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Photocatalytic steady-state methylviologen oxidation in air-saturated TiO_2 aqueous suspension
Initial photonic efficiency and initial oxidation rate as a function of methylviologen concentration and light intensity

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Abstract

Photocatalytic methylviologen oxidation in TiO_2 aqueous suspension has been studied. The initial photonic efficiency has been found to increase dramatically as the light intensity decreases, approaching 34% at extremely low light intensity. The maximum photonic efficiency does not depend on methylviologen concentration and pH of the solution. Increasing the surface methylviologen concentration by increasing the methylviologen concentration in the solution or varying pH causes the photonic efficiency comes to its maximum value at a higher intensity of incident light. The light intensity affects the shape of the dependencies of initial rate versus methylviologen concentration. The model explaining the experimental data has been examined. Two parameters of this model appear to be able to characterize the material of TiO_2 photocatalysts in a quite wide range of conditions. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Methylviologen; TiO_2; Photocatalyst; Oxidation; OH radical

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1. Introduction

A possibility to eliminate the low concentrated organics by their deep photocatalytic oxidation to the extent of mineralization attracts considerable attention of the researchers [1–5]. The TiO_2 based photocatalysts are considered to be the most acceptable for these purposes. Titanium dioxide is non-toxic, corrosion-resisting material which can mineralize practically any organic substance when it is illuminated by mild UV light. At the same time, TiO_2 has some imperfection as a photocatalyst. The main drawback appears to be a low photonic efficiency of photocatalytic reactions which usually does not exceed 10% [6,7]. It is believed that the low photonic efficiency of photocatalytic TiO_2 process is conditioned by a low rate transfer of photogenerated and then trapped electron from TiO_2 particles to dissolved oxygen and the disappearance of photogenerated trapped electrons in recombination processes with holes [2].

Adsorbed methylviologen is known to be a very efficient electron acceptor, therefore, the study of methylviologen oxidation reaction could allow to reveal the regularities of photocatalytic process which are not complicated by recombination of captured electrons and holes, and to determine the maximum efficiency of a TiO_2 based photocatalyst in the photocatalytic oxidation of organics.

2. Experimental

2.1. Reagents and materials

To prepare solutions, we used distilled water, doubly recrystallized methylviologen (1,1′-dimethyl-4,4′-bipyridine dichloride) $MVCl_2$ (chemical purity grade), sodium hydroxide (purity grade). TiO_2 powder (Degussa P25) was used as a photocatalyst.

2.2. Determination of initial reaction rates

All experiments were carried out at room temperature in open quartz glass equipped by transparent quartz window on

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continuous agitation by magnetic stirrer 'MM-2A'. The volume of the sample was 20 ml, it contained a specified amount of methylviologen and TiO_2 suspension (0.02 g/l). pH was controlled by pH meter 'pH-673' (the former USSR).

The suspension was illuminated by filtered light of the high pressure mercury lamp DRSH-1000 (interference filter with maximum filtration at λ=334 nm and water filter for cutting off IR light were used). The intensity of the light incident upon the sample was varied with neutral density filters and measured with thermoresistance LM2 (DDR). The area of the light spot was 1 cm^2. Periodically (at 20 s–10 min intervals), the light was interrupted, and an absorption spectrum was recorded relative to the initial solution by spectrophotometer 'Shimadzu 300 UV' (Japan).

The illumination causes the methylviologen oxidation

$$MV^{2+} + O_2 \overset{TiO_2, h\nu}{\rightarrow} MV_{ox1} + MV_{ox2}$$

that changes the absorption spectrum of the sample. Changes of methylviologen concentration were calculated from the following equation:

$$\Delta[MV^{2+}] = \frac{\Delta D(\lambda)}{\varepsilon_{MV}} \times 1.65,$$

where $\Delta D(\lambda)$ is the change in the optical density of the sample at wavelength λ=270 nm, ε_{MV} an extinction coefficient of methylviologen which was accepted to be $1.5\times10^4\ M^{-1}\ cm^{-1}$, 1.65 a coefficient taking into account the adsorption of the products of methylviologen oxidation [8,9]. The initial rate of the reaction was determined with first four points of the kinetic curve. Initial photonic efficiency was calculated from the following equation:

$$\varphi = \frac{WV}{I_0 S_0} \qquad (1)$$

where W is the initial rate of methylviologen oxidation, V the volume of the sample, I_0 the intensity of the incident light, S_0 the area of the light spot.

2.3. Experimental results

Fig. 1 demonstrates the dependencies of the initial rate and the initial photonic efficiency of methylviologen oxidation on light intensity at two methylviologen concentrations at pH=5.6. Fig. 1 shows that the dependencies of the initial rate on light intensity are not linear and the initial photonic efficiency dramatically increases with decreasing the light intensity. At an extremely low light intensity $I_0 \approx 0.06\times10^{-9}$ einstein $cm^{-2}\ s^{-1}$ and the initial methylviologen concentration $[MV^{2+}]=5\times10^{-5}$ M, the initial photonic efficiency reaches 34%.

The dependencies measured at pH=9 (see Fig. 2) are similar to those at pH=5.6. However, a considerable photonic efficiency (about 30%) at pH=9 and $[MV^{2+}]=5\times10^{-5}$ M is attained at a higher light intensity (about $I_0 \approx 0.5\times10^{-9}$ einstein $cm^{-2}\ s^{-1}$). At high light intensities, lowering of the initial concentration of dissolved methylviologen from $[MV^{2+}]=5\times10^{-5}$ to 0.5×10^{-5} M decreases significantly the initial photonic efficiency (by a factor of about 2). However, at low light intensities such a change of methylviologen concentration does not decrease the initial photonic efficiency so much.

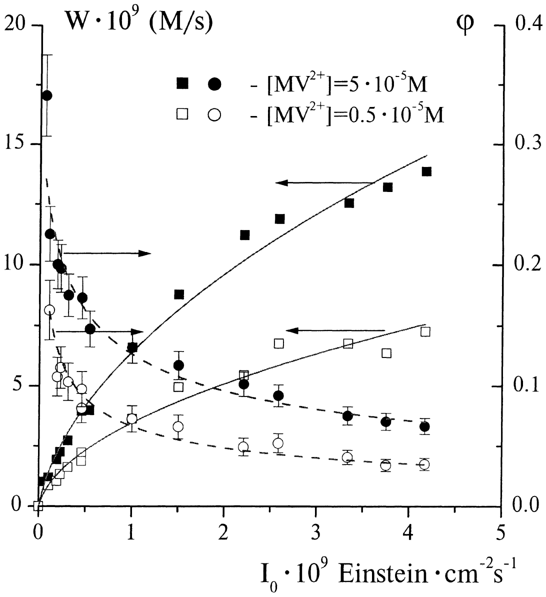

Fig. 1. Initial rate and initial photonic efficiency of methylviologen oxidation vs. light intensity at two methylviologen concentrations in the solution. pH=5.6.

Figs. 3 and 4 demonstrate the dependencies of the initial reaction rate on the initial methylviologen concen-

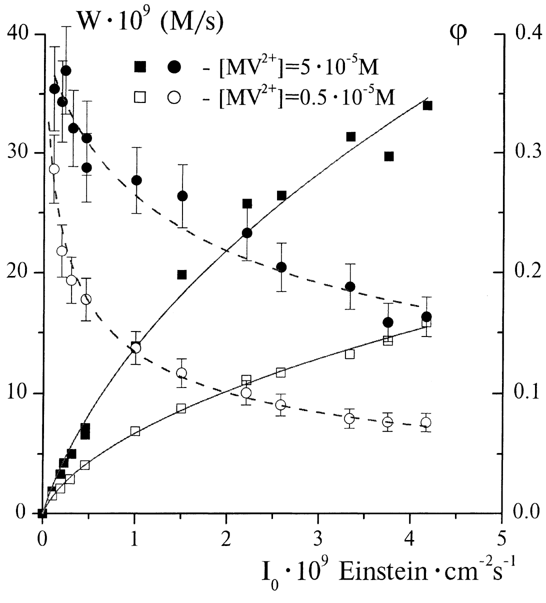

Fig. 2. Initial rate and initial photonic efficiency of methylviologen oxidation vs. light intensity at two methylviologen concentrations in the solution. pH=9.

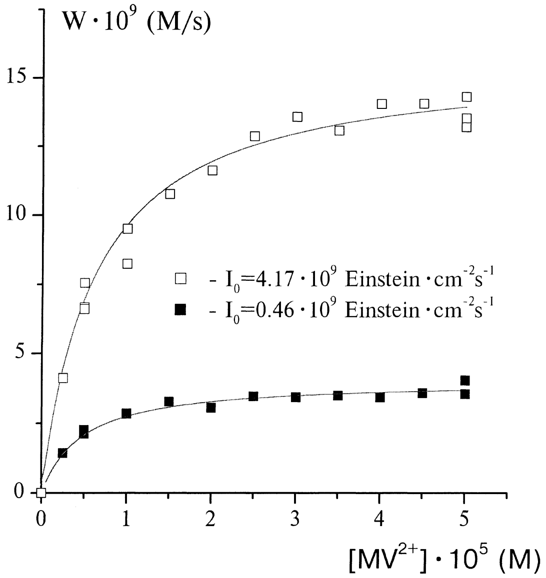

Fig. 3. Initial oxidation rate vs. methylviologen concentration in the solution at two light intensities. pH=5.6.

tration for various light intensities $I_0 \approx 4.17\times10^{-9}$ and 0.46×10^{-9} einstein cm^{-2} s^{-1} at pH 5.6 and 9, respectively. Increasing methylviologen concentration linearly increases the reaction rate at low methylviologen concentration and does not considerably affect the initial reaction rate at high concentration of MV^{2+}. It should be noted that the dependencies of the initial reaction rate on methylviologen concentration at each pH are not proportional to one another. The dependence of the initial reaction rate on methylviologen concentration measured at lower light intensity ($I_0 \approx 0.46\times10^{-9}$ einstein cm^{-2} s^{-1}) reaches the plateau earlier than that measured at higher one ($I_0 \approx 4.17\times10^{-9}$ einstein cm^{-1} s^{-1}) that in agreement with previous results ([3] p. 78, [10]).

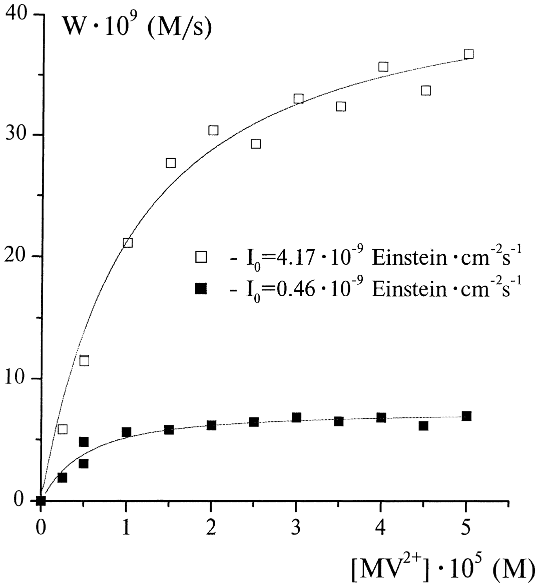

Fig. 4. Initial oxidation rate vs. methylviologen concentration in the solution at two light intensities. pH=9.

Table 1

I_0 (einstein cm^{-2} s^{-1})	K (M^{-1})	
	pH=5.6	pH=9
4.17×10^{-9}	1.4×10^{5}	0.8×10^{5}
0.46×10^{-9}	2.5×10^{5}	1.5×10^{5}

These distinctions are more evident when we try to approximate the experimental data by Langmuir–Hinshelwood type dependency, i.e. according to expression:

$$W = W_m \times \frac{K[MV^{2+}]}{1 + K[MV^{2+}]}.$$

Here $[MV^{2+}]$ is methylviologen concentration in the solution, W_m and K are fitted constants. Table 1 lists the best values of K.

The fitting curves are not shown but they do not distinguish a lot from the solid lines drawn in Figs. 3 and 4.

It is clearly seen from Table 1 that the K value at each pH increases with decreasing light intensity. Langmuir type approximations are given here just as an evidence of changing curves shape with light intensity. A number of mathematical expressions can approximate the experimental data. Below alternative approximation is given.

3. Discussion

3.1. Comparison of the reaction and adsorption–desorption rates

Before proceeding to the process kinetics, which can explain the observed regularities, we shall demonstrate that the shape of experimental dependencies cannot be conditioned by the rate of adsorption–desorption processes.

Schematically the oxidation process could be described as follows:

$$R \underset{\tau_{r,ds}}{\overset{\tau_{r,ad}}{\rightleftarrows}} R_S \xrightarrow{TiO_2, h\nu, \tau} P_S \underset{\tau_{p,ad}}{\overset{\tau_{p,ds}}{\rightleftarrows}} P$$

where R, R_S denote a reagent, P, P_S a product dissolved in the solution, adsorbed on the photocatalyst, respectively, $\tau_{r,ad}$, $\tau_{r,ds}$, $\tau_{p,ad}$, $\tau_{p,ds}$, τ are the typical adsorption/desorption, reaction times. The first process is adsorption/desorption of a reagent, the second one is conversion of the adsorbed reagent into a product, which remains adsorbed, and the third one designates adsorption/desorption of the product. The consideration of products desorption is essential for the reason of slowly desorbing products can block the catalyst surface.

To our knowledge, there is no evidence whether a reagent molecules/ions to be oxidized has to adsorb at TiO_2 photocatalyst particle or it has to be within double electric layer only [11–13]. Hereafter our consideration refers to oxidation of adsorbed molecules albeit it seems to be able to be extended on the molecules/ions localized in vicinity of the photocatalyst particle.

It is known from the literature that an aggregate of titanium dioxide powder suspension 'Degussa P25' consists of primary TiO_2 particles of cubic shape having about 21 nm in size [3].

Let us determine $\tau_{r,ad}$, $\tau_{r,ds}$, $\tau_{p,ad}$, $\tau_{p,ds}$ as the times for that the quantity of molecules/ions in adsorbed layer changes essentially in the processes of reagents/products adsorption/desorption. In the case of reagents, their adsorption time can be expressed as follows:

$$\tau_{r,ad} \sim \frac{R_{ad,m}}{4\pi r \chi [R]}$$

where $R_{ad,m}$ is the maximal number of reagent molecules/ions adsorbed at one TiO_2 particle, [R] the reagent concentration in the solution, r the apparent radii of TiO_2 particle, χ the mutual diffusion coefficient of reagent molecules/ions and a TiO_2 particle. Considering that equation for methylviologen ions and taking $r{=}10^{-6}$ cm, $\chi{\approx}10^{-5}$ cm^2/s and $[MV^{2+}]{=}0.5{\times}10^{-5}$ M, one can find that $\tau_{r,ad}{\sim}3{\times}10^{-6}$ $R_{ad,m}$ (s).

The order of $\tau_{r,ds}$ could be evaluated in the following way. Figs. 3 and 4 allow to believe that at about $[MV^{2+}]{=}0.5{\times}10^{-5}$ M only a half of TiO_2 particle surface centers is occupied by MV^{2+}, and thus, at that methylviologen concentration the adsorption and desorption rates are approximately equal to:

$$4\pi r \chi [R] \sim \frac{R_{ad,m}/2}{\tau_{r,ds}}.$$

That means $\tau_{r,ds}{\sim}\tau_{r,ad}{\sim}3{\times}10^{-6}$ $R_{ad,m}$ (s)

The time of an adsorption–desorption equilibrium achievement could be evaluated from the following expression:

$$\tau_{r,ad\text{–}ds} = \frac{1}{1/\tau_{r,ad} + 1/\tau_{r,ds}}.$$

Thus, in the case of methylviologen at $[MV^{2+}]{=}0.5{\times}10^{-5}$, we can write:

$$\tau_{r,ad\text{–}ds} = \frac{1}{1/\tau_{r,ad} + 1/\tau_{r,ds}} < \tau_{r,ad} \sim 3 \times 10^{-6} R_{ad} \ \ (s).$$

The time needed for the number of adsorbed methylviologen ions change by one is $\tau^1_{r,ad\text{–}ds} \sim 3 \times 10^{-6}$ s.

Increasing methylviologen concentration as well as consideration of the second reagent, dissolved oxygen ($[O_2]{\approx}3{\times}10^{-4}$ M), could only decrease that time. Thus, in our case, $\tau^1_{r,ad\text{–}ds} \leq 3 \times 10^{-6}$ s.

There is some problem in evaluation of $\tau^1_{p,ad\text{–}ds}$ (notations are analogous) for reaction products, MV_{ox1}, MV_{ox1}. As the reaction products MV_{ox1}, MV_{ox1} are rather similar to MV^{2+} [9] and $\tau_{p,ad\text{–}ds} = (1/(1/\tau_{p,ad} + 1/\tau_{p,ds})) < \tau_{p,ds}$, it could be assumed that $\tau^1_{p,ad\text{–}ds} \sim 3 \times 10^{-6}$ s.

Let us now estimate the typical time of photocatalytic conversion of one adsorbed reagent molecule/ion (τ).

This time cannot be lower than $(1/\nu\varphi_{MV})$. Here ν is the number of quanta adsorbed by a primary TiO_2 particle for 1 s. For particles being small enough, ν is known to be determined by the expression

$$\nu = I(2r)^3\alpha(\lambda)\ln 10 = \sigma I.$$

Here $\sigma{=}(2r)^3\alpha(\lambda)\ln 10$ is the cross-section of primary TiO_2 particles adsorption, I the intensity of light incident upon TiO_2 primary particle, $\alpha(\lambda)$ the coefficient of light transmission. Taking $\alpha(\lambda{=}334\,\text{nm}){\approx}6{\times}10^4$ cm^{-1} [14], one can find that $\sigma{\approx}1.1{\times}10^{-12}$ cm^2. In the range of the light intensity under study, $\nu{<}\nu_{max}{\approx}1.3{\times}10^3$ quanta/s. As $\varphi_{MV}{<}1$,

$$\tau > \frac{1}{\nu_{max}} \approx 4 \times 10^{-4}\, s \gg 3 \times 10^{-6}\,\text{s} \geq \tau^1_{ad\text{–}ds}.$$

This means that the photocatalytic reaction cannot disturb the dark adsorption–desorption equilibrium.

The experimental results are in accordance with above conclusion. Figs. 1 and 2 show that the reaction rate increases with light intensity meaning that neither reagent adsorption nor product desorption determine the process rate.

3.2. TiO_2 surface localized photocatalytic process

At first, let us mark out the points that should be put at the bases of a possible scheme (see also [15–20]).

As it is evident from experimental results, photonic efficiency decreases with light intensity, i.e. photonic efficiency falls with decreasing time between photons adsorbed by TiO_2 particle. That means that the interval between photons adsorption is not long enough for the complete relaxation of a photoexited TiO_2 particle to its dark state before adsorption of next photon. That means also that there is an intermediate photogenerated species through that a photoexited TiO_2 particle looses its activity and the life time of that 'key' species should be comparable with the interval between photons adsorption. Consider the dependence of photonic efficiency on light intensity at pH=9, $[MV^{2+}]{=}5{\times}10^{-5}$ M shown in Fig. 2. As the photonic efficiency falls to a half of its maximum value at about $I_0{=}4{\times}10^{-9}$ einstein cm^{-2} s^{-1}, the life time of the species could be evaluated of being about 1 ms. Comparison of the dependencies at $[MV^{2+}]{=}5{\times}10^{-5}$ and $0.5{\times}10^{-5}$ M (Fig. 2), gives that the life time of the species increases with decreasing methylviologen concentration.

Trapped photogenerated electron is commonly accepted as such a 'key' species. Presence of adsorbed methylviologen can seriously decrease trapped photogenerated electron lifetime because that electron can easily transfer to adsorbed methylviologen ion. Unfortunately, the time of that transfer varies drastically from experiment to experiment [21–26]. In present article, we assume that time as being below 1 μs [21,22].

Photogenerated OH radical in absence of photogenerated electrons might be a candidate for the ‘key’ species. Following [11] below we describe the process in terms of average stationary concentrations suggesting that deactivation of a photoexited catalyst particle goes through OH radicals recombination.

Suppose that the oxidation process is caused by $OH^{\bullet}$ radicals, which appear with the rate proportional to the intensity of incident light and disappear in the process of recombination [27] and reaction with organic species. Taking the rate of $OH^{\bullet}$ radicals formation at one particle to be $\varphi_{OH}\sigma I$, the rates of MV^{2+} oxidation and $OH^{\bullet}$ radicals recombination to be $k\mathrm{MV}_{ad}\mathrm{OH}_{ad}$ and $k_r\mathrm{OH}_{ad}^2$, respectively, we can find the stationary concentration of OH_{ad} radicals from the equation:

$$\frac{\mathrm{dOH}_{ad}}{\mathrm{d}t} = 0 = \varphi_{OH}\sigma I - k\mathrm{MV}_{ad}\mathrm{OH}_{ad} - k_r\mathrm{OH}_{ad}^2 \qquad (2)$$

Here φ_{OH} is the photonic efficiency of the $OH^{\bullet}$ radicals formation on the surface of TiO_2 particle, k a rate constant of the reaction between $OH^{\bullet}$ radical and MV located on the surface, MV_{ad} and OH_{ad} are the average stationary number of methylviologen ions and $OH^{\bullet}$ radicals located at the particle surface, k_r is the recombination constant of $OH^{\bullet}$ radicals.

Since the amount of methylviologen ions (MV_{ad}) and hydroxyl radicals (OH_{ad}) on the photocatalyst surface is measured in specimen per a separate particle of photocatalyst, the values of MV_{ad} and OH_{ad} are dimensionless. In this case, the rate constants have dimensionality s^{-1}.

When OH_{ad} is found by Eq. (2), the photonic efficiency of the MV oxidation reaction can be calculated:

$$\varphi = \frac{k\mathrm{OH}_{ad}\mathrm{MV}_{ad}}{\sigma I} = \frac{(k\mathrm{MV}_{ad})^2}{2k_r\sigma I}\left(\left(1+\frac{4k_r\varphi_{OH}\sigma I}{(k\mathrm{MV}_{ad})^2}\right)^{1/2} - 1\right). \qquad (3)$$

To obtain the actual photonic efficiency, averaging over all particles should be done. This procedure is not quite simple. Nevertheless, we believe that averaging will not significantly change the form of dependence of Eq. (3) and will affect only the values of parameters in this equation, so that we can rewrite Eq. (3) as follows:

$$\varphi = \frac{\rho^2}{2I_0}\left(\left(1+\frac{4\varphi_{OH}I_0}{\rho^2}\right)^{1/2} - 1\right) \qquad (4)$$

where $\rho = (k/\sqrt{k_r\sigma})\mathrm{MV}_{ad}$.

Experimental data presented in Figs. 1 and 2 is well approximated by Eq. (4). Results of the experimental data approximation are shown in these figures by solid lines, and parameters of the curves are listed in Table 2.

Table 2

$[MV^{2+}]$ (M)	ρ [a] ($s^{-1/2}$ cm^{-1})	
	pH=5.6	pH=9
0.5×10^{-5}	0.32×10^{7} (0.32)	0.68×10^{7} (0.35)
5×10^{-5}	0.63×10^{7} (0.32)	1.9×10^{7} (0.37)

[a] The φ_{OH} values are indicated in parenthesis.

Data of Table 2 show that $\varphi_{OH}\approx0.34\pm0.02$ and does not depend on methylviologen concentration or pH of the solution. At the same time ρ varies with methylviologen concentration and pH. Comparison of the dependencies of photonic yield on light intensity at pH=5.6 and $[MV^{2+}]=5\times10^{-5}$ M with the dependence at pH=9 and $[MV^{2+}]=0.5\times10^{-5}$ M (Figs. 1 and 2) shows that they are similar. Thus, it has been occasionally found that increasing pH from 5.6 to 9 has the same influence on photonic yield as the methylviologen concentration increase from $[MV^{2+}]=0.5\times10^{-5}$ M to 5×10^{-5} M. Both changes (increasing pH [8] and, obviously, increasing volume methylviologen concentration) result in increasing the surface methylviologen concentration. Thus, it could be assumed that pH of the solution influences photonic yield through changing methylviologen surface concentration. As photonic efficiency dependencies are described with Eq. (4) containing two parameters φ_{OH} and, ρ both of them could depend on $[MV^{2+}]$ and pH via MV_{ad} only. φ_{OH} does not depend on pH or $[MV^{2+}]$ at all. Since $\rho = (k/(k_r\sigma)^{1/2})\mathrm{MV}_{ad}$, $k/(k_r\sigma)^{1/2}$ should not change with $[MV^{2+}]$ and pH. That fact is supported additionally by direct comparison of data of Table 2 and [8]. From direct measurements of [8] at $[MV^{2+}]=5\times10^{-5}$ M, the number of MV_{ad} ions at pH=5.6 is ca. 7 ions per particle, at pH=9, $\mathrm{MV}_{ad}\approx23$, i.e. MV_{ad} increases about three times when pH changes from 5.6 to 9 like ρ does (see Table 2). Thus, it could be accepted that the changes of ρ are caused mainly by variations of MV_{ad}.$(k/(k_r\sigma)^{1/2})$ remains constant at different pH and surface methylviologen concentrations. Taking into account σ, one can find that $k/(k_r)^{1/2} \approx 0.82\,s^{-1/2}$.

The constants φ_{OH}, $k/(k_r)^{1/2}$ should be different for different TiO_2 species (because of difference in volume and surface structure of TiO_2, particle size, etc.) but can characterize activity of each TiO_2 species in a quite wide range of pH, methylviologen concentrations and light intensities.

It is of interest that the highest photonic efficiency of methylviologen oxidation $\varphi=\varphi_{OH}\approx0.34$ actually coincides with the photonic efficiency of methylviologen reduction in aqueous suspension of the same TiO_2 (Degussa P25) [28].

Now let us consider the dependencies of initial rates on the methylviologen concentration. Figs. 3 and 4 show that the value of light intensity affects the shape of those dependencies.

The results obtained may be interpreted in two ways (see also [10]).

First, the photodesorption of methylviologen from the TiO_2 particle surface into solution may occur. Increasing illumination increases the OH radical concentration (the localized positively charged holes) at the particle surface, and thus, makes the TiO_2 particle charge more positive. This should result in partial photodesorption of positively charged

Table 3

I_0 (einstein cm^{-2} s^{-1})	K (M^{-1})	
	pH=5.6	pH=9
4.17×10^{-9} 0.46×10^{-9}	1.4×10^5	0.6×10^5

methylviologen, and thus, leads to a complete occupation of the TiO_2 surface centers at a higher methylviologen concentration in the solution. The constant K has to diminish its value as we see from the experiments (see Table 1).

Changing TiO_2 particle charge to a more positive value in the presence of methylviologen is possible in principle but needs additional supports [29].

On the other hand, the model suggested above can explain all experimental results without additional complications. Suppose that MV_{ad} follows Langmuir–Hinshelwood type dependence. As $\rho = (k/\sqrt{k_r\sigma})MV_{ad}$, we can write:

$$\rho \approx \rho_m \frac{K[MV^{2+}]}{1+K[MV^{2+}]} \tag{5}$$

where ρ_m, K are constants depending on pH.

At high light intensities when $(4\varphi_{OH}I_0)/\rho^2 \gg 1$, Eq. (4) can be reduced to $\varphi \approx \varphi_{OH}^{1/2} I_0^{-1/2} \rho$ that with Eq. (5) can be rewritten as follows:

$$\varphi \approx \varphi_{OH}^{1/2} I_0^{-1/2} \rho_m \frac{K[MV^{2+}]}{1+K[MV^{2+}]} \tag{6}$$

At high light intensities, photonic efficiency (φ) and initial oxidation rate (W) should follow Langmuir–Hinshelwood type curve.

With decreasing I_0, the shape of the dependence of φ on $[MV^{2+}]$ according to Eq. (4) starts to deflect from Eq. (6) reaching the plateau at lower $[MV^{2+}]$. Numerical analysis shows that the data of Figs. 3 and 4 could be well fitted with Eq. (4) (taking into account Eqs. (1) and (5)) with K listed in Table 3.

Corresponding approximation curves are shown in Figs. 3 and 4 with solid lines.

The model under discussion has an assumption that is not evident and needs to be additionally based. That is the assumption that the rate of $OH^\bullet$ radials formation does not depend on the light intensity and surface concentration of the reagents. This appears to be true when an active acceptor of photogenerated electrons is used.

The suggested scheme of $OH^\bullet$ radicals formation is depicted in Fig. 5. The evaluations made above show that a primary TiO_2 particle adsorbs photons rather rarely, i.e. one photon a 10^{-3} s. In the present article, we assume that the typical time of photogenerated interface electron transfer from TiO_2 particle to methylviologen becaution is much less [21,22]. Thus, the TiO_2 primary particle is free from photogenerated electron (not localized or localized as Ti^{3+}) when a photon is adsorbed (state 1, Fig. 5).

Being based on the studies of elementary processes [3,21–45] and strongly simplifying the findings, the following model may be suggested. Adsorption of a photon with photonic efficiency near 1 results in formation of a non-localized electron and a hole:

$$TiO_2 \xrightarrow{h\nu} e + h, \quad (1 \to 2) \tag{r.1}$$

This step is depicted in Fig. 5 as changing the state of the TiO_2 particle from 1 to 2.

Then the non-localized electron is captured by the surface center to form Ti_s^{+3} (∼180 fs [30], 30 ps [33], 5 ns [3]):

$$e + Ti_s^{4+} \to Ti_s^{3+}, \quad (2 \overset{\varphi_{23}}{\to} 3) \tag{r.2}$$

The time seems to increase with the depth of the trap [2].

This step is depicted in Fig. 4 as changing the state of the TiO_2 particle from 2 to 3. Only the recombination of the non-localized electron and hole appears to be able to compete with the process of electron localization

$$e + h \to \text{heat}, \quad (2 \to 1) \tag{r.3}$$

which corresponds to returning TiO_2 particle back to initial state 1 (Here we neglect the recombination of non-localized

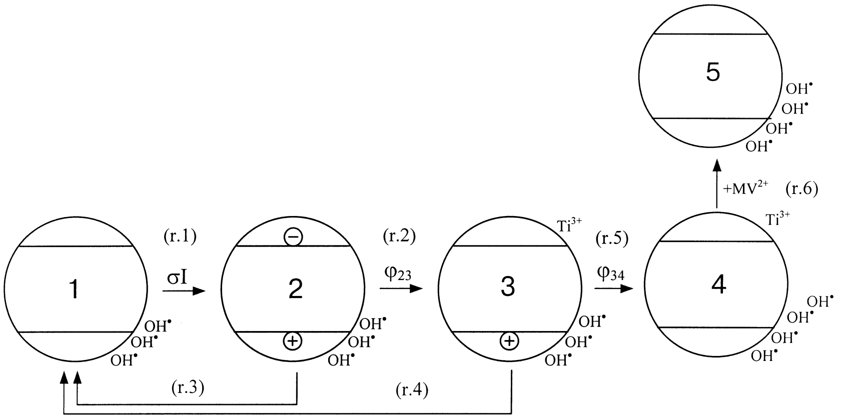

Fig. 5. The scheme of $OH^\bullet$ radicals formation.

electron with localized hole ($OH^{\bullet}$ radical) because the recombination time is about 100 ns [2] that is much higher than the time needed for electron localization).

The photonic efficiency (φ_{23}) of the formation of state 3 is equal to the share of TiO_2 particles which are able to reach state 3 from state 2.

Then the captured electron and non-localized hole have two main choices. They can either recombine (~30 ns [33])

$$h + Ti_s^{3+} \rightarrow Ti_s^{4+} + \text{heat}, \quad (3 \rightarrow 1) \tag{r.4}$$

which corresponds to the returning of TiO_2 particle back to initial state 1, or the non-localized hole can localize, forming new OH radical (~30 ns [33])

$$h + OH_s^- \rightarrow OH_s{}^{\bullet}, \quad (3 \xrightarrow{\varphi_{34}} 4) \tag{r.5}$$

Here we neglect the bulk electron–hole recombination. It seems to be valid for given size of TiO_2 particles because of about 10% of TiO_2 units are the surface ones and potentially recombination centers. The volume concentration of recombination centers of common semiconductors or oxides having semiconductor properties is much lower.

The process of OH radical formation is depicted in Fig. 5 as changing the state of the TiO_2 particle from 3 to 4. Only φ_{34} part of TiO_2 particles, being in the state 3, can reach state 4.

After that the localized electron mainly reduces methylviologen (below 1 μs [21,22])

$$Ti_s^{3+} + MV^{2+} \rightarrow Ti_s^{4+} + MV^{\bullet +} \tag{r.6}$$

which in turn transfers the photogenerated electron to oxygen and turns back to becaution state:

$$MV^{\bullet +} + O_2 + H^+ \rightarrow MV^{2+} + HO_2{}^{\bullet}$$

Thus, according to that scheme, the photonic efficiency of the OH radical formation is equal to $\varphi_{OH}=\varphi_{23}\varphi_{34}$. Increasing the light intensity increases the frequency of TiO_2 particle passing from state 1 to state 5 but does not change the photonic efficiency of the OH radical formation.

It should be noted that after adsorption of a photon, TiO_2 particle relaxes from state 2 to state 5 for less than 1 μs. Since TiO_2 particle will have adsorbed the next photon about 1 ms later, the probability of this happening when TiO_2 particle goes from state 2 to state 5 is very low (below $1\,\mu s/1\,ms=10^{-3}$). The fact that the average photogenerated electron/hole concentration is well below unit strongly simplifies the consideration. In the case of average concentration comes near unit, a strict description demands a stochastic approach [33].

It has to be pointed out that the present scheme to be valid only if the reaction (r.6) is slower than reaction (r.5) (because otherwise methylviologen concentration would affect the φ_{34} and in turn the photonic efficiency of the OH radical formation) and faster than recombination of trapped electrons with OH radicals. Some ambiguity remains here and other schemes are possible [15–20].

It should be noted also that the times of primary photocatalytic processes given above should be treated with caution because they should dramatically vary from sample to sample. In addition, most of them have been measured at flash experiments where high power impulse is used and as a rule more than one electron–hole pair generated in each TiO_2 particle for a short time of laser pulse. On contrary, steady-state experiments are conducted at much lower light intensities where photoexited TiO_2 particle have some time to relax before adsorption of next photon.

4. Summary and conclusions

The reaction rate and the photonic yield of methylviologen photocatalytic oxidation over TiO_2 at different pH, methylviologen concentration and light intensities have been measured.

1. Neither the process of reagents adsorption nor the products desorption limit the reaction rate of methylviologen photocatalytic oxidation over TiO_2.
2. Both pH and volume methylviologen concentration affect photonic yield possibly through methylviologen concentration in vicinity of photocatalyst surface.
3. Illumination of TiO_2 leads to formation of long living species (~1 ms) through that deactivation of exited catalyst goes. The lifetime of that species increases with decreasing methylviologen concentration.
4. The model assuming deactivation of photoexited TiO_2 particle through OH radicals recombination has been examined. With two parameters (the quantum yield of OH formation and the ratio of reaction and recombination constants), which remain unchanged at different pH, methylviologen volume concentrations and light intensities, this model is able to describe the photocatalyst activity in a quite wide range of experimental conditions.
5. Decreasing light intensity as well as increasing surface methylviologen concentration results in increasing photonic yield. The maximum value of photonic yield is quite high and equals 34%.

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