Activity and selectivity of photocatalysts in photodegradation of phenols

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ABSTRACT

Photodegradation of phenol and 4-chlorophenol over six different TiO_2 samples was tested in order to establish whether an interconnection between the activity and selectivity of photocatalysts exists. The obtained experimental data were analyzed using correlation analysis. Some correlations between the activity in phenol(s) photodegradation and selectivity toward formation of primary intermediate products were established. The type of correlations depends on the type of studied photoreactions. The discussion of the observed correlations between the activity and selectivity of photocatalysts is given in terms of the difference of surface concentrations of electrons and holes and corresponding surface active sites which might be dependent on the types of dominating surface faces. On the basis of the obtained results of correlation analysis it was assumed that a higher activity of photocatalysts could be achieved provided that both reduction and oxidation reaction pathways occur with equally high efficiency.

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1. Introduction

Most attention in fundamental and applied studies in the area of heterogeneous photocatalysis is directed toward exploration of the factors, which determine three main characteristics of photocatalysts: photoactivity, spectral sensitivity and selectivity [1–10]. The problem of the enhanced (photo)activity of photocatalysts has attracted major attention among researchers dealing with heterogeneous photocatalysis. This is explained by the fact that photocatalysis has found the most application for degradation of organic pollutants in water and air that requires the strong oxidation power sufficient to decompose most organic molecules to simple mineralized products. Obviously, such a problem does not require much attention to more delicate characteristics such as selectivity of photocatalysts. In fact even the problem of increased spectral sensitivity to visible light has been recalled as a tool to increase the overall photoactivity of photocatalysts by taking such a simplified approach as "the more light absorbed, the higher the activity would be". Detailed research however, demonstrated that the reality is not so simple and flat and the consequences of the

extension of the spectral range of photocatalyst activity to its extrinsic light absorption by various chemical or physical modifications are more complex [6,8,11–14] and can lead to decay of photoactivity and chemical power of photocatalysts.

The least attention was ever attracted by such characteristics as selectivity of photocatalysts and its relation to other major parameters. Only a few studies have been focused on measurement of selectivity and exploration of the factors determining its magnitude, such as reagent concentration, pH of solution, light intensity and so on [6,15–18]. In our studies we have explored the connection between the origin of the extrinsic absorption responsible for the increase of the spectral sensitivity to visible light and selectivity of photocatalyst dependent on wavelength of the actinic light [18–20]. Recently the understanding of the practical significance of the photocatalyst selectivity has emerged. It is dictated by the fact that many hazardous organic contaminants are represented by complex molecules whose complete mineralization requires utilization of the energy of quite a large number of photons that makes the process inefficient energy-wise. Moreover, at some stages of the multistep photodegradation of organic molecules more hazardous and chemically stable intermediates can be formed. Thus, exploration of factors affecting photocatalyst selectivity becomes practically essential for learning how to drive the organic contaminant degradation toward formation of benign reaction products

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without complete mineralization. Of particular interest might be the search for the interconnection between the activity and selectivity of photocatalysts.

2. Activity and selectivity of photocatalysts

As demonstrated in our earlier studies [6,17–20] there are two possible causes for selectivity of a photocatalyst in the case when the rate of the surface photochemical reaction is dictated by the surface concentration of photocarriers (electrons for reduction or holes for oxidation reaction pathways, respectively). The first cause originates from the ratio between surface concentrations of electrons and holes at the surface of photoactive material. Consequently, alteration of this ratio caused by various factors leads to changes in the ratio between the efficiencies of oxidation and reduction surface reactions for the molecules possessing both electron-acceptor and electron-donor behavior. For example, if a given reaction product (P_i) is formed by a reduction pathway during the photo-stimulated surface reaction with reagent (R) interacting with both electrons (e) and holes (h), the surface selectivity toward formation of the given product (S_{P_i}) can be presented as:

$$S_{P_i} = \frac{d[P_i]/dt}{d[R]/dt} = \frac{k_{e,i}[e]}{\sum_i k_{e,i}[e] + \sum_j k_{h,j}[h]} \qquad (1)$$

Here $k_{e,i}$ and $k_{h,j}$ are rate constants for a given reaction pathway. Obviously, a similar expression can be written for the products formed by the oxidation reaction pathway (it is assumed by default, that the reaction rate does not depend on the reagent concentration. That corresponds to saturation of the reaction rate dependence on reagent concentration for the Langmuir–Hinshelwood like kinetics). As evident from Eq. (1) the selectivity of the photocatalyst is determined by the ratio between the surface concentration of electrons and holes.

The second cause for selectivity is related to formation of the surface active sites of different types, which therefore have different activity and selectivity. These different types of surface active sites can be formed through photoexcitation of localized surface and sub-surface electronic states (intrinsic defects and/or dopant states) or through formation on different types of surface structure (dominating surface plane, for instance). This type of selectivity is clearly observed for the molecules demonstrating only electron-donor or electron-acceptor behavior though it is typical for any surface photochemical reaction. In this case the selectivity of the

surface toward formation of given reaction product can be presented as:

$$S_{P_i} = \frac{d[P_i]/dt}{d[R]/dt} = \frac{k_{e,i}}{\sum_i k_{e,i}} \qquad (2)$$

and is determined by the ratio of a given reaction rate constant, characteristic of a given sort of active site, to the sum of reaction rate constants corresponding to all possible types of active site on the surface of photocatalyst (note that rate constants here are clearly apparent and implicitly include the surface concentrations of the active sites). Obviously this factor (ratio of rate constants) is also significant for selectivity caused by the first scenario (see Eq. (1)).

From the scientific point of view the strongest parameter characterizing the activity of photocatalysts is the quantum yield of interfacial photochemical process [21,22], which is the ratio between the number of reacted or produced molecules (per unit time) and the number of photons absorbed by the photocatalyst (per unit time). Therefore, the quantum yield characterizes the ability of the photocatalyst to convert the energy of absorbed light into the interfacial chemical sequence. At the same time, from a practical point of view, it is important to know the activity of the photocatalyst with respect to incident light. In the latter case it is wise to use the parameter named photonic efficiency, which represents the ratio between the number of reacted or produced molecules (per unit time) and the number of incident photons (per unit time). However, in general, both parameters (quantum yield and photonic efficiency) are spectrally variable and thus, can be determined precisely for monochromatic light only [6,18–20]. Consequently, the problem of photocatalyst characterization in terms of its activity requires the quite complex measurements of the spectral distribution of corresponding parameters. The problem can be experimentally simplified provided that comparable photocatalysts possess similar light absorption properties (for example, different TiO₂ photocatalysts) and are studied using the same light sources with the same spectral distribution of light intensity. In such a scenario the (initial or stationary) rates of interfacial chemical processes can be used to estimate the relative acitivities of the photocatalysts. Whatever parameter is selected for activity characterization it relates to the rate of surface photostimulated reaction which by definition depends on the sum of the rate constants (including the concentration of the surface active sites) and on the surface concentration of charge carriers involved into chemical reaction. Moreover, according to charge balance by Gerischer [23] the true (photo)catalytic process is characterized by the
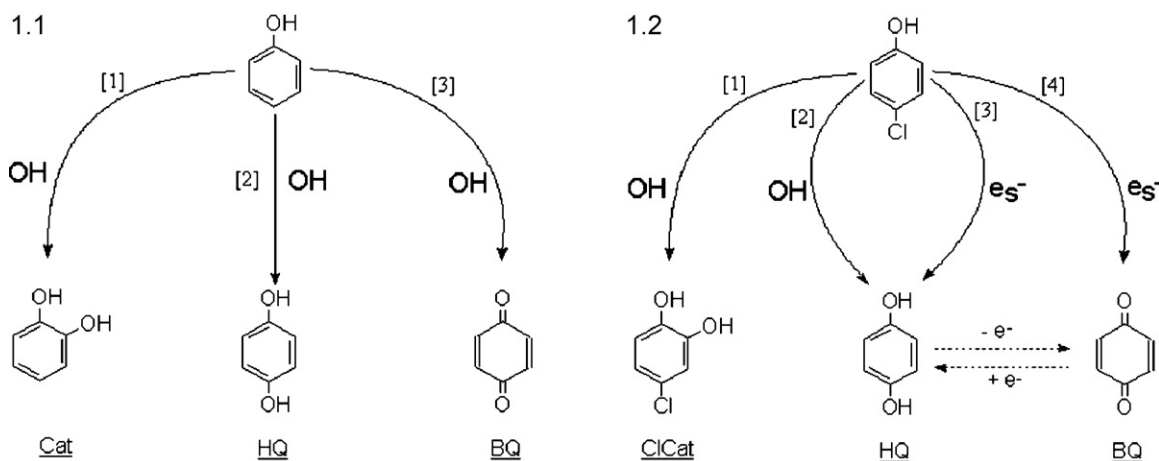
Scheme 1. (a) Mechanism of phenol photodegradation leading to formation of major intermediate reaction products: catechol (Cat), hydroquinone (HQ) and benzoquinone (BQ). (b) Mechanism of 4-chloro-phenol photodegradation leading to formation of intermediate reaction products: 4-chlorocatechol (ClCat), hydroquinone (HQ) and benzoquinone (BQ).

equality of the rates of consumption of electrons and holes in overall reaction:

$$d[e]/dt = d[h]/dt \tag{3}$$

These issues let one assume that there could be a connection between activity and selectivity of photocatalysts. To explore this possibility and its eventual causes in the present work we study activity and selectivity of TiO_2 photocatalysts in selected test photoprocesses on the basis of correlation analysis.

To estimate the activities and possible connection with selectivities of six selected photocatalysts we chose to test them in reactions of heterogeneous photodegradation of phenol and 4-chlorophenol. The reason for such selection was that the major pathway of phenol photodegradation is photooxidation, while both photooxidation and photoreduction are equally effective in photodegradation of 4-chlorophenol [15–17] (see Scheme 1(a and b)).

Accordingly, selectivity of the photocatalyst toward formation of major primary intermediates: hydroquinone (HQ), benzoquinone (BQ), and catechol (Cat) during photodegradation of phenol can be presented as:

$$S_{HQ} = \frac{d[HQ]/dt}{d[PhOH]/dt} = \frac{k_{HQ}}{\sum_i k_i} \tag{4.1}$$

$$S_{BQ} = \frac{d[BQ]/dt}{d[PhOH]/dt} = \frac{k_{BQ}}{\sum_i k_i} \tag{4.2}$$

$$S_{Cat} = \frac{d[Cat]/dt}{d[PhOH]/dt} = \frac{k_{Cat}}{\sum_i k_i} \tag{4.3}$$

Since, the major reaction pathway of phenol photodegradation is oxidation the selectivity toward intermediate products is determined by the ratio between corresponding rate constants. That means that the difference in selectivity between different photocatalysts can be explained in terms of the difference in surface structure and formation of different surface active sites.

At the same time selectivity toward major primary intermediates of 4-chloro-phenol photodegradation formed by both oxidation and reduction reaction pathways, depends also on the ratio between the surface concentrations of electrons and holes. Note that according to Eqs. (5.1)–(5.3) selectivity toward benzoquinone, formed mainly by reduction pathway, increases with the ratio between electrons and holes at the surface while selectivity toward 4-chlor-catechol decreases. Accordingly, selectivity toward hydroquinone, which can be formed by both reduction and oxidation pathways, depends on the ratio between corresponding rate constants.

$$S_{HQ} = \frac{d[HQ/dt]}{d[ClPhOH]/dt} = \frac{(k_{HQ}[OH]) + k'_{HQ}[e][ClPhOH]}{\left(\sum_i k_i[OH] + \sum_j k_j[e]\right)[ClPhOH]}$$

$$= \frac{k_{HQ} + k'_{HQ}\{[e]/[h]\}}{\sum_i k_i + \sum_j k_j\{[e]/[h]\}} \tag{5.1}$$

$$S_{BQ} = \frac{d[BQ/dt]}{d[ClPhOH]/dt} = \frac{(k'_{BQ}[e])[ClPhOH]}{\left(\sum_i k_i[OH] + \sum_j k_j[e]\right)[ClPhOH]}$$

$$= \frac{k'_{HQ}\{[e]/[h]\}}{\sum_i k_i + \sum_j k_j\{[e]/[h]\}} \tag{5.2}$$

$$S_{ClCat} = \frac{d[ClCat]/dt}{d[ClPhOH]/dt} = \frac{(k_{ClCat}[OH])[ClPhOH]}{\left(\sum_i k_i[OH] + \sum_j k_j[e]\right)[ClPhOH]}$$

$$= \frac{k_{ClCat}}{\sum_i k_i + \sum_j k_j\{[e]/[h]\}} \tag{5.3}$$

3. Experimental

Six TiO_2 photocatalyst samples were tested in the present study, namely: Degussa P-25 ($50\,m^2\,g^{-1}$), Hombikat UV100 ($300\,m^2\,g^{-1}$), ST-41 ($10\,m^2\,g^{-1}$), ST-21 ($50\,m^2\,g^{-1}$) FTL-200 ($10\,m^2\,g^{-1}$ (nanorods)) produced by Ishihara and ($2.9\,m^2\,g^{-1}$) produced by Kanto Chem. According to the XRD data Hombikat UV100, ST-41 and ST-21 samples possess the anatase crystal structure, FTL-200 and Kanto Chem. are the samples of rutile type modification, and P-25 consists of 78% anatase and 22% rutile. Phenol and 4-chlorophenol (Aldrich) reagents were used as received. Phenol's photodegradation in presence of TiO_2 photocatalyst samples was carried out in aqueous slurry solution enclosed in glass spherical reactor with a flat quartz light-inlet window. TiO_2 sample loading was 1 g/l. pH of the solution was adjusted by adding HCl to be at pH = 3.0. The initial (before dark adsorption) concentration of phenol was 1×10^{-3} M, and the concentration of 4-chloro-phenol was 7.8×10^{-4} M. Tested solution was constantly stirred at 800 rpm. The solution was kept in the dark for 1 h to approach adsorption equilibrium. Broadband irradiation with Xe-lamp (300 W, Oriel) was employed in phenol(s) photodegradation experiments. The monitoring of time evolution of phenol(s) concentration as well as the detection of major intermediate products was carried out by HPLC method (Schimadzu-LC2010).

4. Results and discussion

To compare the photoactivities and selectivities of different TiO_2 photocatalysts and to perform the correlation analysis we measured the initial rates of phenols photodegradation and formation of corresponding intermediates. A necessary condition for such analysis is that the rate of corresponding photoprocess should scale linearly with the light intensity and be independent of reagent concentration. This can be achieved by alteration of reagent concentration due to effect of dependence of the reaction rate on reagent concentration and light intensity [24–26]. Obviously, linear dependence of the rates of reagent consumption provides the independence of photocatalyst selectivity of light spatial distribution within reactor and of non-uniform irradiation of the photocatalyst surface, while independence of the reaction rate of reagent concentration corresponds to highest possible photoactivity of photocatalyst at given light intensity. Such required conditions were achieved for all tested heterogeneous systems. Some examples of linear dependencies of reaction rates on light intensity are shown in Figs. 1 and 2.
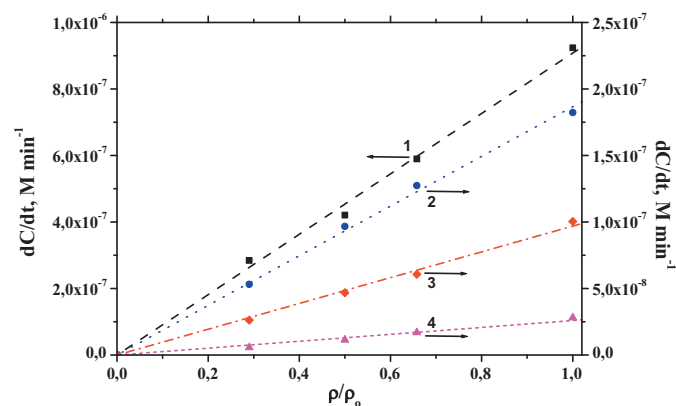

Fig. 1. Dependencies of the rates of phenol photodegradation (1) over TiO_2 (ST-41) and formation of intermediated products: hydroquinone (2), benzoquinone (3), and catechol (4) on relative intensity of actinic light (ρ/ρ_o).
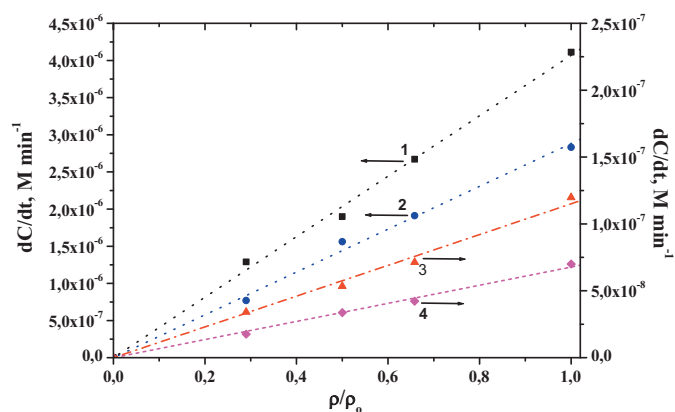
Fig. 2. Dependencies of the rates of 4-chloro-phenol photodegradation (1) over TiO₂ (Kanto Chem.) and formation of intermediated products: hydroquinone (2), benzoquinone (3), and 4-chloro-catechol (4) on relative intensity of actinic light (ρ/ρ_o).

Fig. 4. Relative activity (normalized by maximal rate of phenol photodegradation, PhOH) and selectivity toward formation of major intermediates (hydroquinone, HQ, benzoquinone, BQ, and catechol, Cat) during phenol photodegradation over tested samples.
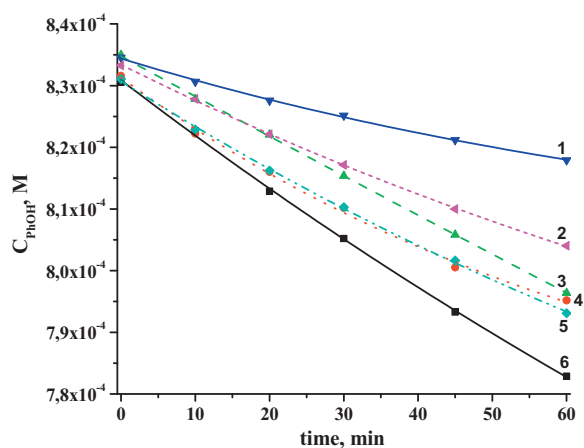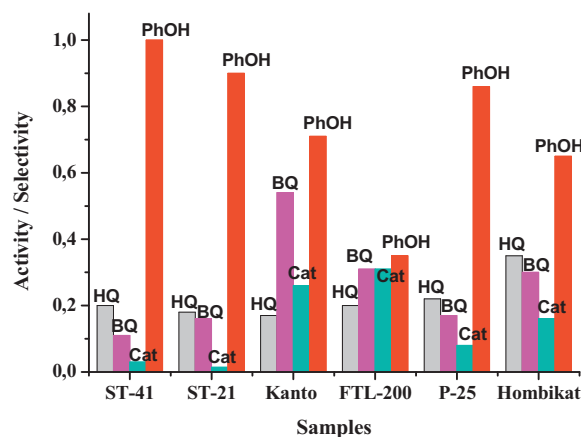

Fig. 3. Time evolution of phenol concentration during its photodegradation over tested TiO₂ samples: 1 – FTL-200; 2 – Hombikat UV100; 3 – Kanto Chem.; 4 – ST-21; 5 – Degussa P25; 6 – ST-41.

The time evolutions of phenol photodegradation over 6 different TiO₂ photocatalysts are presented in Fig. 3. In addition, the kinetic behavior of three major primary intermediates, namely hydroquinone, benzoquinone, and catechol, were tracked during phenol photodegradation.

The ratio between the initial rates of formation of major intermediates and the initial rates of phenol photodegradation presented in Table 1 can be considered as an initial selectivity of selected photocatalysts toward formation of the major primary intermediates. For example, the selectivity toward the formation of hydroquinone (HQ) was count as:

$$\text{selectivity(HQ)} = \frac{dC(\text{HQ})/dt}{dC(\text{PhOH})/dt}$$

The initial rates and values of relative activity and selectivity of corresponding processes are summarized in Table 1 and shown in Fig. 4.

Note that other primary reaction products, different from the selected ones, can be also formed during phenol(s) photodegradation (see, for example, [27]), thus the mass-balance of the selected intermediates does not necessary approach 1. However, the objective of the present study does not require following the evolution of all intermediates.

As evident from the experimental data the activity of selected photocatalysts in phenol photodegradation process increases as FTL-200 < Hombikat UV100 < Kanto Chem. < Degussa P25 < ST-21 < ST-41. Remarkably, experimental results show that the surface area of the samples is not the major factor affecting their activity (see Table 1).

One may expect that photostimulated formation of the same type of surface active sites on the same surface plane should result in the same selectivity since the given type of surface active sites should induce the same chemical sequence regardless of any other photocatalyst characteristics such as surface area, particle size, surface density of the active sites and so on. Thus, the experimentally observed difference in values of selectivity of different TiO₂ photocatalysts clearly demonstrates the difference in surface chemistry of the photocatalysts in spite of the fact that the major pathway of phenol photodegradation in all tested systems is an oxidation. Accordingly, the observed difference in selectivity can be attributed to different surface densities of the active sites of different types and/or to different surface structure, that is a difference in dominating surface faces for different TiO₂ photocatalysts. Note that the latter may concern not only the difference between anatase and rutile but also the difference in dominating surface faces for the same crystal structure which is possible for nanoparticles with a
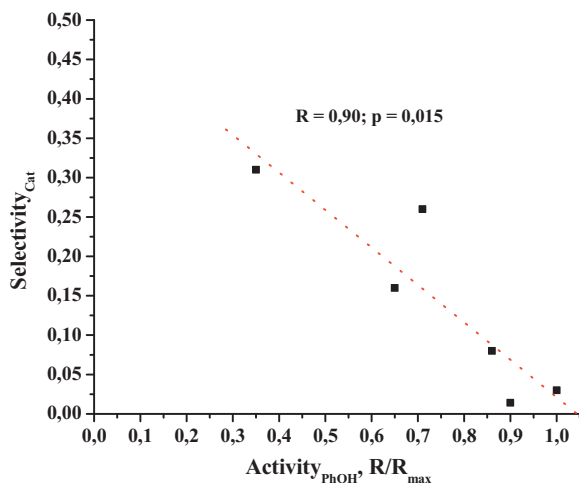
Table 1
Activity and selectivity of tested TiO₂ photocatalysts in phenol photodegradation. Initial rates of phenol photodegradation and formation of major intermediates (hydroquinone, HQ, benzoquinone, BQ, and catechol) and relative activity (normalized by maximal rate) and selectivity of tested samples.

Sample/surface area	Phenol dC/dt (M min⁻¹)/rel. activity	HQ dC/dt (M min⁻¹)/selectivity	BQ dC/dt (M min⁻¹)/selectivity	Catechol dC/dt (M min⁻¹)/selectivity
ST-21 50 m² g⁻¹	8.3×10^{-7}/0.90	1.5×10^{-7}/0.18	1.3×10^{-7}/0.16	1.2×10^{-8}/0.014
ST-41 10 m² g⁻¹	9.2×10^{-7}/1.00	1.8×10^{-7}/0.20	1.0×10^{-7}/0.11	2.8×10^{-8}/0.03
FTL-200 10 m² g⁻¹	3.2×10^{-7}/0.35	6.4×10^{-8}/0.20	1.0×10^{-7}/0.31	1.0×10^{-7}/0.31
Kanto Chem. 2.9 m² g⁻¹	6.5×10^{-7}/0.71	1.1×10^{-7}/0.17	3.5×10^{-7}/0.54	1.7×10^{-7}/0.26
Degussa P25 50 m² g⁻¹	7.9×10^{-7}/0.86	5.2×10^{-7}/0.22	1.7×10^{-7}/0.17	5.0×10^{-7}/0.08
Hombikat UV100 300 m² g⁻¹	6.0×10^{-7}/0.65	2.1×10^{-7}/0.35	1.8×10^{-7}/0.30	0.95×10^{-7}/0.16

Fig. 5. Correlation between activity of tested photocatalysts in phenol photodegradation and their selectivity toward formation of catechol.

Fig. 6. Time evolution of concentration of 4-chloro-phenol during its photodegradation over tested TiO_2 samples: 1 – Degussa P25; 2 – Hombikat UV100; 3 – ST-21; 4 – ST-41; 5 – FTL-200; 6 – Kanto Chem.

Fig. 7. Correlation between the activities of tested photocatalysts in photodegradation of phenol and 4-chloro-phenol.

different prehistory (such as method and conditions of synthesis, pretreatments and so on).

The results of correlation analysis show that no significant correlation is observed between the selectivity toward formation of hydroquinone and benzoquinone and activity of photocatalysts ($R = 0.04$ at $p = 0.94$ for hydroquinone, and $R = -0.54$ at $p = 0.27$ for benzoquinone. Here R is a correlation coefficient and p is a significance level). However, there is quite significant negative correlation for selectivity toward catechol formation and activity of photocatalysts ($R = -0.9$ at $p = 0.015$) (Fig. 5).

In other words, the higher the selectivity toward formation of catechol is, the lower the total activity of the photocatalyst in phenol photodegradation. In the set of tested photocatalyst samples this behavior partly correlates with bulk crystal structure (anatase vs. rutile). Note, however, that the difference in activity and selectivity observed in the present study can be often observed within the set of the samples of the same crystal structure pretreated at different conditions [28,29]. Besides, the number of the photocatalyst samples of two different modifications is not sufficient for significant correlation. Therefore, the negative correlation between selectivity toward catechol formation and photoactivity of photocatalyst, cannot be *a priori* attributed to the influence of crystal structure.

Another well-known factor affecting the activity of photocatalysts is the type of interfacial chemical reaction. Fig. 6 shows the time evolution of the 4-chlorophenol concentration during its photodegradation over tested photocatalyst samples.

As evident from the presented data the activity of photocatalysts grows as Degussa P25 < ST41 < ST21 < Hombikat UV100 < FTL-200 < Kanto. Thus, anatase samples demonstrate lower activity than rutile samples in photodegradation of 4-chlorophenol. Correlation analysis shows that there is no correlation between the activity of photocatalysts in photodegradation of phenol and 4-chloro-phenol (see Fig. 7; $R = -0.33$, $p = 0.52$). Therefore, one may conclude that the term "*activity of photocatalyst*" strongly depends on the studied reaction. At the same time, note, that the difference in activity between the anatase and rutile samples can be also attributed to the different sample prehistory and not to the difference in crystal structure.

The kinetic behavior of three major primary intermediates, namely hydroquinone, benzoquinone, and chlorocatechol, was monitored during 4-chlorophenol photodegradation. Note, that unlike the phenol photodegradation, photodecomposition of 4-chlorophenol can go through both reduction and oxidation
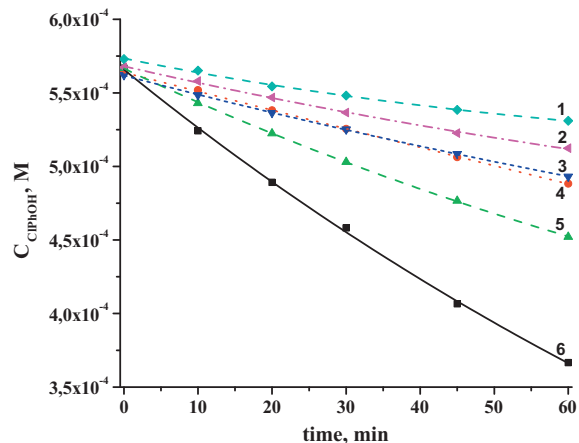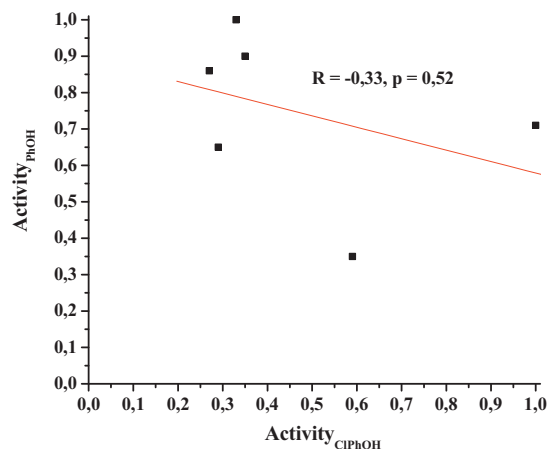
pathways; chlorocatechol is formed as a product of photooxidation through interaction with OH-radicals, while benzoquinone is formed mainly through the primary reduction pathway; hydroquinone can be formed through both reduction and oxidation pathways [16–18]. The initial rates of corresponding processes are summarized in Table 2 and the photocatalyst selectivities toward major primary intermediates are presented in Fig. 8.

The experimental data on selectivity demonstrate the difference in surface chemistry taking place in different photocatalysts. No significant correlation is observed between the selectivity toward formation of both benzoquinone and 4-chloro-catechol and photoactivity of photocatalysts ($R = 0.26$ at $p = 0.62$ for benzoquinone and $R = -0.47$ at $p = 0.35$). However, unlike phenol photodegradation there exist the strong positive correlation ($R = 0.983$ at $p = 0.00045$) between selectivity toward hydroquinone formation and photocatalyst activities (see Fig. 9).

Note that according to Scheme 1(b) the hydroquinone can be formed effectively by both reduction and oxidation pathways. At the same time the effective photocatalytic process occurs provided that the overall efficiency of oxidation pathways is equal to the overall efficiency of reduction pathways (see Eq. (3)). Otherwise, deviation from the catalytic equilibrium (Eq. (3)) results in transformation of charge balance to Eq. (6) [30]:

$$(d[e]/dt) + (d[F]/dt) = (d[h]/dt) + (d[V]/dt) \qquad (6)$$

Table 2

Activity and selectivity of tested TiO$_2$ photocatalysts in 4-chlorophenol photodegradation. Initial rates of 4-chloro-phenol photodegradation and formation of major intermediates (hydroquinone, HQ, benzoquinone, BQ, and chlorocatechol) and relative activity (normalized by maximal rate) and selectivity of tested samples.

| Sample	4-Chlorophenol dC/dt (M min^{-1})/rel. activity	HQ dC/dt (M min^{-1})/selectivity	BQ dC/dt (M min^{-1})/selectivity	Cl-Catechol dC/dt (M min^{-1})/selectivity
ST-21	1.35×10^{-6}/0.33	5.7×10^{-7}/0.42	7.7×10^{-7}/0.57	4.1×10^{-9}/0.003
ST-41	1.34×10^{-6}/0.33	5.1×10^{-7}/0.38	5.6×10^{-7}/0.42	2.5×10^{-7}/0.19
FTL-200	2.40×10^{-6}/0.59	1.0×10^{-6}/0.42	1.4×10^{-6}/0.57	3.4×10^{-8}/0.014
Kanto Chem.	4.11×10^{-6}/1.00	2.8×10^{-6}/0.68	1.2×10^{-6}/0.30	7.0×10^{-8}/0.017
Degussa P25	1.10×10^{-6}/0.27	2.4×10^{-7}/0.22	1.2×10^{-7}/0.11	2.1×10^{-7}/0.19
Hombikat UV100	1.21×10^{-6}/0.29	1.8×10^{-7}/0.15	2.2×10^{-7}/0.12	0.6×10^{-7}/0.03
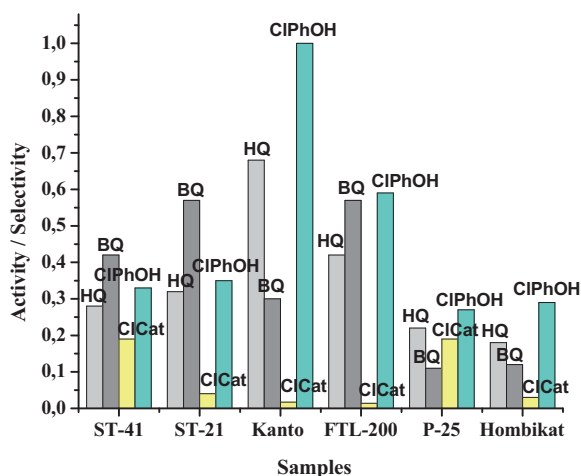
Fig. 8. Relative activity (normalized by maximal rate of 4-chloro-phenol photodegradation, ClPhOH) and selectivity toward formation of major intermediates (hydroquinone, HQ, benzoquinone, BQ, and 4-chloro-catechol, ClCat) during 4-chloro-phenol photodegradation over tested samples.

where F and V are electrons and holes trapped by bulk defects, which leads to acceleration of the bulk charge recombination and decreasing of the photocatalyst activity. Since formation of hydroquinone effectively consumes both electrons and holes these reaction pathways create a favorable condition for photodegradation of 4-chloro-phenol being truly catalytic and suppressing bulk recombination. Therefore, the higher the selectivity of the photocatalyst surface toward formation of hydroquinone, the higher the activity of photocatalyst during 4-chloro-phenol photodegradation. That was observed for the Kanto Chem. sample,
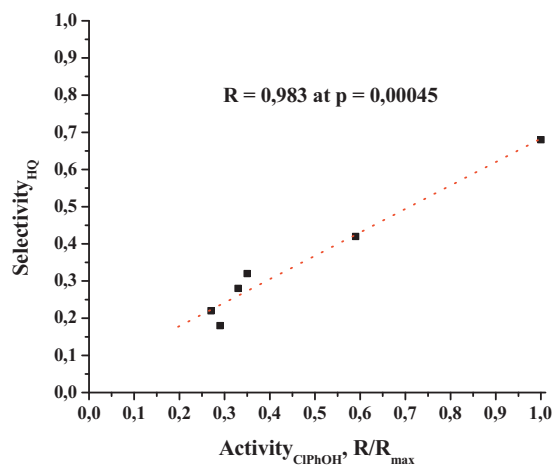
which demonstrates the highest activity and the highest selectivity toward formation of hydroquinone.

Unlike macro crystals with their clearly manifested crystal faces, the dominant surface planes in nanoparticles are strongly affected by the method and conditions of synthesis. Concomitantly, from general considerations one may expect a difference in the selectivity of various planes of photocatalyst particles in the course of photoprocesses, caused by a different atomic structure, magnitude and distribution of surface charge, dominant type of defects such as surface active centers, etc. Such differences in particle dominating faces were demonstrated in [31–35]. Consequently, if the nanoparticle surface structure is dominated by a face with a strong selectivity toward an oxidation (or reduction) process, the particle will accumulate charge resulting in the limitation of the overall activity of nanoparticles by the rate of the slowest non-dominant process that is not characteristic of the dominant face. Clearly, the condition for maximal activity of a particle corresponds to a situation when the ratios between various surface planes provide equal selectivities of the particle with respect to oxidation and reduction reaction pathways. Therefore, by changing the ratio between various surface planes during the synthesis, one can achieve the desired optimal efficiency of the photoactive nanomaterial.

5. Conclusion

Application of the correlation analysis to experimental data obtained for phtodegradation of phenol and 4-chlorophenol over six tested TiO$_2$ photocatalyst samples results in establishing the correlation between the activity and selectivity of photocatalysts. The type of this correlation strongly depends on the type of testing reaction. The negative correlation between the activity of photocatalysts toward photodegradation of phenol whose primary step occurs by oxidation pathway only, and selectivity toward formation of primary intermediate product – catechol is established. This suggests that the surface active sites responsible for the formation of catechol are less active in phenol photodegradation. In turn, the positive correlation between the activity of photocatalysts toward photodegradation of 4-chloro-phenol whose primary steps can go through both oxidation and reduction reaction pathways, and the photocatalyst's selectivity toward formation of primary intermediate product – hydroquinone, produced by both oxidation and reduction pathways, is found. Thus, a higher activity of photocatalysts can be expected provided that both reduction and oxidation reaction pathways occur with equally high efficiency. No other significant correlations including correlation between the activities of photocatalysts in phenol and 4-chloro-phenol photodegradation, were observed.

Acknowledgments

Fig. 9. Correlation between activity of tested photocatalysts in 4-chloro-phenol photodegradation and their selectivity toward formation of hydroquinone.

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