyst amounts were in the 0.1–0.8 g L^{-1} range.

The standardized procedure of the runs was the following one and it was strictly observed. The photoreactor *without the immersed lamp* was filled with a fixed volume of the benzyl alcohol aqueous solution of known concentration and pure oxygen (or air for a few runs) was bubbled for 1 h under magnetic stirring (bubbling and stirring were never interrupted in the course of runs); then the desired amount of catalyst was added and samples (5 cm^3) of the suspension were taken at fixed intervals of time until the dark equilibrium conditions were reached (about 30 min after catalyst addition). At that time the lamp *outside the photoreactor* was switched on and time was allowed for reaching steady state conditions of irradiation (about 5 min). Once the irradiation did not change, the lamp was immersed into the suspension and that time was taken as the zero time of the photoreactivity run; samples (5 cm^3) for analysis were withdrawn every 15 min in the first 2 h of the run and then every 0.5 or 1 h. The samples were immediately filtered by means of a cellulose acetate filter (Millipore) with pore diameter of 0.45 μm.

The quantitative determination and identification of the species present in the reacting suspension was performed by means of a HPLC (Beckman Coulter, System Gold 126 Solvent Module and 168 Diode Array Detector), equipped with a Luna 5 μ Phenyl-Hexyl column (250 mm long × 2 mm i.d.) using standards (Sigma–Aldrich). The eluent consisted of: 17.5% acetonitrile, 17.5% methanol, 65% 40 mM KH_2PO_4 aqueous solution. All the used chemicals (Sigma–Aldrich) had a purity >99.0%.

3. Photoadsorption determination

For heterogeneous photocatalytic processes, it is generally agreed that the expression for the degradation rate of organic substrates on TiO_2 surfaces in the presence of oxygen follows (with minor variations) the Langmuir–Hinshelwood (LH) model, which is widely used in liquid- and gas-phase systems [17–23]. This model successfully explains the kinetics of reactions that occur between two adsorbed species, a free radical and an adsorbed substrate, or a surface bound radical and a free substrate. In the LH model adsorption equilibrium is assumed to be established at all times so that the rate of reaction is taken to be much less than the rate of adsorption or desorption. The concentrations of adsorbed species are therefore determined by adsorption equilibrium as given by the suitable isotherm (Langmuir, Freundlich, etc.). Reaction is assumed to occur between adsorbed species whose coverage on the catalyst surface is always in equilibrium with the species concentration in the fluid phase so that the rate determining step of the photocatalytic process is the surface reaction. It is useful to report that the simple rate form of the LH approach may have origins which take into account different photoreaction mechanisms [24–26].

In batch photocatalytic reactors working in liquid–solid regime the depletion of a species is the combined result of photoadsorption and photoconversion processes. To describe this, a mole balance applied to the species at whatever time [20] can be represented as:

$$n_T = n_L + n_S \tag{4}$$

where n_T is the total number of moles present in the photoreactor, n_L the number of moles in the fluid phase and n_S the number of moles photoadsorbed on the solid. When Eq. (4) is divided by the volume of the liquid phase, V, one obtains:

$$C_T = C_L + \frac{n_S}{V} \tag{5}$$

where C_T is the total concentration of the species and C_L the concentration in the liquid phase. By assuming that the Langmuir adsorption isotherm [13] and its underlying assumptions are suitable to describe photoadsorption, the equilibrium coverage for photoadsorption on solid catalyst is described by the following relationship:

$$\theta = \frac{n_S}{WN_S^*} = \frac{K^* C_L}{1 + K^* C_L} \tag{6}$$

where θ is the fractional coverage of the surface, N_S* the maximum capacity of moles adsorbed on the unit mass of irradiated solid, W the mass of catalyst and K* is the photoadsorption equilibrium constant which is a measure of the intrinsic photoreactivity of the catalyst surface. By solving Eq. (6) with respect to n_S and substituting in Eq. (5), the result is:

$$C_T = C_L + \frac{WN_S^*}{V}\frac{K^* C_L}{1 + K^* C_L} \tag{7}$$

The total disappearance rate of substrate per unit surface area, r_T, is assumed to be of first order with respect to the substrate coverage:

$$r_T \equiv -\frac{1}{S}\frac{dn_T}{dt} = k\theta \tag{8}$$

in which S is the catalyst surface area and k the first order rate constant. Owing to the fact that in the course of the runs the oxygen concentration in the liquid phase did not change and therefore also the oxygen coverage on the catalyst surface remained constant, the dependence of r_T on oxygen coverage [18,19] is included in the kinetic constant. Introducing in Eq. (8) the liquid volume, V, the surface area per unit mass of catalyst, S_S, and the Langmuir relationship (Eq. (6)) produces:

$$-\frac{V}{WS_S}\frac{dC_T}{dt} = k\frac{K^* C_L}{1 + K^* C_L} \tag{9}$$

Taking the derivative of Eq. (7) with respect to time, it yields:

$$\frac{dC_T}{dt} = \left[1 + \frac{WN_S^* K^*}{V}\frac{1}{(1 + K^* C_L)^2}\right]\frac{dC_L}{dt} \tag{10}$$

Substituting Eq. (10) into the lhs term of Eq. (9), rearranging and separating the variables, the following differential equation is obtained:

$$-\frac{V}{WS_S K^*}\frac{dC_L}{C_L} - \frac{V}{WS_S}dC_L - \frac{WN_S^*}{S}\frac{dC_L}{C_L(1 + K^* C_L)} = k\,dt \tag{11}$$

It is important to outline that Eq. (11) gives the evolution with irradiation time of the concentration in the liquid phase of a species which is in photoadsorption equilibrium on the catalyst surface over which the species undergoes a slow transformation process. In other words, for a batch photocatalytic run the substrate concentration values measured in the liquid phase at a certain time represent the substrate concentration in equilibrium with an (unknown) substrate amount photoadsorbed on the catalyst surface. This feature belongs to all the measured values of substrate concentration except to the initial one. The substrate concentration measured at the start of a photoreactivity run is characteristic of a system without irradiation. As a consequence, when a kinetic model is fitted to the experimental data, the regression analysis must be done with the concentration values measured in the course of the run excluding the value of initial substrate concentration because the condition of the initial concentration value (dark) is not that of the other ones (irradiated).

On this ground integration of Eq. (11) must be performed with the condition that at $t = 0$ the substrate concentration in the liquid phase is that in equilibrium with the initial photoadsorbed amount, $C_{L,0}$; this parameter is unknown but it may be determined by the regression analysis carried out with the experimental data obtained after the start of irradiation. The integration yields:

$$\frac{1}{K^*}\frac{V}{WS_S}\ln\frac{C_{L,0}}{C_L} + \frac{V}{WS_S}(C_{L,0} - C_L) + \frac{WN_S^*}{S}\ln\left(\frac{1 + K^* C_L}{1 + K^* C_{L,0}}\frac{C_{L,0}}{C_L}\right) = kt \tag{12}$$

Eq. (12) contains four unknown parameters, K*, N_S*, k and $C_{L,0}$, whose determination may be carried out by a best fitting procedure.

A direct determination of those parameters can be done, however, in the following way. k and $C_{L,0}$ may be easily determined by considering two asymptotic situations, i.e. very high or very low substrate concentration. At very high concentrations of substrate the following inequality may be assumed to hold:

$$K^* C_L \gg 1 \tag{13}$$

In this case $\theta = 1$, i.e. $n_S = WN_S$*, and from Eq. (7) one obtains:

$$C_T = C_L + \frac{WN_s^*}{V} \tag{14}$$

The total disappearance rate of substrate per unit surface area, r_T, gets of zero order so that Eq. (9) can be written as:

$$-\frac{V}{WS_S}\frac{dC_T}{dt} = k \tag{15}$$

Taking the derivative of Eq. (14) with respect to time, it yields that $dC_T/dt = dC_L/dt$. Substituting this equality in Eq. (15) and rearranging, one obtains:

$$-\frac{dC_L}{dt} = \frac{WS_S}{V}k \tag{16}$$

Integration of Eq. (16) with the same initial condition used for Eq. (12) yields the following relationship:

$$C_L = C_{L,0} - \frac{WS_S}{V}kt \tag{17}$$

which is a linear relationship between the concentration values measured in the solution and the irradiation time. The intercept and slope values allow to determine the $C_{L,0}$ and k values.

At very low concentrations of substrate the following inequality may be assumed to hold:

$$K^* C_L \ll 1 \tag{18}$$

In this case $\theta = K^*C_L$, i.e. $n_S = W\ N_S^*K^*C_L$, and from Eq. (7) one obtains:

$$C_T = C_L + \frac{WN_S^*}{V}K^* C_L \tag{19}$$

The total disappearance rate of substrate per unit surface area, r_T, gets of first order with respect to the substrate concentration and Eq. (9) can be written as:

$$-\frac{V}{WS_S}\frac{dC_T}{dt} = kK^* C_L \tag{20}$$

By following the same procedure previously described and integrating, one obtains:

$$\ln C_{\mathrm{L}} = \ln C_{\mathrm{L},0} - \frac{WS_{\mathrm{S}}kK^*}{V + WN_{\mathrm{S}}^*K^*}t \tag{21}$$

which is a linear relationship in a semilogarithmic plot of concentration values versus the irradiation time. The intercept value allows to determine the $C_{\mathrm{L},0}$ value while the slope contains two parameters, K^* and N_{S}^*, that may be determined in the following way.

From the photoreactivity runs for which the 13 and 18 hold, the values of $C_{\mathrm{L},0}$ may be determined. Applying the molar balance expressed by Eq. (5) to the start of irradiation, i.e. the zero time, yields:

$$C_{\mathrm{T},0} = C_{\mathrm{L},0} + \frac{n_{\mathrm{S},0}}{V} \tag{22}$$

in which $C_{\mathrm{T},0}$ is the total concentration of substrate and coincides with the concentration of initial solution and $n_{\mathrm{S},0}$ is the number of photoadsorbed moles in equilibrium with the solution at $C_{\mathrm{L},0}$ concentration. In the statement of Eq. (22) it is assumed that only photoadsorption can occur on the surface of irradiated particles of catalyst and that the whole particles are irradiated. Eq. (22) allows to determine the $n_{\mathrm{S},0}$ value corresponding to a certain $C_{\mathrm{L},0}$:

$$n_{\mathrm{S},0} = V(C_{\mathrm{T},0} - C_{\mathrm{L},0}) \tag{23}$$

All the $n_{\mathrm{S},0}$–$C_{\mathrm{L},0}$ couples of values are related by the Langmuir model (Eq. (6)):

$$\frac{n_{\mathrm{S},0}}{WN_{\mathrm{S}}^*} = \frac{K^*C_{\mathrm{L},0}}{1 + K^*C_{\mathrm{L},0}} \tag{24}$$

Inverting the terms of Eq. (24) and rearranging, one has:

$$\frac{1}{n_{\mathrm{S},0}} = \frac{1}{WN_{\mathrm{S}}^*K^*C_{\mathrm{L},0}} + \frac{1}{WN_{\mathrm{S}}^*} \tag{25}$$

Introducing Eq. (23) into Eq. (25) and multiplying Eq. (25) by $C_{\mathrm{L},0}$ yield Eq. (26), which is the linear form of Eq. (24):

$$\frac{C_{\mathrm{L},0}}{C_{\mathrm{T},0} - C_{\mathrm{L},0}} = \frac{V}{WN_{\mathrm{S}}^*K^*} + \frac{V}{WN_{\mathrm{S}}^*}C_{\mathrm{L},0} \tag{26}$$

where $C_{\mathrm{L},0}/(C_{\mathrm{T},0} - C_{\mathrm{L},0})$ is a dependent variable, $C_{\mathrm{L},0}$ an independent variable, $V/WN_{\mathrm{S}}^*K^*$ the linear coefficient and V/WN_{S}^* the angular coefficient of the straight line. Thus, by plotting $C_{\mathrm{L},0}/(C_{\mathrm{T},0} - C_{\mathrm{L},0})$ versus $C_{\mathrm{L},0}$ one can determine the maximum adsorption capacity, N_{S}^*, and photoadsorption equilibrium constant, K^*, respectively, through the slope and linear coefficient of the straight line.

The determination of the value of K^* allows to check the inequalities expressed by Eqs. (13) and (18). For the runs for which the previous inequalities do not hold, Eq. (12) must be used for determining the only unknown parameter contained in it, i.e. the $C_{\mathrm{L},0}$ value.

4. Results and discussion

As expected, no photodegradation of benzyl alcohol was observed in oxygenated solution under irradiation but without catalyst. In the presence of catalyst but without irradiation no oxidation of benzyl alcohol was detected but a small adsorption of benzyl alcohol was measured. The photoreactivity runs carried out by bubbling pure oxygen or air gave the same results so that it may be concluded that the oxygen coverage is equal to unity for all the runs.

Figs. 1 and 2 report the photoreactivity results obtained from representative runs carried out at different initial benzyl alcohol concentrations and two lamp powers; for all of these runs the same amount of catalyst was used. Fig. 3 reports the results obtained from runs carried out with different amounts of catalyst; for all these runs the same initial benzyl alcohol concentration and lamp power were used. In Figs. 1–3, the concentration values reported for the zero time correspond to those of the starting solution, i.e. without catalyst and irradiation.

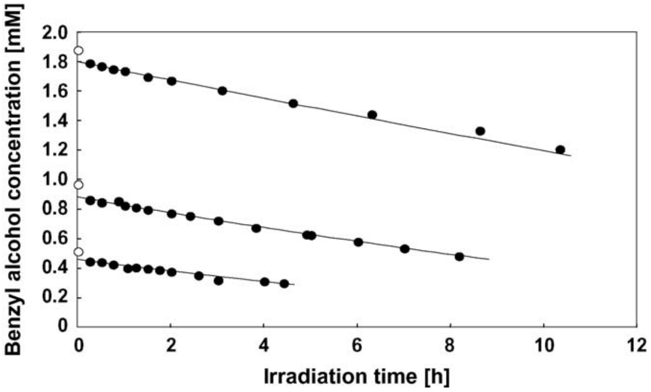

Fig. 1. Experimental values of benzyl alcohol concentration versus irradiation time. Catalyst amount: 0.4 g L^{-1}, lamp power, 125 W. The empty symbols indicate the concentration of starting solution. The solid lines represent the photoadsorption model (Eq. (12)).

Benzyl aldehyde was the intermediate product detected in the course of benzyl alcohol photocatalytic oxidation, CO_2 being the other oxidation product. No other intermediates were detected in all the course of the runs indicating that at the used experimental conditions the produced aldehyde does not compete with alcohol for photoadsorption and oxidation. This feature together with the low degradation rate exhibited by the home prepared catalyst favors the studied system in accomplishing the assumptions of photoadsorption model.

The data of the runs carried out at equal mass of catalyst and lamp power have been first fitted to the model in order to have an estimate of the parameters values. The data at high initial concentration of benzyl alcohol have been fitted to Eq. (17) and those at low initial concentration to Eq. (21). The data obtained by these fitting procedures have been used to determine K^* and N_{S}^* by means of Eq. (26). As inequalities 13 and 18 were not strongly satisfied, the general equation of the proposed model (Eq. (12)) has been used to determine the values of $C_{\mathrm{L},0}$, k, K^* and N_{S}^*, that best fitted the experimental data of each run. The continuous lines

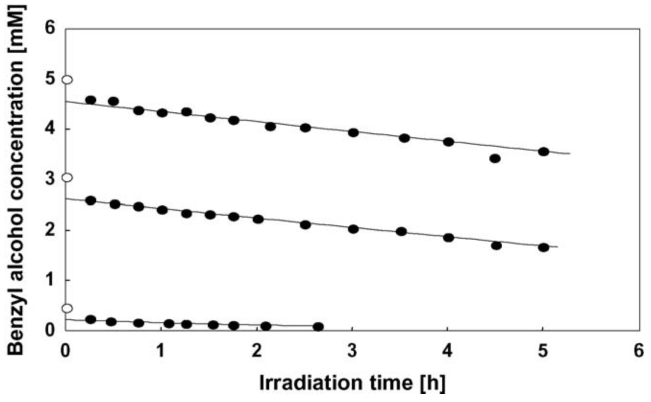

Fig. 2. Experimental values of benzyl alcohol concentration versus irradiation time. Catalyst amount: 0.4 g L^{-1}, lamp power, 500 W. The empty symbols indicate the concentration of starting solution. The solid lines represent the photoadsorption model (Eq. (12)).

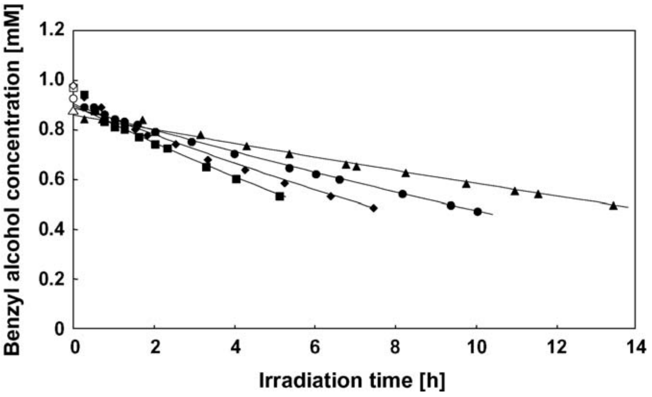

Fig. 3. Experimental values of benzyl alcohol concentration versus irradiation time. Catalyst amount: (▲) 0.1 g L^{-1}; (●) 0.2 g L^{-1}; (◆) 0.6 g L^{-1}; (■) 0.8 g L^{-1}. Lamp power, 125 W. The empty symbols indicate the concentration of starting solution. The solid lines represent the photoadsorption model (Eq. (12)).

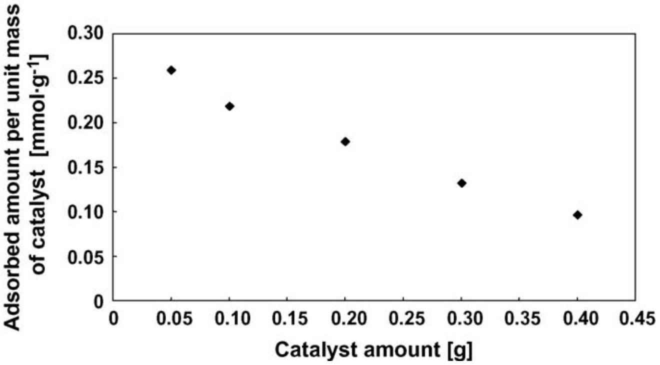

Fig. 5. Photoadsorbed amount of benzyl alcohol per unit mass of catalyst versus the mass of catalyst. Initial benzyl alcohol concentration, 1 mM, lamp power, 125 W.

drawn through the data of Figs. 1–3 represent Eq. (12) and a very satisfactory fitting ($R^2 > 0.99$) may be noted. The values of k, K^* and N_S^*, obtained by the best fitting procedure, are reported later (see Fig. 6).

The suitability of Langmuir model to describe the photoadsorption phenomenon has been checked by using the linear form of Langmuir equation (Eq. (26)). Fig. 4 reports the values of the $C_{L,0}/(C_{T,0} - C_{L,0})$ group obtained from runs carried out at equal mass of catalyst and lamp power versus the benzyl alcohol equilibrium concentration. The straight lines drawn through the data represent Eq. (26) and a very good fitting ($R^2 > 0.99$) may be noted. The slopes and linear coefficients of lines allow to determine the N_S^* and K^* values corresponding to these runs; these values are almost the same of those determined by means of Eq. (12) (error percentage, ±4%). Fig. 4 also reports the adsorption results obtained in the absence of irradiation, i.e. in the dark. A least-squares best fitting procedure allows to determine the values ($R^2 > 0.99$) of the Langmuir equilibrium constant and the maximum adsorption capacity in the absence of irradiation, i.e. $K = 0.35\ \mathrm{m^3\ mol^{-1}}$ and $N_S = 4.57 \times 10^{-6}\ \mathrm{mol\ g^{-1}}$ of catalyst.

The effect of catalyst amount on photoadsorption capacity is shown in Fig. 5. This figure reports the benzyl alcohol moles photoadsorbed per unit mass of catalyst versus the catalyst amount; the reported data refer to runs carried out at equal initial benzyl alcohol concentration and lamp power. From the observation of data of Fig. 5, it may be noted a decrease of specific photoadsorption capacity by increasing the catalyst amount, differently from that expected on thermodynamic basis for which an increase of catalyst amount determines a corresponding increase of adsorbed substrate. This finding may be explained by considering that an increase of catalyst amount determines an increase of photons absorbed by the suspension but the photon flow absorbed *by the unit mass of catalyst* decreases. As photoadsorption is likely to be strongly dependent on absorbed photon flow, the increase of catalyst amount is eventually detrimental for specific photoadsorption.

The consideration that the photon flow absorbed by the unit mass of catalyst is the parameter mainly affecting the photoadsorption phenomenon is strengthened by the results reported in Fig. 6. This figure reports the values of the model parameters, K^*, N_S^* and k, versus the absorbed photon flow per unit mass of catalyst. The K and N_S values obtained from dark experiments are also reported. It may be noted that all parameters increase by increasing the specific photon absorption. While it is known that in thermal catalysis a temperature increase determines an increase of kinetic and equilibrium adsorption constants, the results of Fig. 6 also show a beneficial effect of absorbed photons on the photoadsorbed amount of solute. This effect is very noticeable if a comparison is done between irradiated and dark conditions. The values of K^* and N_S^* are one and two orders of magnitude, respectively, higher than those obtained in the absence of irradiation. Under irradiation the catalyst surface changes from hydrophobic to hydrophilic character, this change depends on photon absorption. The photoadsorbed amount of solute shows first a sharp increase with absorbed photons, this increase being less important at high photon absorption. This behaviour should indicate that the number of photoactive sites increases with photon absorption until a value is reached for which an increase of

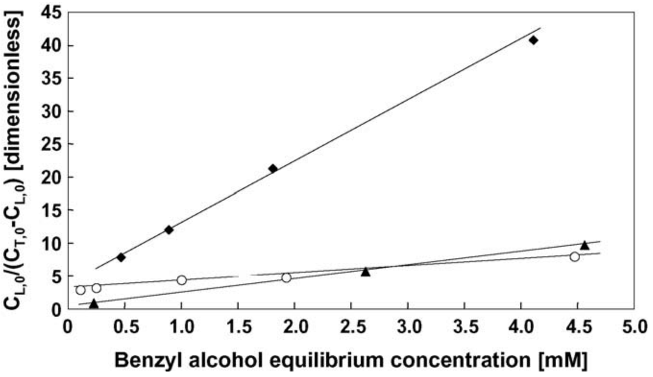

Fig. 4. Linear form of Langmuir model. The left hand side term of Eq. (26), $C_{L,0}/(C_{T,0} - C_{L,0})$, versus $C_{L,0}$ for runs carried out under irradiation with lamp power of 125 W (◆), 500 W (▲) and in the dark (○). The dark data are multiplied for 10^{-3}. The solid lines represent the Langmuir photoadsorption model (Eq. (26)).

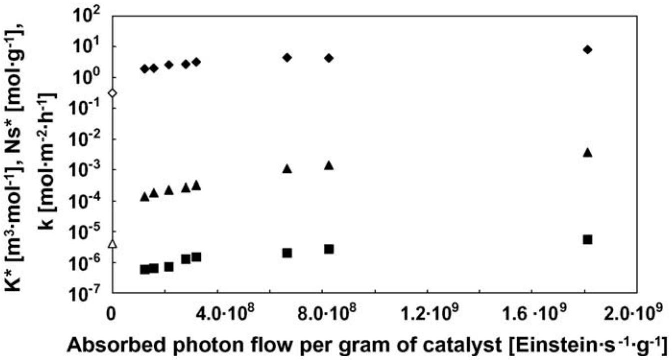

Fig. 6. Values of model parameters (see Eq. (12)) versus the absorbed photon flow per unit mass of catalyst. (◆) K^*; (▲) N_S^*; (■) k. The empty symbols refer to dark conditions.

absorbed photon does not affect the amount of photoadsorbed substrate. This limiting amount should be characteristic of the catalyst surface and the physicochemical features of solute and medium (such as pH, ionic strength, etc.).

5. Conclusions

The method here proposed for the determination of photoadsorption capacity under reaction conditions gives valuable information on the influence of absorbed photons on kinetics and thermodynamics of a photocatalytic reaction. The basic assumptions of model are that: (i) photoadsorption is fast with respect to the reaction; and (ii) the Langmuir isotherm is suitable for describing photoadsorption. The Freundlich isotherm has been also tested in the present investigation but the results were not so satisfactory as those obtained with the Langmuir isotherm. It is likely that the chemical features of solute determine the type of isotherm most suitable for modeling the photoadsorption phenomenon. The finding that the parameters of the model (K^*, $N_S{}^*$ and k) depend on the absorbed photon flow is a clear clue that under the concept of photoadsorption other information is conceived therefore suggesting that a more detailed kinetic model is needed. Work is in progress on this point.

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