

Photocatalytic activity of spectro-pure titanium dioxide: Effects of crystalline structure, specific surface area and sorption properties

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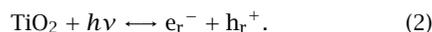
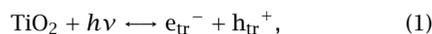
ABSTRACT. Dispersed optically pure anatase, rutile and two-phase samples of titanium dioxide were prepared using a sol-gel technique. In particle of two-phase samples, the anatase nuclei are surrounded by a rutile envelope. Content of anatase in the two-phase particles varied between 20 and 80%. Particles of all the TiO₂ samples had a globular shape of diameter between 10 and 30 μm. When compared to the corresponding technical-grade samples, the optically pure anatase and rutile demonstrated higher photocatalytic activity in the destruction of tetradecylpyridinium chloride, Methylene Blue and tetrachlorofluorescein as well as in reduction of Cr₂O₇²⁻, MnO₄⁻, [Fe(CN)₆]³⁻ and [Fe(CN)₆]⁴⁻. The photocatalytic reactions bring about the reduction of the inorganic anions to yield water insoluble substances and mineralization of the organic compounds. Rate constant of the all above processes do not depend on specific surface area of TiO₂ and adsorption of the substrates on the TiO₂ samples. The rutile calcined at 1027K exhibits the highest specific rate constants. Exposure to γ-radiation increases photocatalytic activity of the dispersed TiO₂. The influence of TiO₂ and substrate on the photocatalytic reactions is caused by the influence of these factors on the formation of reactive electron hole pair and on the efficiency of the interfacial electron transfer.

1. INTRODUCTION

Photocatalytic reactions of organic or inorganic compounds on wide-bandgap semiconductors can be used for the destruction (mineralisation) of water contaminants [1-3]. Nowadays, among the various semiconductors studied, titanium dioxide dispersed or in the form of film is thought as one promising photocatalytic agent because of its high activity in combination with nontoxicity, high stability and availability. Much work has been carried out on kinetics and mechanisms of the photocatalytic processes assisted by TiO₂. However, conflicting conclusions may be encountered in literature about the correlation between photocatalytic activity and crystalline structure of TiO₂. The following examples can be given as an illustration. Thus, anatase is more active as compared with rutile in the destruction of organic dyes [4, 5] but rutile shows higher activity in the photocatalytic mineralisation of trichloroethylene [6]. Opinions differ also widely about influence of sorption properties of titanium dioxide on its photocatalytic activity. Likewise little work has been carried out on the association between efficiency of the photocatalytic process and specific surface area of the dispersed TiO₂. Here we present a study of the effects of adsorption properties, specific surface area and crystalline structure on photocatalytic activity of the dispersed TiO₂ in mineralisation of tetradecylpyridinium chloride,¹ Methylene Blue, tetrachlorofluorescein as

well as in reduction of MnO₄⁻, Cr₂O₇²⁻, [Fe(CN)₆]³⁻ and [Fe(CN)₆]⁴⁻.

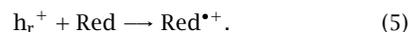
The basic principles of heterogeneous photocatalysis on TiO₂ can be summarized shortly as follows [2, 3, 18]. Photoexcitation of the semiconductor leads to the formation of the unreactive (1) or reactive (2) electron holes pair. For colloidal TiO₂, the hole trapping occurs in a few hundred nanoseconds, whereas electron trapping processes in the picoseconds time frame



The electron, e_r⁻, and the hole, h_r⁺, can recombine on the surface or in the bulk of the particle in few nanoseconds



or can be trapped by acceptor (A) or donor (D) on the surface of the particle

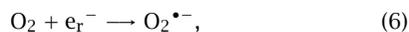


In the absence of the suitable electron acceptors or hole scavengers, the electron-hole recombination represents the energy dissipation route.

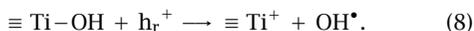
¹ Abbreviations: TDPy⁺ Cl⁻-tetradecylpyridinium chloride; MB⁺ Cl⁻-Methylene Blue; TCF-tetrachlorofluorescein; A-anatase;

R-rutile; X%A Y%R-the two-phase titanium dioxide containing X and Y percentages of anatase and rutile, respectively.

The photocatalytic degradation of organic materials in aqueous solutions by TiO₂ in the presence of oxygen seems to originate from the generation of hydroxide or superoxide radicals which react with substrates or the radical ions derived from the substrates



Hydroxide radicals are also generated in oxidation of surface hydroxyls by h⁺



It is well known that doping titania with metal transition ions can have a profound impact on the photogeneration of the electrons and holes in the TiO₂ lattice (see, for example, [7]). Deposition of transition metal ions onto TiO₂ may trigger electron or hole trapping that plagues analysis of influence crystalline structure, specific surface area and other physicochemical factors on photocatalytic activity of TiO₂. Therefore, the spectro-pure samples of TiO₂ studied in this work enable to compare photocatalytic behavior of various TiO₂ samples.

2. EXPERIMENTAL

2.1. Preparation and investigation of the TiO₂ samples. The optically pure TiO₂ was prepared by thermal hydrolysis of titanium tetrachloride in hydrochloric acids solutions in the presence of the anatase or rutile nuclei by the procedure proposed in [8–10], which allow to keep stray ions to a minimum in all the titanium dioxide modifications. Addition of anatase nuclei, results in the optically pure anatase or in the two-phase titanium dioxide with the anatase nuclei and the rutile envelope depending on synthesis conditions. Content of anatase in the two-phase particles was varied between 20 and 80% that was determined with the help of X-ray analysis.

After synthesis, the TiO₂ samples were calcined at 473, 573 and 1073 K followed by washing by water and dried at 473 K for 48 hours. The content of stray ions (Fe, Co, Cr, Ni, Cu, Mn, V) in the prepared materials did not exceed 10⁻⁵%.

The TiO₂ particles had a globular shape of diameter between 10 and 30 μm. Specific surface area in the range fell 3 to 200 m²/g. Part of the TiO₂ samples was irradiated with γ-rays in a setup with ⁶⁰Co as the gamma-emitter. Dose power was 4.3 × 10⁻² Gy/s.

2.2. Sorption and photolysis procedures. Adsorption of the substrates by TiO₂ from aqueous solutions was studied by the standard procedure [11]. Concentrations of the substrates in solutions were measured spectrophotometrically. Experimental relative error for determination of adsorbed substrate, *a*, was within 10%.

The light source for the photodegradation experiments was the low-pressure mercury lamp BUV-30 (30 W, Ukraine) which emits about 83% light energy at 253.6 nm. The photocatalytic reactor was a quartz tube of 2.5 cm across provided with a stirrer. Rotation speed was 120 vpm. The reactor was 1 cm distant from the lamp. In the photocatalytic experiments, concentration of TDPy⁺Cl⁻ and the dyes was 0.09 g/l and 0.03 g/l, respectively. Concentration of K₂Cr₂O₇ was 0.06 g/dm³ and that of KMnO₄, K₃[Fe(CN)₆] and K₄[Fe(CN)₆] was 0.3 g/dm³. The solid/liquid ratio was about 1 : 170.

Prior UV irradiation, the TiO₂ suspension in substrate solution was magnetically stirred in the dark to attain the adsorption/desorption equilibrium between the substance and the TiO₂ particles. Sorption and kinetics of the photocatalytic reactions were studied at pH 3 apart from specified experiments.

The reaction products were analyzed by UV, ¹HNMR spectroscopy (Varian 300) and mass-chromatography (INCOS 50, Finnigan Corporation.)

3. RESULTS

3.1. Sorption of the substrates on TiO₂. Sorption of the substrates has been studied with the object of understanding implications of sorption for the photocatalytic reactions. Sorption kinetics was exponential for the majority of the TiO₂ samples regardless of their crystalline structure. The time taken to the attainment of the sorption equilibrium was defined by substrate rather than crystalline structure of the TiO₂ sample. The equilibrium was reached in 35, 2 and 0.5 h for TDPy⁺Cl⁻, MB⁺Cl⁻ and TCF, respectively. The sorption capacity of anatase was about one order of magnitude higher compared to rutile. Sorption capacity of the two-phase samples depended only slightly on the anatase/rutile ratio. The samples bearing 65% anatase demonstrated the highest sorption capacity among the two-phase samples, which was close to that of anatase.

Sorption of TDPy⁺Cl⁻ and MB⁺Cl⁻ on anatase occurred in two stages. In the course of the first one with duration of about 10 hours, anatase absorbs about 90% of the substrate amount, which can be adsorbed in the given experimental conditions. Length of the second sorption stage exceeded 20 h. The two-step kinetics was also noted for sorption of MB⁺Cl⁻ on anatase.

Sorption of the TDPy⁺ and MB⁺ cations decreased as pH solution is reduced (Figure 1(a)). By contrast, sorption of the anions Cr₂O₇²⁻, [Fe(CN)₆]³⁻ or MnO₄⁻ increases with decreasing pH (Figure 1(b)). The influence of pH on sorption of the indicated substrates can be derived from amphoteric nature of the OH groups on the TiO₂ surface. At all pH, correlation between *a* and specific surface area is lacking for sorption of TDPy⁺ and MB⁺ on anatase, rutile and the two-phase modification.

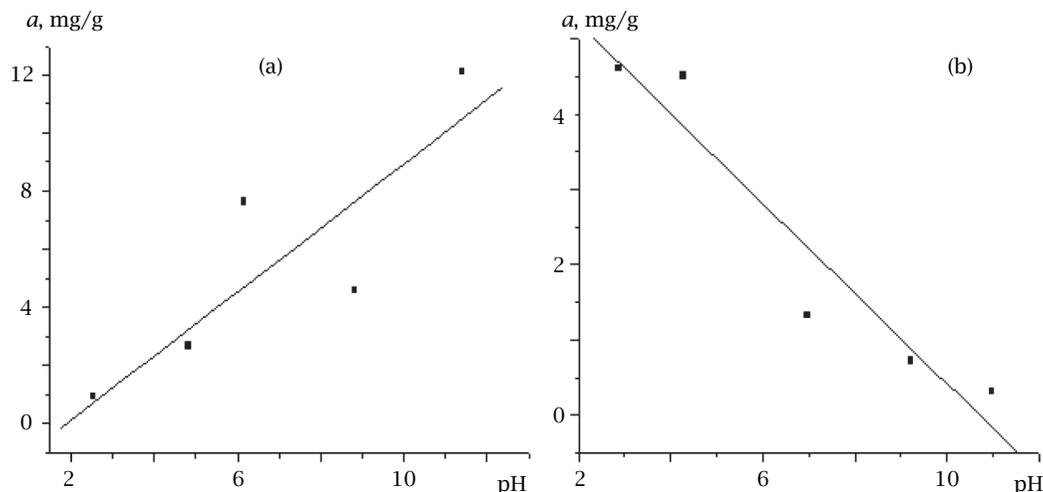


Figure 1. The pH dependences of adsorption of TDPy^+Cl^- (a) and inorganic anions (b) on anatase.

Sorption isotherms for all the above compounds relative to the L-type (Langmuir type) in terms of the Giles classification [12]. The L_2 -isotherms, taking hyperbolic form, describe sorption of all the substrates on rutile and on the two-phase TiO_2 with the anatase content less than 60% as well as sorption of MB^+Cl^- , $[\text{Fe}(\text{CN})_6]^{3-}$ and TDPy^+Cl^- on anatase (Figure 2). The isotherms, which do not exhibit a plateau area, govern sorption of TCF, MnO_4^- , $\text{Cr}_2\text{O}_7^{2-}$ on anatase and on the two-phase TiO_2 , containing above 60% anatase.

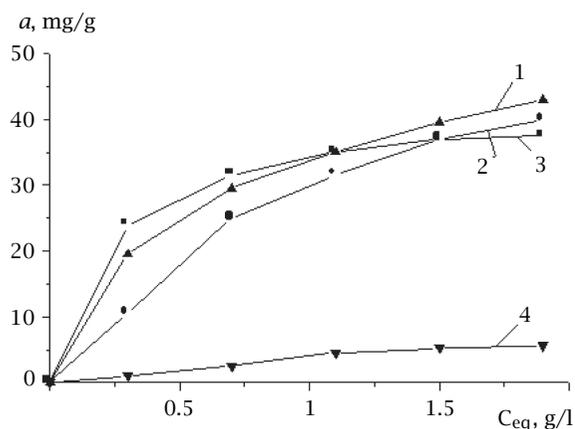


Figure 2. Isotherms of TDPy^+Cl^- adsorption on the dispersed titanium dioxide. 1-65%A 35%R, 2-75%A 25%R, 3-A, 4-R.

3.2. Products of the photochemical and photocatalytic reactions in aqueous solutions TDPy^+Cl^- . UV irradiation of TDPy^+Cl^- in aqueous solutions during 3 hours resulted in a yellow compound, which was tolerant to UV light over the course of 20 hours. This product, however, being unstable in dark in the presence of oxygen, is converted into initial compound. Conceivably, the product being discussed is formed in

the photochemical reduction of the TDPy^+ cations to form neutral radicals TDPy^\bullet . Recombination of the latter can yield yellow bipyridinium compound in the presence of oxygen [13].

Irradiation of TDPy^+Cl^- in aqueous solution of in the presence of TiO_2 produces the destruction of both the pyridinium ring and the long aliphatic chain that was evident from the ^1H NMR spectra of the reaction products. Thus the ^1H NMR spectrum of the products, isolated from reaction mixture after 3 hour irradiation, displayed only the signals belonging to lower alcohols, ketones and aldehydes.

3.3. MB^+Cl^- and TCF. UV irradiation of MB^+Cl^- in water over 3 hours initiates very small destruction of the dye. In the presence of TiO_2 , total bleaching of MB^+Cl^- solution takes place in 3 hours. This photocatalytic reaction is partial reversible. Regeneration of MB^+ occurred in part after separation of aqueous solution from TiO_2 . The reversible product is Leucomethylene Blue in concordance with [17]. The total mineralization of the dye occurs in a consequence of subsequent reactions of the leuco compound that is evident from the following data. A fraction of irreversible products of the photocatalytic reaction increased with increasing duration of UV irradiation. Thus about 80% MB is regenerated after 3 hours irradiation. The destruction of all amount of the dye occurred in 40 hours UV irradiation. *N,N*-Dimethyl-1,4-phenylenediamine, phenol and carbon oxides were found among the products of the MB^+Cl^- destruction using mass-chromatography.

Total destruction of TCF occurs in the course of 3 hours under UV irradiation. Addition of the photocatalyst accelerated the destruction in 6 times.

3.4. Inorganic anions. Aqueous solution of potassium dichromate is inconvertible under the action of UV irradiation. In the presence of TiO_2 , irradiation of the

Table 1. Photocatalytic activity of the TiO₂ modifications in the destruction of TDPy⁺Cl⁻.

TiO ₂ samples	Temperature of calcination, K	S _{sp} , m ² /g	k _d (×10 ⁴), s ⁻¹	k _d /S _{sp} , gs ⁻¹ m ⁻²
A	473	95	1.5	0.0158
A	473	305	1.4	0.0046
A	493	214	0.9	0.0042
A	493	313	0.6	0.0019
A	473	199	1.5	0.0075
R	1273	-	2.2	-
R	473	95	1.2	0.0126
R	1123	-	1.9	-
R	1123	3	1.8	0.633
19%A 81%R	773	54	1.1	0.0204
25%A 75%R	473	197	0.7	0.0036
40%A 60%R	473	93	0.4	0.0043
65%A 35%R	573	195	1.0	0.0051
67%A 33%R	573	183	0.6	0.0033
75%A 25%R	573	185	1.1	0.0059
80%A 20%R	623	165	0.7	0.0042

Table 2. Photocatalytic activity of the TiO₂ samples in the destruction of MB⁺Cl⁻.

TiO ₂ samples	S _{sp} , m ² /g	k _d (×10 ⁴), s ⁻¹	k _d /S _{sp} , g s ⁻¹ m ⁻²
A	95	0.9	0.0095
A	199	2.2	0.0112
R	3	0.4	0.133
R	95	0.3	0.0032
19%A 81%R	54	0.6	0.0111
30%A 70%R	-	0.1	-
40%A 60%R	93	0.2	0.0022
65%A 35%R	195	1.1	0.0056
80%A 20%R	165	1.3	0.0079

dichromate solution gives rise to a green Cr(III) compound water insoluble. Solution of potassium permanganate is decomposed by UV light to give brown MnO₂ dispersion. Rate of the MnO₄⁻ decomposition is about 5 times faster with TiO₂ present. Potassium ferricyanide is resistant to exposure to both visible and UV light over 3 hours. Addition of TiO₂ to the aqueous ferricyanide solution being UV irradiated leave a dark-blue sedimentation of ferrocyanide (Turnbullis Blue). UV irradiation of potassium ferrocyanide in the absence of TiO₂ gives sediment of ferrocyanide (Prussian Blue). In the presence of TiO₂, the reaction is nearly six times faster.

3.5. Kinetic of the photocatalytic reactions. All the investigated reactions obey the first order kinetics. The observed rate constants can vary by more than order of magnitude depending on nature of TiO₂ and substrate (Tables 1-4). The rate constants of the above photocatalytic reactions are not dependent on mixing speed.

Rate constants of all the photocatalytic reactions are found to depend on pH of the solution. The photocatalytic reactions of TDPy⁺Cl⁻, MB⁺Cl⁻ and [Fe(CN)₆]³⁻ exhibit the highest rate constant in acidic

solutions (Figure 3). The maximum rate constants were found at pH 7 for the photocatalytic destruction of TCF and reduction of Cr₂O₇²⁻.

3.6. Photocatalytic activity of the gamma irradiated TiO₂. The photocatalytic activity of the γ -rayed TiO₂ has been studied in view of increasing

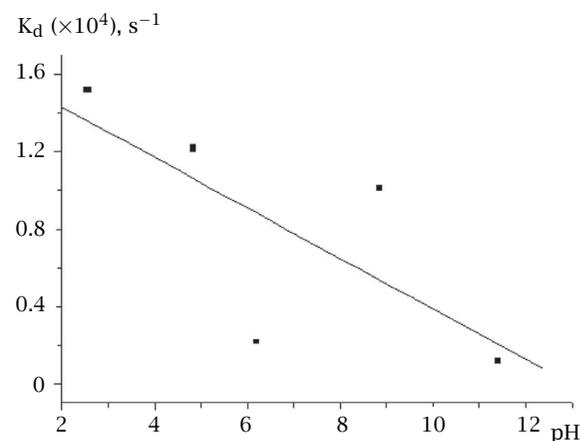


Figure 3. The dependence of k_d vs. pH for the destruction of TDPy⁺Cl⁻.

Table 3. *Photocatalytic activity of the TiO₂ samples in the destruction of TCF.*

TiO ₂ samples	S _{sp} , m ² /g	k _d (×10 ⁴), s ⁻¹	k _d /S _{sp} , g s ⁻¹ m ⁻²
R	3	0.6	0.2
R	95	0.7	0.0074
65%A 35%R	195	1.8	0.0092
80%A 20%R	165	0.8	0.0048

Table 4. *Photocatalytic activity of the TiO₂ samples in reduction of inorganic anions.*

TiO ₂ samples	S _{sp} , m ² /g	KMnO ₄		K ₃ [Fe(CN) ₆]		k ₂ Cr ₂ O ₇	
		k _d ×10 ⁴ , s ⁻¹	k _d /S _{sp} , g s ⁻¹ m ⁻²	k _d ×10 ⁴ , s ⁻¹	k _d /S _{sp} , g s ⁻¹ m ⁻²	k _d ×10 ⁴ , s ⁻¹	k _d /S _{sp} , g s ⁻¹ m ⁻²
A	95	6.1	0.064	0.8	0.008	2.9	0.030
R	95	0.2	0.002	1.3	0.014	2.8	0.029
R	3	1.6	0.53	0.09	0.03	0.7	0.223
40%A 60%R	93	4	0.043	1.4	0.015	1.5	0.016
65%A 35%R	195	7.3	0.037	2.6	0.013	3.5	0.018
75%A 25%R	185	5	0.027	1.7	0.09	1.7	0.009

catalytic activity of various solid substances in dark processes [14, 15]. In this work, we established that prior γ -irradiation of the dispersed TiO₂ rises rate of the photocatalytic destruction of both TDPy⁺Cl⁻ and MB⁺Cl⁻ at the optimum absorbed dose around 500 Gy (Table 5). The irradiated TiO₂ samples did not change noticeably their photocatalytic activity within a month. The cause of the radiation effects could be the formation of the electron or hole defects on the particles surface or in the near-surface region as well as the generation of hot atoms or free radicals in the radiation-induced destruction of surface residues.

Table 5. *Photocatalytic activity of the irradiated TiO₂ samples in the destruction of MB⁺Cl⁻ and TDPy⁺Cl⁻.*

Titanium dioxide	S _{sp} , m ² /g	Dose, Gy	k _d (×10 ⁴), s ⁻¹	
			MB ⁺ Cl ⁻	TDPY ⁺ Cl ⁻
R	3	-	0.4	1.9
		300	0.4	1.5
		500	1.0	2.6
		700	0.3	2.1
40%A 60%R	93	-	0.2	0.4
		300	0.4	0.4
		500	0.3	0.7
		700	0.3	Not done

4. DISCUSSION

Total combination of the facts obtained using the optical pure specimens allows providing an insight into the function of the TiO₂ reactivity on adsorption, specific surface area and crystalline structure. Although the processes involving the above substrates are chemically distinct they share a number of traits, analysis of which may benefit for an active search of new photocatalytic agents around TiO₂.

4.1. Correlation of photocatalytic and sorption properties of TiO₂.

Frequently occurring opinion is that the absorbed molecules are mainly subjected to photocatalytic transformation. This has let to believe (see, for instance, [14]) that photocatalytic activity may be related directly to sorption ability of TiO₂ like the inorganic anions involved. The last-named statement should particularly apply to the processes involving electron transfer between TiO₂ and substrate. Admittedly, the role of sorption was not studied for the majority of photocatalytic processes.

For the most reactions has been studied in this work, k_d increases with increasing *a* (Figure 4) although corresponding correlation coefficients were very small (Table 6). Correlation k_d with adsorption is also lacking for the reactions of various substrates proceeding on a common photocatalyst (Figure 5). The TDPy⁺Cl⁻ destruction features an inversed dependence of k_d

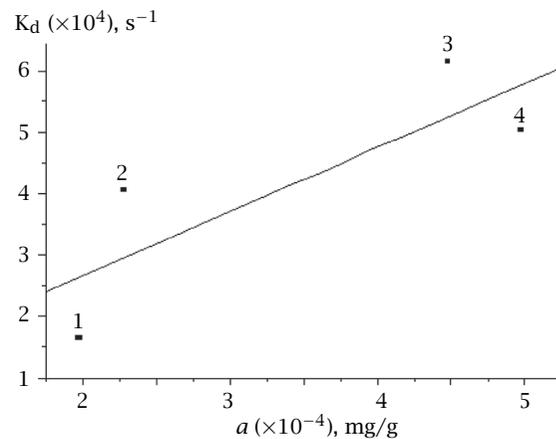


Figure 4. *The correlation between k_d and a for the photocatalytic reduction of MnO₄⁻. 1-R, 2-40%A 60%R, 3-A, 4-75%A 25%R.*

Table 6. Correlation coefficients k_d with adsorption and specific surface area.

Substrate	Correlation coefficients	
	a	S_{sp}
TDPy ⁺ Cl ⁻	-0.72	-0.32
MB ⁺ Cl ⁻	0.4	0.76
TCF	0.5	-0.19
[Fe(CN) ₆] ³⁻	0.42	0.92
MnO ₄ ⁻	0.6	0.66
Cr ₂ O ₇ ²⁻	0.12	0.64

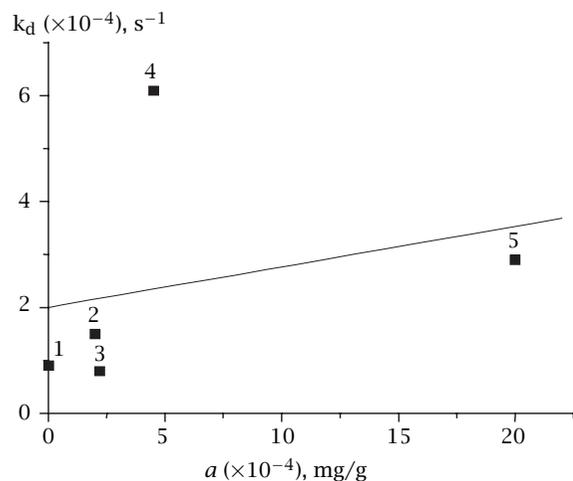


Figure 5. The dependence of k_d vs. a for the destruction reactions on anatase. 1-MB⁺Cl⁻, 2-TDPy⁺Cl⁻, 3-[Fe(CN)₆]³⁻, 4-MnO₄⁻, 5-Cr₂O₇²⁻.

vs. a . Some TiO₂ samples having small sorption capacity demonstrated high photocatalytic activity and conversely.

Besides, correlation was not found between rate constants and the time taken to the attainment of the equilibrium. UV Irradiation should disturb the system from the equilibrium state in systems with long time, taken to attainment of the sorption/desorption equilibrium, and high rate of photocatalytic reaction, for example, in the TDPy⁺Cl⁻/TiO₂ systems. In such cases, however, rate constants did not noticeably reduce with time that also shows that sorption does not play a leading role in the reactions under study.

All these results are to allow conclusion that sorption properties are not governing factor for photocatalytic activity of TiO₂ that may be attributable to the involvement of labile complexes between the substrates and the TiO₂ surface in the photocatalytic reactions.

4.2. Photocatalytic activity and specific surface area. One popular statement resides in the fact that rate of photocatalytic processes can be essentially accelerated by increasing specific surface area, S_{sp} , of photocatalyst. In this connection, we analyzed the influence of this factor on rate constants of the above

processes. Thereupon the question has been arisen whether the surface of the TiO₂ pores should be taken into consideration. Reactions (6)–(8), which not only results in highly reactive species but also prevent the electron hole recombination, can proceed both in pores and outside area of the TiO₂ particles. Therefore, the total specific surface area seems to be used in the calculations of the specific rate constants of the photocatalytic reactions on TiO₂.

For the destruction of [Fe(CN)₆]³⁻, k_d rises clearly as S_{sp} increases (Figure 6). However, plausible link between k_d and S_{sp} is lacking in the majority cases. Interestingly that k_d decreases with rising S_{sp} for the destruction of TDPy⁺Cl⁻ and TCF (Table 6). Negative correlation coefficients, while small in absolute value, were found for the processes involving only anatase, rutile or the two-phase modification.

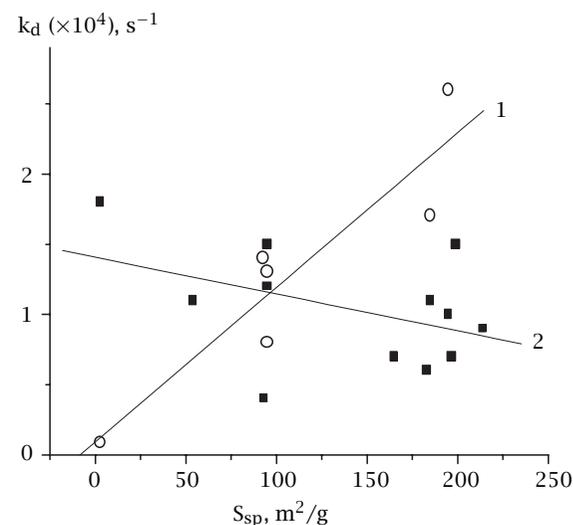


Figure 6. The dependence of k_d vs. S_{sp} for the photocatalytic reactions of [Fe(CN)₆]³⁻ (1) and TDPy⁺Cl⁻ (2).

Rate constant of heterogeneous photocatalytic reaction should indubitably increase with specific surface area of a photocatalyst. In specific cases, such link can be masked by influence of stronger factors like crystalline structure, nature and concentration of residuals on TiO₂ surface etc. However, the destruction of TDPy⁺Cl⁻ discussed immediately above shows that correlation between k_d and S_{sp} can be lacking even for the catalysts having identical crystalline structure and treated in a similar manner. This phenomenon is dealt with in the next paragraph.

4.3. Influence of crystalline structure. Rate constants of the destruction reactions of the organic substrates being studied can differ not more than by 5–6 times depending on TiO₂ nature (Tables 1–3). The influence of the TiO₂ crystalline structure is stronger for the

transformations of the inorganic anions, rate constants of which can differ in 30 times (Table 4).

The measure of photocatalytic activity of the TiO₂ modifications can be specific rate constant, k_d/S_{sp} , according to the principles of reaction kinetics in heterogeneous systems. This measure has been used as a characteristic of photocatalytic reactions on TiO₂ [16].

For all the reactions under study, the rutile calcinated at 1073 K exhibits the highest k_d/S_{sp} (see Figure 7). Concentration of OH-groups on the rutile surface is much less than that for anatase [18]. Hence specific activity of the TiO₂ photocatalysts is not associated with surface concentration of hydroxyls. Probably surface concentration of OH-groups is sufficient for trapping all the holes even on the rutile TiO₂ surface or/and reactions (6) and (7) play prior role in the photochemical destruction.

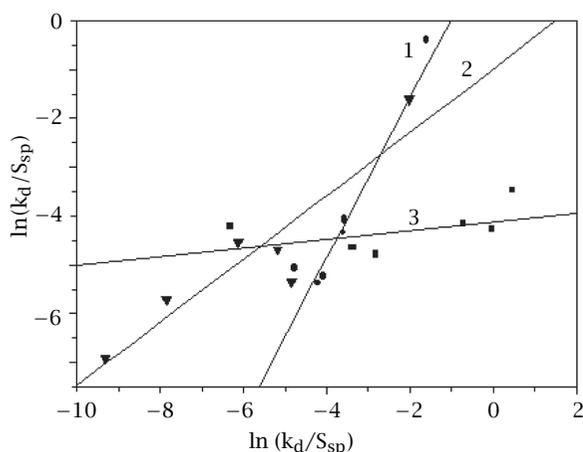


Figure 7. Correlations between specific rate constants for various pairs of the photocatalytic reactions. 1-Cr₂O₇²⁻/TDPy⁺Cl⁻, 2-MB⁺Cl⁻/TCF, 3-MnO₄⁻/[Fe(CN)₆]³⁻.

As opposite to rate constants, the links are revealed between k_d/S_{sp} , describing various reactions (Figure 7). Correlation coefficient exceeds 0.9 in most cases. On first inspection, the above pair correlations of k_d/S_{sp} are surprising. However, they suggest that these all processes have common stages sensitive to crystalline structure.

The photocatalytic reactions involved are distinguished by responsivity towards alteration of TiO₂ nature that can be illustrated with the help of Figure 7. So, the k_d/S_{sp} values are closely related to each other for the photocatalytic reduction of MnO₄⁻ regardless of the photocatalyst used in contrast to the reactions of MB⁺Cl⁻, TCF, Cr₂O₇²⁻ and TDPy⁺Cl⁻.

Under low light intensity, the following relation holds for process rate, ν , [19]

$$\nu = \phi_p I_a. \quad (9)$$

where $\phi_p = \eta_r \eta_i \eta_p$; η_r is the efficiency of the formation of the reactive electron-hole pair; η_i is the efficiency of the interfacial electron transfer; η_p is the efficiency of product formation; I_a is light intensity.

The efficiency of the formation of the reactive electron hole pair should not be substrate dependent. The following expansion holds for η_i

$$\eta_i = k_r / (k_3 + k_r), \quad (10)$$

where k_3 is rate constant of the electron hole recombination (3), k_r is rate constant of primary product generation (reactions (4)–(8)). Interfacial electron-transfer rate constant is bound to rise with as the Gibbs free energy of electron transfer reduced in line with essential principle of electron transfer [20]. Thus, for very fast interfacial electron transfer $k_r \gg k_3$ and η_i is invariant with TiO₂ nature and specific surface. For such systems rate constants of photocatalytic reactions would be closely related for various TiO₂ modifications. Apparently, this is true for photocatalytic reduction of MnO₄⁻ which is the strongest oxidant among the substrates studied.

Obviously η_p may be relatively independent of changes in TiO₂ properties whereas η_r and η_i seem to change considerably. However, if the influence of TiO₂ nature on k_d/S_{sp} is specified by η_r , all the correlations k_d^y/S_{sp}^y vs. k_d^x/S_{sp}^x should have a similar slope that is inconsistent with the experimental evidences (Figure 7). Only yield of the interfacial electron transfer hinges upon both nature of the photocatalyst and substrate. This gives reason to believe that η_i is the term which is the most sensitive to TiO₂ properties and it defines principally influence of TiO₂ and substrate on rate of examined photocatalytic reactions.

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