

Spectral dependence of quantum yields in gas–solid heterogeneous photosystems

Influence of anatase/rutile content on the photostimulated adsorption of dioxygen and dihydrogen on titania

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Abstract

In this study we explored the photostimulated adsorption of dioxygen and dihydrogen gases on the surface of Degussa P25 titania particles subsequent to a thermal pre-treatment at 600 and 850 K, which of consequence varied the typical anatase/rutile ratio (83–17%, respectively). The focus was to probe how the anatase/rutile content modified the spectral dependence of the quantum yields of photoadsorption of O₂ and H₂. Dioxygen is photoadsorbed preferentially on the anatase component of the P25 titania specimen, inasmuch as no photoadsorption occurs on an *ultrapure* rutile particle surface. By contrast, dihydrogen photoadsorbs on both polymorphic structures on the particle surface. A model is proposed wherein the Degussa titania is taken to be composed of rutile domains (surface and bulk) in an otherwise sea of anatase. These represent nothing more than surface defects, which when excited with appropriate radiation generate photoelectrons that spillover onto the anatase phase and photostimulate the adsorption of the acceptor molecules (oxygen). © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Heterogeneous system; Titanium dioxide; Photoadsorption; Quantum yield

1. Introduction

Photocatalysis represents a field of research at the interface between photochemistry and catalysis. Numerous current and potential applications of photocatalysis require a greater understanding of the nature of photocatalysis and of the factors that affect the efficiency(ies) of photocatalytic processes. Starting from the catalytic approach toward studies of photocatalysis, the major focus and efforts of many research groups is to increase the activity and selectivity of photocatalysts. The influence of the chemical composition and the synthetic methods to prepare catalysts of various particle sizes on the photocatalytic process, together with an examination of the effects of pH, light intensity, and other parameters on the efficiencies of photocatalytic processes have been investigated extensively [1–14]. As well, the efficiency of processes in complex photochemical systems may depend strongly on the spectral variation of the actinic radiation used to drive the photo-induced events. From this

point of view, we expect to observe spectral dependencies of the activity and selectivity of catalysts in a complex photochemical system such as the photocatalytic one.

In our previous theoretical approach [15], we examined a number of physical factors that might affect the activity and selectivity of photocatalysts. One particular factor was the absorption coefficient of the solids whose spectral variation under certain conditions can lead to spectral variations in the activity and selectivity of the photocatalyst. Some of the first experimental indications of the existence of spectral dependencies of photocatalyst activity in gas–solid heterogeneous systems were obtained in the late 1930s by Kasparov and Terenin [16]. Later this effect was also investigated by the research groups of Solonitsyn [17,18] and Zakharenko and Cherkashin [19] who observed spectral dependencies of quantum yields of simple surface photochemical processes in gas–solid systems using a specially designed black-body-like reactor.

In a recent study [20] we demonstrated that the spectral dependence of the quantum yield was also typical of liquid–solid photocatalytic heterogeneous systems (phenols–TiO₂) as well (see, e.g., Fig. 1). Moreover, the spectral dependence

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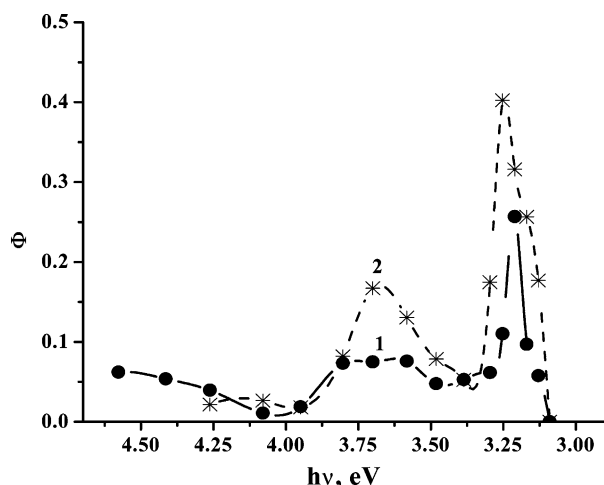


Fig. 1. Spectral dependencies of the quantum yields for the photodegradation of (1) phenol and (2) 4-chlorophenol over Degussa P25 TiO₂. From Ref. [20] (Copyright by the American Chemical Society).

of the quantum yield scaled closely with the spectral changes in the electronic transitions of the solid. Interestingly, the maxima of the spectral dependencies corresponded to the energies of the direct and indirect transitions in the semiconductor solid.

In the present article we report on the evolution of the spectral dependencies of the quantum yields of surface photochemical processes (e.g., photostimulated adsorption of oxygen and hydrogen) as they are influenced by the evolution of the phase composition of the photocatalyst, TiO₂.

2. Experimental

Powdered titanium dioxide samples of Degussa P25 and Aldrich were used as received, unless noted otherwise. They were contained in a quartz black-body-like cell specially designed by Solonitzyn and Basov [17,21] to measure quantum yields of heterogeneous photoreactions (Fig. 2; sample thickness was 5 mm; diameter of internal sphere was ca. 2 cm; diameter of light inlet window was 2.5 mm). The reaction cell was connected to a high-vacuum setup equipped with an oil-free pump system; the ultimate gas pressure in the cell was ca. 10⁻⁷ Pa. The gas pressure in the reactor was measured with a modified Pirani-type manometer with sensitivity 35 mV/Pa for oxygen and 42 mV/Pa for hydrogen. The illuminating system consisted of a 120 W xenon lamp DKSH-120 (MELZ) and a monochromator MSD-1 (LOMO) for wavelength selection. The resolution was about 0.05 eV in the 2–3 eV range reducing to about 0.1 at 5 eV.

The incident light irradiance was measured using a thermoelement (IOFI; sensitivity, 20 mV W⁻¹). Cutoff glass filters (LOMO) were used to eliminate the detrimental scattered light behind the output slit of the monochromator. Metal-supported neutral quartz filters (Vavilov SOI) were used to change the intensity of the actinic light. In order

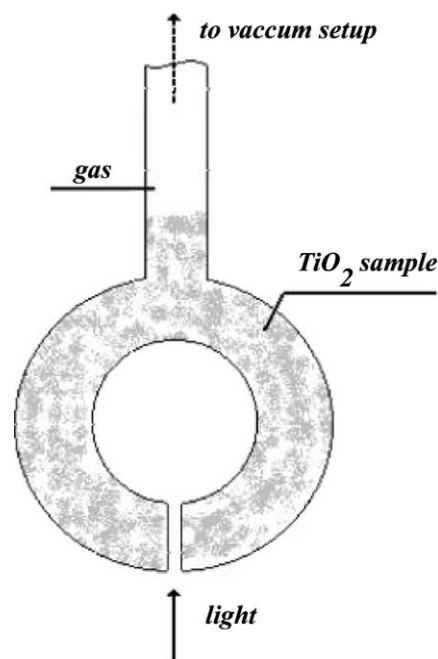


Fig. 2. Black-body-like photoreactor used to measure the quantum yields of photostimulated processes in gas–solid heterogeneous systems (see Footnote 1). From Ref. [17].

to remove adsorbed water and organic impurities from the surface, the metal-oxide samples were previously heated at 600 K in one set of experiments and at 850 K in another set under a normal atmosphere (air) and under an oxygen atmosphere ($p \approx 100$ Pa) for several days. The products of thermodestruction and desorption were removed from the system using a liquid nitrogen trap and under constant pumping at ambient temperatures. Prior to every measurement the samples were pre-heated in an oxygen atmosphere at $T = 600$ K for 15–20 min and cooled down under dynamic vacuum conditions.

Calculations of the quantum yields, Φ , of surface photochemical processes were based on the definition of the quantum yield in use in photochemistry (see Eq. (1)) as the ratio of the rate of turnover of molecules (dN_{mol}/dt (molecules s⁻¹)) taking part in the photoreaction and the rate of photons absorbed by the photocatalyst system ($dN_{h\nu}/dt$ (photons s⁻¹):

$$\Phi = \frac{dN_{\text{mol}}/dt}{dN_{h\nu}/dt} \quad (1)$$

The experimental reaction rate dN_{mol}/dt (molecules s⁻¹) was obtained from the following equation:

$$\frac{dN_{\text{mol}}}{dt} = \frac{dP}{dt(t \rightarrow 0)} \left[\frac{V_{\text{reactor}}}{\kappa T} \right] \quad (2)$$

and the rate of photons absorbed by the system, as defined by $dN_{h\nu}/dt$ (photons s⁻¹), was obtained from the following equation:

$$\frac{dN_{h\nu}}{dt} = A_{\lambda} \rho S_{\text{reactor}} \quad (3)$$

where V_{reactor} is the volume of the reactor occupied by the gases, $dP/dt_{t \rightarrow 0}$ is the experimentally measured initial (maximal) reaction rate (in units of Pa s^{-1}), κ the Boltzmann's constant, and T the Kelvin temperature (K); A_λ the absorbance of the heterogeneous system at the given wavelength, λ , ρ the light intensity at the given wavelength (in units of $\text{photons s}^{-1} \text{m}^{-2}$), and S_{reactor} the illuminated area of the reactor's window. The expression for the experimentally determined quantum yield is then given by the following equation:

$$\Phi_\lambda = \frac{(dP/dt)_{(t \rightarrow 0)}(V_{\text{reactor}}/\kappa T)}{A_\lambda \rho S_{\text{reactor}}} \quad (4)$$

In all our experiments we used the black-body-like cell (Fig. 2); due to its geometry the absorbance of the system at all wavelengths was $A_\lambda = 1$.¹ In this case also, S_{reactor} was the cross-section of the light inlet opening in the reactor cell. Note that in such experiments the actual illuminated surface, S , of the powdered sample is always an unknown quantity. Obviously, the theoretical estimation of S , which depends on the dispersion of the sample and on its absorbance and reflectance, presents a difficult challenge, which to our knowledge has not yet been resolved. Moreover, illumination of the sample surface is strongly non-uniform, whereas the definition of the quantum yield in heterogeneous systems requires that the surface be uniformly irradiated. It is relevant to note, however, that the quantum yield Φ does not depend on S as long as the rate of reaction is directly proportional to the irradiance of the incident light [17]. The latter condition is also essential in order to avoid a dependence of the quantum yield on light irradiance, and to measure the maximal quantum yield of the photochemical process in the heterogeneous system. In this manner, Φ can then be used to compare results with those obtained in other laboratories [9,22].

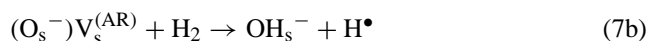
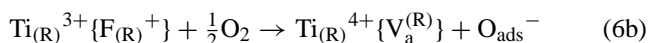
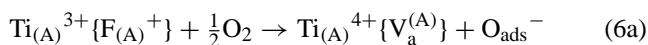
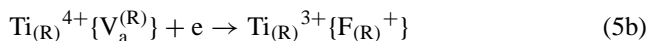
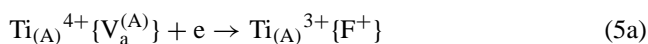
In preliminary experiments we detected the existence of the interdependence of the reaction rate on light irradiance and on the gas pressure (concentration), which we showed earlier to be typical for other heterogeneous systems [9,23]. Consequently, we needed to determine the pressure range within which the rate of photoadsorption scaled linearly with light irradiance. At a pressure of 2 Pa for both oxygen and hydrogen gases the linear dependence of the reaction rate on light irradiance obtained for both titania samples. Thus,

¹ Any system under illumination can reflect the light (with fraction of reflected light R), transmit (with fraction of transmitted light T), absorb it (with the fraction of absorbed light A). The total balance can be represented as: $A+R+T = 1$. Note that no ideally reflective sample exists, so R of the sample is never equal to 1. Due to geometry of "black body" reactor (see Fig. 2) the fraction of reflected light $R \rightarrow 0$ since the area of inlet window is much smaller than the area of the internal sphere of reactor covered with the metal oxide. The thickness of the sample (5 mm) is sufficient enough to assume that the sample is optically "black" for transmitted light, that is $T \rightarrow 0$. This assumption can be easily confirmed using diffuse reflectance spectroscopy. Consequently, the light going into the internal sphere of the reactor through the inlet window is absorbed completely, that is $A = 1$ for any wavelength used to irradiate the system.

the experimentally measured quantum yields reported here are independent of the surface area irradiated; as such they correspond to the true quantum yields.

3. Results and discussion

In the present study we examine the spectral dependencies of the quantum yields of photostimulated adsorption of hydrogen donor molecules and oxygen acceptor molecules. On a sufficiently dehydroxylated surface of TiO_2 , adsorption of donor molecules occurs on hole surface active centers (O_s^- -like) formed on trapping photogenerated holes by surface defects such as cation vacancies V_c , which result in the formation of surface V-type centers. Adsorption of acceptor molecules takes place at electron surface active centers (e.g., Ti^{3+} , F^+ , and F-like²) formed on trapping photoelectrons by surface defects such as, e.g., displaced or low-coordinated titanium cations $\text{Ti}_{\text{def}}^{4+}$ and anion vacancies V_a in the anatase (A) and rutile (R) forms. Eqs. (5a)–(7b) summarize some of the events:



At the sufficiently high pressures used in our experiments, chemical interactions become the dominant pathways for the decay of surface-active centers. The physical pathways for decay of these centers through recombination and/or thermoionization are negligible. The rate, and hence the efficiency, of photo-stimulated adsorption is then dictated by the rate (efficiency) of generation of the corresponding surface active centers, which will depend on the photophysical properties of the catalyst examined.

The experimental spectral dependencies of the quantum yields of photostimulated adsorption of oxygen and

² The notation F-type center has been brought from the solid state physics and spectroscopy of solids where its meaning is the anion vacancy with trapped electron(s). The classic example of F center is the one in alkali halide crystals where it represents the anion vacancy with one trapped electron that makes such center neutral with respect to the lattice. In metal oxides anion vacancy has two positive charges relative to the lattice. Consequently, the trapping of one electron creates a single positively charged defect named F^+ center, whereas the trapping of the second electron forms neutral F center. Both centers together with Ti^{3+} behave as active centers of adsorption of gas acceptor molecules. The reason why we use the language of solid spectroscopy is that identification of active centers of photoadsorption on metal oxides as F-type centers in original works has been made using UV-Vis and ESR spectroscopy where such notation is typical.

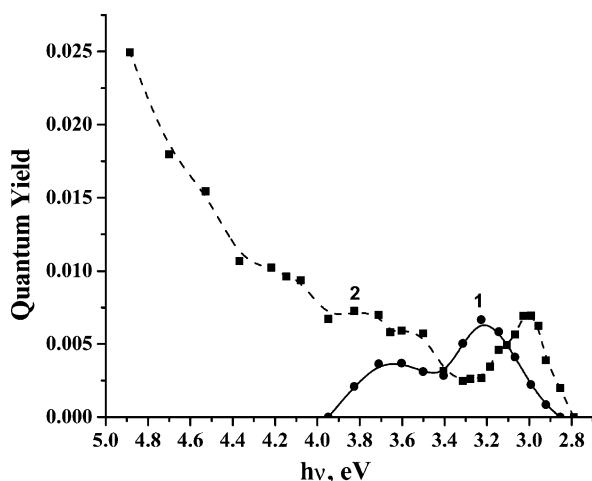


Fig. 3. Spectral dependencies of the quantum yields of photostimulated adsorption of (1) dioxygen and (2) dihydrogen on the surface of Degussa P25 TiO₂ specimen pre-treated at 600 K.

hydrogen molecules on the surface of Degussa P25 TiO₂ specimen that was pre-treated at $T = 600$ K are presented in Fig. 3. These spectral dependencies display a multi-band spectra-like structure with maxima at ca. 3.0, 3.12(sh) 3.55, 3.8, 4.1, and 4.55(sh) eV for dihydrogen and at 3.20 and 3.65 eV for dioxygen. The lowest energy maxima correspond to the energies of the bandgap indirect transitions in the rutile and anatase components in the Degussa P25 sample, respectively; other maxima correspond to the direct electronic transitions from the valence bands to the conduction bands. They are in good agreement with maxima positions obtained in our earlier study for the liquid–solid systems (TiO₂ Degussa P25—phenols) (see Fig. 1) [20]. The multi-band spectra of the quantum yield spectral dependence result from an overlap of the absorption bands that correspond to the different electronic transitions [15]. In such case, the total experimental quantum yield can be represented by the following equation:

$$\Phi = \frac{R}{A\rho} = \frac{\sum_i A_i \Phi_i}{\sum_i A_i} \quad (8)$$

for which the total reaction rate R is given by the following equation:

$$R = \sum_i R_i = \sum_i A_i \rho \Phi_i \quad (9)$$

where R_i is the rate of the elementary reaction under excitation in the i th single absorption band, A_i the absorbance in the i th single absorption band, and Φ_i the corresponding quantum yield of the reaction. The total number of absorbed photons per unit time is given by $A\rho = \rho \sum_i A_i$, where A is the total absorbance at a given wavelength. Note that according to Eq. (8) the necessary condition to observe the spectral dependence of the quantum yield is the different values of the quantum yields Φ_i for each single absorption band corresponding to the i th electronic transition.

In spite of the qualitative similarity between the spectra of the quantum yields in gas–solid and liquid solid systems, the relative values of the maxima in the gas–solid system differ from those in the spectrum of the quantum yield obtained for liquid–solid systems [20]. We infer that this is caused by variations in the ratio between the anatase and rutile phases in the Degussa P25 titania specimen from the pre-treatment stage. In fact, as demonstrated by an X-ray structural analysis, in its original state the Degussa P25 titania specimen used contains ca. 83% anatase and ca. 17% rutile, whereas after the pre-treatment at $T = 600$ K the sample is composed of ca. 50% anatase and 50% rutile. Note that the temperature of the pre-treatment stage is sufficiently less than the temperature of the phase transition from anatase to rutile known for TiO₂. Nonetheless, a certain amount of the anatase polymorph in the Degussa P25 sample has undergone some phase transformation.

It is interesting that the temperature of the pre-treatment stage, as used herein, corresponds to the temperature range wherein a drastic decrease of the activity of Degussa P25 titania was observed by Augugliaro et al. [7] for the photooxidation of phenol. We suppose that the greater influence of the surface in polycrystals plays an important role in phase transformations that occur at lower temperatures (below the phase transition temperature). Further, increasing the pre-treatment temperature to $T = 850$ K causes the nearly complete transformation of the Degussa P25 specimen into the rutile (97%) form under our conditions. The latter is reflected in the spectral dependencies of the quantum yields of photostimulated adsorption of both dioxygen and dihydrogen gases. The first major maximum in Fig. 4 is seen at about 2.9–3.0 eV corresponding to the indirect transition energies in rutile for such a specimen. Note that for the original state of the Degussa P25 titania, the first maximum observed in the spectral dependence of the quantum yields in the photooxidation of the phenols (Fig. 1) occurred at

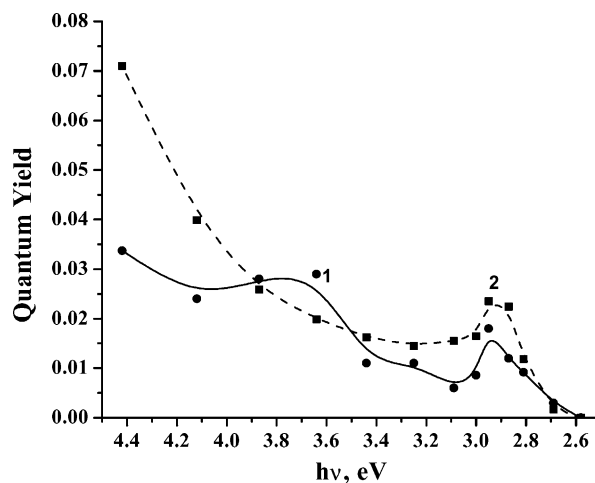


Fig. 4. Spectral dependencies of the quantum yields of photostimulated adsorption of (1) dioxygen and (2) dihydrogen on the surface of Degussa P25 TiO₂ specimen pre-treated at 850 K.

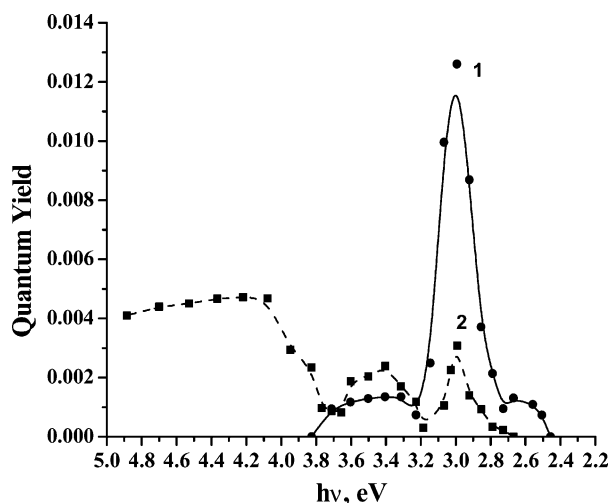


Fig. 5. Spectral dependencies of the quantum yields of photostimulated adsorption of (1) dioxygen and (2) dihydrogen on the surface of a TiO_2 (Aldrich, rutile) specimen pre-treated at 600 K.

3.20 eV. In Fig. 3, the lowest energy maximum for the photoadsorption of dioxygen is seen at 3.20 eV (bandgap of anatase), whereas for the photostimulated adsorption of dihydrogen it is seen at ca. 3.0 eV (bandgap of rutile).

We now compare the spectral dependencies of the quantum yields of photochemical processes on the surface of Degussa P25 TiO_2 pre-treated at $T = 850$ K with those obtained for the “Aldrich” TiO_2 specimen (Fig. 5) pre-treated at $T = 600$ K to remove adventitious organic impurities. This latter specimen contains only the rutile phase before (original state) and after the pre-treatment. It is also relevant to compare the present results with the spectral dependencies of the quantum yields reported earlier for the ultrapure powdered rutile.

We suggest that the different values of the quantum yields for the photochemical processes on the surface of rutile and anatase, as accounted for by Eq. (8), are the reason for the spectral variations of the total quantum yield in the system. However, we cannot preclude the notion that an overlap of the absorption spectra of the two phases of TiO_2 , as encountered in the Degussa P25 specimen, may also result in a multi-band-like structure of the spectral dependencies of quantum yields in a narrow range of the values of the parameters (e.g. variations in absorption coefficients, differences in diffusion lengths of the carriers, and the anatase/rutile ratio) of the catalysts. Nonetheless, such overlap cannot be the sole factor that describes the whole spectral dependence, since we also observe a multi-band-like spectra of the quantum yields for specimens that contain only one phase (e.g., rutile; see Fig. 5).

To describe qualitatively the experimental spectral dependencies of the quantum yields we deduce [20] that relaxation of carriers produced from the different electronic transitions to higher energy states down to the bottom of the conduction band for the electrons (or to the top of the valence band for the holes) is not fast enough to compete with surface

chemical processes. In other words, the hot carriers generated in the higher energy states are involved in the formation of surface-active centers of photostimulated adsorption. Differences in the physical parameters of hot carriers (lifetimes, mobilities, and trapping cross-sections of carriers by the surface active centers) are responsible for the different quantum yields in each single i th absorption band, and thus for the spectral dependence of the total quantum yield of the surface photochemical processes.

It is relevant to note the maxima of the spectral dependence of the photoadsorption of dioxygen on Degussa P25 TiO_2 , which correspond to the energy of electronic transitions that are typical of the anatase form only, whereas for the photoadsorption of dihydrogen the maxima correspond to the energy of electronic transitions in both the anatase and the rutile forms contained in the Degussa P25 sample. This is in keeping with earlier results that photoadsorption of dioxygen does not occur on an otherwise ultrapure rutile surface (high purity grade IREA rutile TiO_2 , Moscow) at ambient temperature, but does so at 100 K (see Footnote 1). The latter observation may be due either to a low thermal stability of the surface-active centers for oxygen photoadsorption, or to a high recombination rate of the carriers through these electron surface active centers. Strangely, however, oxygen photoadsorption does occur on the Aldrich TiO_2 specimen surface and on the surface of the Degussa P25 sample pre-treated at 850 K, which was shown to consist of 97% rutile with the major maximum in the spectral dependence of the quantum yield corresponding to the bandgap energy of rutile (3.0 eV). We infer that differences in activity between the Degussa and the Aldrich samples toward the photoadsorption of acceptor oxygen molecules are governed by differences in their surface structural details that manifest themselves particularly in the different acidities of the two specimens.

The kinetic curves of solution pH changes after introducing the titania samples in water are presented in Fig. 6. The total surface area of all the specimens was kept the same at 5 m^2 . In its original state, the Degussa P25 specimen surface has more acid character. Surface acidity has in fact increased after the pre-treatment procedure, whereas the behavior of the Aldrich sample after the same thermal pre-treatment at 600 K remains invariant. Evidently, the surface of Degussa P25 titania has undergone significant changes that increase its acidity. Such changes have generated a new surface structure that causes the rutile component of the TiO_2 specimen to be inactivated toward the photoadsorption of dioxygen. Note also that the quantum yields of photochemical processes occurring on the surface of the Degussa specimen pre-treated at the higher temperature (850 K) are greater than for those taking place on the surface of the sample pre-treated at 600 K. This is caused by a thermostimulated formation of additional surface defects (surface active centers) owing to removal of stronger bonded hydroxyl groups at the higher temperature.

We deduce that phase transformation from anatase to rutile during the pre-treatment at the lower temperature (600 K) in the presence of oxygen creates a low-defect rutile surface

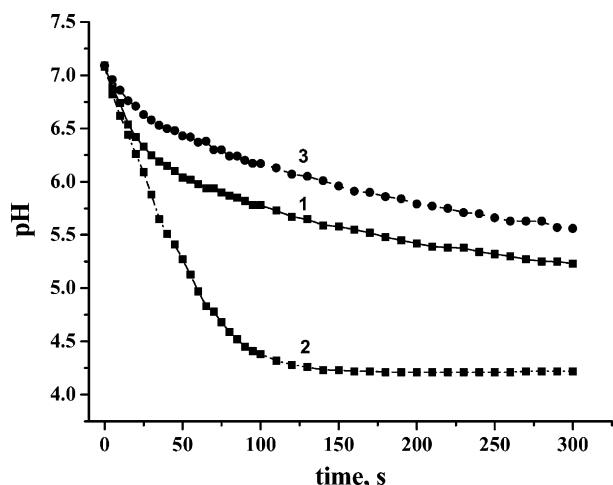
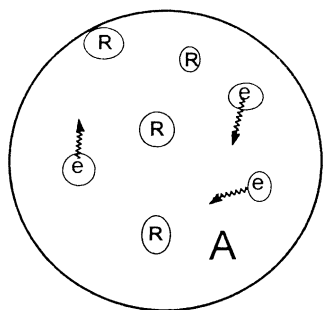


Fig. 6. Temporal kinetic changes taking place on introducing a TiO_2 specimen into water: (1) Degussa P25 in its original state; (2) Degussa P25 titania after the thermal pre-treatment at 600 K; (3) Aldrich rutile specimen before and after the thermal pre-treatment also at 600 K.

vis-à-vis the potential electron active centers (e.g., anion vacancies, low-coordinated Ti^{4+}), which will preclude the photostimulated adsorption of oxygen on the rutile surface in a manner similar to the behavior of ultrapure rutile (see above). That is, the thermal pre-treatment suppresses the anion vacancies in rutile more so than it does in the anatase phase. Moreover, photogenerated electrons in the rutile domains (R; see below), which can in essence be considered as surface defects in the Degussa P25 titania specimen, may spillover onto the anatase component (A). Only the anatase surface is active in the electron-involving processes of



Degussa P25 TiO_2

Eqs. (5a)–(6b) (see Fig. 3). At the higher pre-treatment temperature (850 K), when the anatase-to-rutile transformation is nearly complete, thermal dehydroxylation creates new active centers on the rutile surface, which becomes reactivated (see Fig. 4) toward the photoadsorption of the acceptor molecules oxygen. In other words, the pre-treatment at the higher temperature creates more surface defects and a higher energetic surface structure as demonstrated by the pH evolution. Unfortunately, simple experiments such as these provide no indicators as to what sort of surface transformation(s) is responsible for such pH behavior. Other

methods are required to probe the peculiar characteristics of the particle surface. Studies in this direction are in progress and will be reported at a later date.

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