

Spectral Selectivity of Photocatalyzed Reactions Occurring in Liquid–Solid Photosystems

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The photocatalyzed transformations of phenol (PhOH) and 4-chlorophenol (4CIPhOH) in irradiated TiO₂ (P25) aqueous dispersions were reexamined to assess the spectral dependencies of the selectivities of the primary oxidative and/or reductive steps in the formation of the primary intermediates catechol (Cat), hydroquinone (HQ), and benzoquinone (BQ) for PhOH and chlorocatechol (ClCat), HQ, and BQ for 4CIPhOH. These selectivities depend on the relative surface concentrations of the electrons and holes at the various wavelengths, which in turn hinge on the spectral variations of the absorption coefficients of the photocatalyst. The rates of degradation of PhOH and of 4CIPhOH, together with the rates of formation of the primary intermediate species, scaled linearly with photon flow from the irradiation source, as required if quantum yields and selectivities of formation of the intermediates are to be correctly evaluated. As expected, the selectivities of formation of the intermediates in phenol were spectrally invariant, whereas those for the 4-chlorophenol were spectrally variant. The average of the spectrally integrated selectivities for the formation of Cat, HQ, and BQ for phenol ranged from 0.18 to 0.24 (error ca. ± 0.02), whereas the corresponding ones for the formation of ClCat, HQ, and BQ from 4-chlorophenol ranged between 0.18 and 0.32. With a minor exception, these selectivities compare remarkably well with those determined under broadband irradiation (0.20–0.24 for phenol and 0.15–0.26 for 4-chlorophenol).

Introduction

As a fundamental and applied (technological) field of science, photocatalysis continues to be an important component of modern chemistry in the twenty-first century. Research in this area has evolved significantly during the last two decades and has enriched the knowledge base with regard to mechanisms, the development of new technologies for the storage and conversion of solar energy, and the environmental detoxification of liquid and gaseous ecosystems, as well as the photochemical production of new materials, among several others. To date, most of the research in photocatalysis has been directed at increasing the activity of the photocatalysts^{1–13} by optimization of experimental conditions, by synthesis of new types of photocatalysts, and by chemical and physical modification(s) of the photocatalysts that includes their sensitivity to visible light. By comparison, however, relatively little has been achieved on the selectivity of photocatalysts. A few research groups have examined and demonstrated catalyst selectivity during photocatalytic processes.^{2,4,14–17} In particular, Richard and co-workers¹⁴ studied the dependence of the selectivity on reagent concentration, and Theurich et al.⁴ demonstrated the dependence of the selectivity on the type of photocatalyst and on the pH, among other parameters. Accordingly, we expect to witness in photocatalysis, as part of photochemistry, changes in selectivity with the spectral variation of the actinic light. Such a phenomenon was observed nearly two decades ago by the research groups of Kuzmin¹⁶ and Ryabchuk¹⁷ for the photo-stimulated processes in gas–solid heterogeneous photosystems.

Our recent studies^{18,19} have focused on identifying those factors that influence the spectral variation of photocatalytic activity (e.g., spectral dependence of the quantum yield of

photocatalytic processes) as well as the selectivity of photocatalysts. The goal of our current work is to examine and demonstrate the existence of the spectral selectivity of photocatalysts in liquid–solid heterogeneous photosystems.

Experimental Section

Materials. The photocatalyst P25 TiO₂ was kindly provided by Degussa Canada Ltd. Phenol and 4-chlorophenol were Aldrich reagents and were used as received. Solvents for liquid chromatography were Omnisolv HPLC grade, and the water was doubly distilled.

Procedures. All experiments were carried out at pH \sim 3 (HCl). Typically, irradiation of a phenol solution in an air-equilibrated dispersion with a TiO₂ loading of 0.3 g L^{−1} was carried out in a sphere-like Pyrex reactor using an Oriel 1000-Watt Hg/Xe lamp as the light source whose radiation was filtered through a water filter to remove IR radiation. Appropriate wavelengths of illumination were selected using a monochromator (spectral resolution ca. ± 5 nm). Nonselective “gray” metal–supported Pyrex filters were used to attenuate the photon flow, when needed.

Rates of the photocatalyzed degradation of phenol (PhOH) and 4-chlorophenol (CIPhOH) were determined by monitoring the time evolutions of the concentrations of the aromatic compounds during irradiation utilizing liquid chromatographic methods on a Waters HPLC chromatograph (501 pump and a Waters μ Bondapak C18 column) interfaced to a Shimadzu flow cell for absorption recording. The Shimadzu UV-265 spectrophotometer was also interfaced to an IBM PC computer for data acquisition and handling. Chosen initial concentrations of the substrates used were 0.23 mM for phenol and 0.20 mM for 4-chlorophenol to provide the maximal reaction rates at the experimental conditions used (saturation of rate dependence on

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concentration of reagent and linear dependence of rate on photon flow²⁰). Control experiments at selected wavelengths and under broadband irradiation were also performed to assess the contribution of direct photolysis of 4-CP in solution and in the presence of colloidal SiO₂ to the overall photocatalyzed degradation. In all cases, this contribution was negligibly small relative to the photodegradation occurring under photocatalytic conditions. Recording parameter settings, data collection, and data processing were carried out using the Spectroscopy Interface Software, Version 3, provided by Shimadzu Scientific Instruments, Inc.

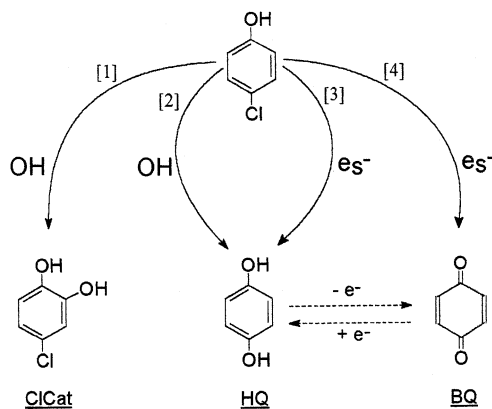
Results

In the present studies we considered the spectral variation of the photocatalyst's initial selectivity (S_i) defined as

$$S_i = \frac{\left(\frac{dC_i}{dt}\right)_{t \rightarrow 0}}{\left(\frac{dC_r}{dt}\right)_{t \rightarrow 0}} \quad (1)$$

where $(dC_i/dt)_{t \rightarrow 0}$ is the initial rate of formation of a given intermediate and $(dC_r/dt)_{t \rightarrow 0}$ is the initial rate of photodegradation of phenols resulting in the formation of that intermediate. Cathecol (Cat), hydroquinone (HQ), and benzoquinone (BQ) were identified as the major intermediates in the photodegradation of phenol and chlorocatechol (ClCat), hydroquinone, and benzoquinone were the major intermediates for the degradation of 4-chlorophenol, in accordance with previous studies on the degradation of phenols.^{2,4,19} In addition, formation of phenol and 2,5,4'-trihydroxybiphenyl were also observed. However, in our study of the spectral selectivity we monitored only the processes of formation of major intermediates since these are formed during the primary stages of phenolic degradation,^{4,19} whereas the other intermediates result from the degradation of primary intermediates, which necessitates their interaction with electrons and holes at secondary stages of the processes. Consequently, in our measurements of the initial selectivity these secondary processes are negligible. This allowed us to simplify our considerations of an otherwise very complex mechanism of the degradation of phenols. For the same reasons we did not consider the "electron shuttle" mechanism of the interconversion between BQ and HQ⁴ (see Scheme 1 below).

SCHEME 1



Before starting the measurements of the spectral dependencies of selectivity (S_i) of heterogeneous photocatalytic systems, it was important to demonstrate that selectivity does not depend on the photon flow (or light intensity) under the experimental conditions used (see eq 2). Otherwise, the existence of the

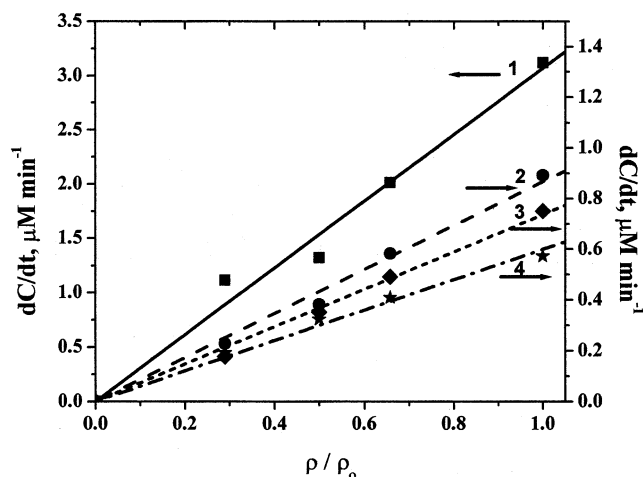


Figure 1. Dependencies of the initial rates of the degradation of (1) phenol and rates of formation of (2) cathecol, (3) benzoquinone, and (4) hydroquinone on the photon flow of the incident light (broadband irradiation).

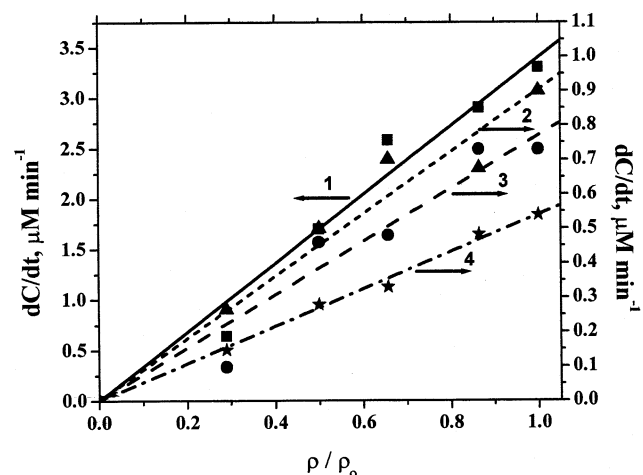


Figure 2. Dependencies of the initial rates of the degradation of (1) 4-chlorophenol and rates of formation of (2) hydroquinone, (3) chlorocatechol, and (4) benzoquinone on the photon flow of the incident light (broadband irradiation).

spectral dependence of selectivity might be shadowed by the spectral variation of the photon flow of the light source. This condition was satisfied as the linear dependencies of the initial rates of degradation of phenols and formation of intermediates on photon flow were indeed observed.

$$S_i = \frac{\left(\frac{dC_i}{dt}\right)_{t \rightarrow 0}}{\left(\frac{dC_r}{dt}\right)_{t \rightarrow 0}} = \frac{A\rho}{A'\rho} \neq f(n(\rho)) \quad (2)$$

where ρ is the photon flow of the light acting on the heterogeneous photosystem and A and A' are constants.

The results of our measurements show that, under broadband irradiation at the prevalent experimental conditions, the initial rates of the degradation of phenol and formation of major intermediates (cathecol, chlorocatechol, hydroquinone, and/or benzoquinone) scale linearly with photon flow. Consequently, the selectivity of the TiO₂ photocatalyst toward the formation of major intermediates does not depend on photon flow in the range of light intensity changes used and under the other experimental conditions (see, for example, Figures 1 and 2). This is particularly significant if the rates are to be used to

TABLE 1: Summary of Photocatalyst Selectivities in the Formation of Major Intermediates during the Photocatalytic Degradation of Phenol and 4-Chlorophenol As Obtained Experimentally under Broadband Irradiation and Given as the Average of the Spectral Dependence of the Corresponding Selectivities after Spectral Integration

reagent	method	CiCat	Cat	HQ	BQ
phenol	broadband irradiation	n/a ^a	0.23 ^b	0.2	0.24
	spectral integration	n/a	0.24	0.18	0.24
4-chlorophenol	broadband irradiation	0.22		0.26	0.15
	spectral integration	0.2		0.32	0.18

^a n/a = not applicable. ^b Estimated error in the selectivities is ± 0.02 .

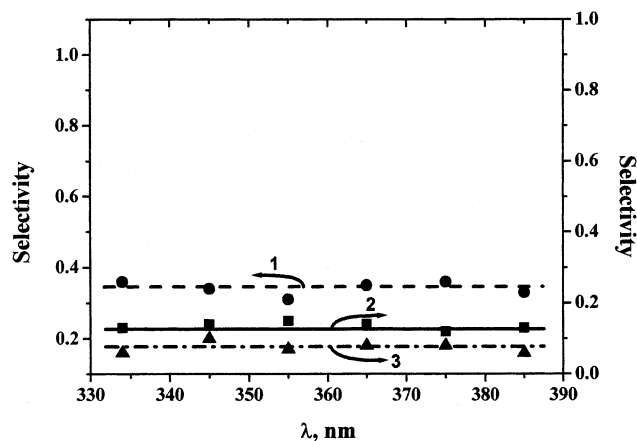


Figure 3. Spectral dependencies of the initial selectivity of formation of (1) hydroquinone, (2) cathecol, and (3) benzoquinone during the photocatalyzed degradation of phenol.

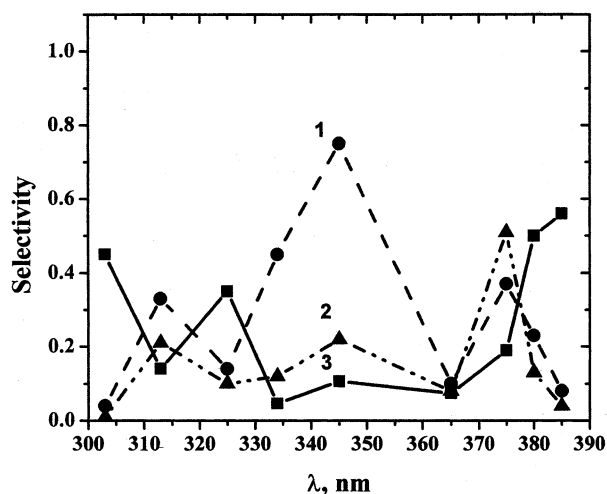


Figure 4. Spectral dependencies of the initial selectivity of formation of (1) hydroquinone, (2) benzoquinone, and (3) chlorocatechol during the photocatalyzed degradation of 4-chlorophenol.

describe the quantum yield of the process. Otherwise, the expected spectral variation of selectivity would be dictated by an alteration of the photophysical/photochemical properties of the heterogeneous photosystems only. The estimated experimental selectivities for broadband irradiation toward the formation of major intermediates averaged over different light intensities are summarized in Table 1.

The experimental dependencies of the spectral variations of the initial selectivity of TiO_2 photocatalyst toward the formation of intermediates during the photodegradation of phenol and 4-chlorophenol are presented in Figures 3 and 4, respectively. As expected, no spectral variation was observed for the phenol degradation, whereas a spectral variation was indeed observed

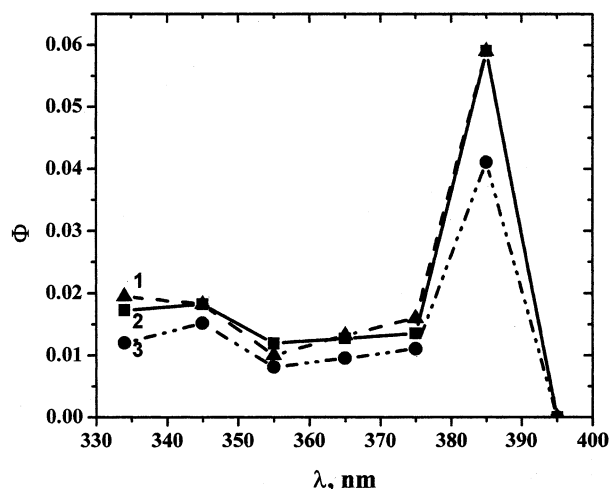


Figure 5. Spectral dependencies of the initial quantum yields of formation of (1) benzoquinone, (2) cathecol, and (3) hydroquinone during the photocatalyzed degradation of phenol.

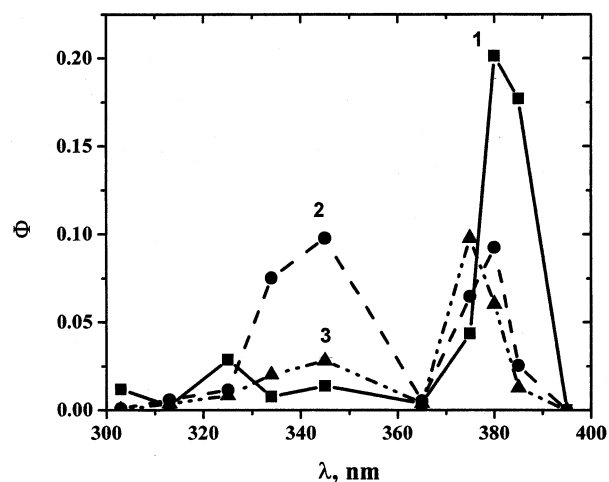


Figure 6. Spectral dependencies of the initial quantum yields of formation of (1) cathecol, (2) hydroquinone, and (3) benzoquinone during the photocatalyzed degradation of 4-chlorophenol.

in the photodegradation of 4-chlorophenol. The average values of the selectivity of the photocatalyst toward the formation of the major intermediates were estimated using eq 3. Note that

$$S_{\text{av}} = \frac{\int S_{(h\nu)} d h\nu}{\int d h\nu} \quad (3)$$

for the photodegradation of phenol, the average selectivities are in excellent accord with those obtained under broadband excitation, whereas they are slightly different for the photodegradation of 4-chlorophenol (see Table 1).

Using the experimentally obtained spectral dependencies of the quantum yield $\{\Phi_{r(h\nu)}\}$ of photodegradation of phenol and 4-chlorophenol reported in our previous study,¹⁹ it is now possible through eq 4 to assess the spectral dependencies of

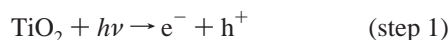
$$\Phi_{i(h\nu)} = \Phi_{r(h\nu)} S_{i(h\nu)} \quad (4)$$

the initial quantum yields of formation of the major intermediates considered, $\Phi_{i(h\nu)}$, from the experimentally determined selectivities $S_{i(h\nu)}$. The relevant results are illustrated in Figures 5 and 6.

Discussion

Traditional simplified mechanisms of heterogeneous photocatalysis typically involve the photoexcitation of the catalyst

(step 1), which leads to formation of free charge carriers



(electrons, e^- , and holes, h^+). These carriers are subsequently trapped on the surface (steps 2 and 3); they are then poised to



react with organic molecules as indicated in steps 4–6 (**note:** henceforth, it is understood that $\bullet\text{OH}$ implies a surface hydroxyl radical). In accord with earlier studies, the degradation of phenol involves only oxidative pathways (step 4), whereas both reductive (interaction with surface electrons; step 5) and oxidative pathways (interaction with photogenerated $\bullet\text{OH}$ radicals; step 6) are involved in the photodegradation of 4-chlorophenol to yield the different intermediates^{2,4} displayed in Scheme 1. Consequently, in the initial (primary) steps of the photodegradation of 4-chlorophenol we expect to detect the different distributions of primary intermediates as determined by the relative efficiencies of the reduction and oxidation steps. In the degradation of phenol, the primary product distribution should be constant regardless of the excited state(s) of the photocatalyst. In turn, the key factor to control the relative efficiencies of the reductive and oxidative steps in the 4-chlorophenol degradation is the ratio between the surface concentrations of electrons and holes ($\bullet\text{OH}$). In fact, the initial rates of formation of the three major primary intermediates in the degradation of 4-chlorophenol can be represented by three different events: (a) oxidative formation of chlorocatechol (path 1 in Scheme 1) for which the pseudo-first-order rate is given by eq 5, (b) oxidative and reductive formation of hydroquinone



(paths 2 and 3 of Scheme 1) for which the pseudo-first-order rate can be described by eq 6, and (c) reductive formation of benzoquinone, the pseudo-first-order rate of which is given by eq 7.

$$\left(\frac{dC}{dt}\right)_{(\text{ClCat})} = k_1[\bullet\text{OH}] \quad (5)$$

(paths 2 and 3 of Scheme 1) for which the pseudo-first-order rate can be described by eq 6, and (c) reductive formation of

$$\left(\frac{dC}{dt}\right)_{(\text{HQ})} = k_2[\bullet\text{OH}] + k_3[e_s^-] \quad (6)$$

benzoquinone, the pseudo-first-order rate of which is given by eq 7.

$$\left(\frac{dC}{dt}\right)_{(\text{BQ})} = k_4[e_s^-] \quad (7)$$

The total initial rate of 4-chlorophenol degradation is summarized by eq 8a, with eq 8b representing the rate constants of the overall oxidative pathway, and eq 8c summarizing the rate constants of the overall reductive pathway.

$$\left(\frac{dC}{dt}\right)_{(\text{ClPhOH})} = k'[\bullet\text{OH}] + k''[e_s^-] \quad (8a)$$

$$k' = k_1 + k_2 + \sum k_i \quad (8b)$$

$$k'' = k_3 + k_4 + \sum k_j \quad (8c)$$

The initial selectivity of the photocatalyst toward the formation of the three major intermediates can then be described by eqs 9–11, where $\gamma = [e_s^-]/[\bullet\text{OH}]$ is the ratio between the surface concentrations of electrons and holes.

$$S_{\text{ClCat}} = \frac{k_1[\bullet\text{OH}]}{k'[\bullet\text{OH}] + k''[e_s^-]} = \frac{k_1}{k' + k''\gamma} \quad (9)$$

$$S_{\text{HQ}} = \frac{k_2[\bullet\text{OH}] + k_3[e_s^-]}{k'[\bullet\text{OH}] + k''[e_s^-]} = \frac{k_2 + k_3\gamma}{k' + k''\gamma} \quad (10)$$

$$S_{\text{BQ}} = \frac{k_4[e_s^-]}{k'[\bullet\text{OH}] + k''[e_s^-]} = \frac{k_4\gamma}{k' + k''\gamma} \quad (11)$$

Clearly, as evidenced by eqs 9–11, the variation of the parameter γ leads to the changes in selectivity of the photocatalyst. In our previous study^{18,19} we demonstrated that the spectral variation of γ is governed by the spectral distribution of the absorption coefficient α of the photocatalyst provided that the diffusion length of electrons and holes are different. In particular, for a semi-infinite crystal this dependence can be described as¹⁸

$$\gamma = \frac{[e_s^-]}{[\bullet\text{OH}]} = B \frac{\alpha L_e + \beta}{\alpha L_e + 1} \quad (12)$$

where $\beta = L_e/L_h$ is the ratio between the diffusion lengths of electrons and holes, respectively, and B is a constant. This implies that γ depends on the absorption coefficient α and the shape of the spectral dependencies is determined by the magnitude of β . The ratio $[e_s^-]/[h_s^+]$ decreases for $\beta > 1$ (i.e., for $L_e > L_h$) and increases for $\beta < 1$ (i.e., for $L_e < L_h$) with increasing absorption coefficient α .¹⁸ In turn, the spectral changes of γ will cause the spectral response of the selectivity of photocatalysts, which can lead to changes in the route of the major reaction pathway.

In the case of phenol degradation, the selectivity toward any major primary intermediate is given by

$$S_{\text{PhOH}} = \frac{k_r[\bullet\text{OH}]}{k_t[\bullet\text{OH}]} = \text{constant} \quad (13)$$

where k_r is the rate constant for the formation of a given intermediate and k_t is the sum of rate constants of all the primary steps involved in the photodegradation of phenol. Consequently, the selectivity of the photocatalyst in this particular case is independent of the spectral variation of the irradiation in accord with the experimental data (Figure 3).

According to eqs 9–11, the spectral variation of the selectivity is dictated by the spectral variation of γ . The ratio between the selectivity of the photocatalyst for the evolution of ClCat and BQ yields eq 14, which reflects the spectral variation of γ ; that

$$\frac{S_{\text{ClCat}}}{S_{\text{BQ}}} = \frac{k_4[e_s^-]}{k_1[\bullet\text{OH}]} = (\text{const})\gamma \quad (14)$$

is the spectral variation of the ratio between the surface concentrations of electrons and holes. The experimental spectral dependence of $S_{\text{ClCat}}/S_{\text{BQ}}$, which scales with the $[e_s^-]/[h_s^+]$ ratio, is presented in Figure 7.

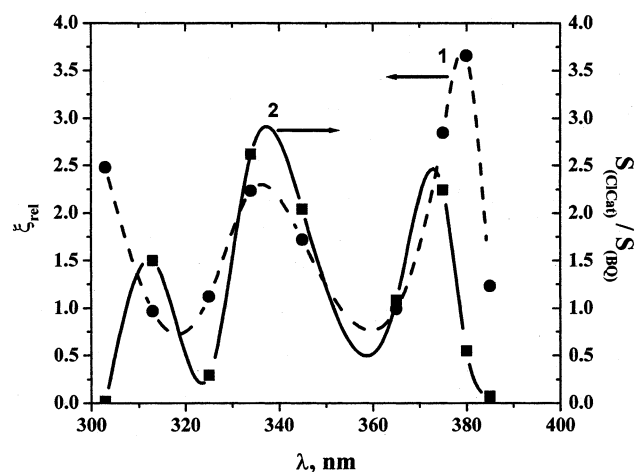


Figure 7. Spectral dependencies of (1) the relative photonic efficiency of the photocatalyzed degradation of 4-chlorophenol and of (2) the experimental ratio between the initial selectivities of formation of chlorocatechol and benzoquinone.

Earlier¹⁹ we demonstrated that the relative photonic efficiency of the photodegradation of 4-chlorophenol with respect to the photodegradation of phenol could be represented as

$$\xi_{\text{rel}} = 1 + \frac{k_{\text{re}}[e_s^-]}{k_{\text{rh}}[h_s^+]} = 1 + (\text{const})'\gamma \quad (15)$$

Accordingly, its spectral dependence should correlate with the spectral dependence of the ratio between the selectivity of the photocatalyst toward the formation of chlorocatechol (CICat) and benzoquinone (BQ); see eq 14. Indeed, a reasonably good, albeit semiquantitative, correlation exists (Figure 7), but it is nonetheless remarkable since the two constants in eq 14 and 15 are different.

Conclusions

In the present study we have demonstrated experimentally that the selectivity of the photocatalyst in heterogeneous photocatalytic processes is spectrally dependent, a phenomenon that we had earlier predicted theoretically¹⁸ using a simple model. This spectral dependence is caused by the spectral variation of the absorption coefficient of the solid, which leads to the spectral variation of the ratio of the surface concentrations of electrons and holes, provided that the diffusion lengths of the carriers are different. The spectral changes of the absorption coefficient of the photocatalyst alter the depth of the subsurface space in the solid where photogeneration of electrons and holes occurs. Consequently, different values of the diffusion lengths of the electrons and holes lead to different quantities of electrons and holes photogenerated in the bulk of the photocatalyst that can reach the surface and change the ratio of the surface concentrations of the two charge carriers. These are then poised to participate in surface chemical reactions. The different concentrations of the carriers at the different wavelengths of excitation change the relative efficiency of the oxidative and reductive steps, and thus the selectivity of the photocatalyst. Accordingly, the selectivity becomes spectrally dependent. This phenomenon governs the overall reaction pathway and should thus be a useful consideration if the goal in the photocatalytic transformation of substrates is to produce certain desired, value-added new products in heterogeneous photochemistry.²¹

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- (21) An astute reviewer suggested that, since reaction control of the type discussed herein is based on differing rates of surface-trapped electrons and hole formation reactions, the semiconductor particle should become charged. In this regard, it is relevant to note that different concentrations of electrons and holes on the surface exist in isolated semiconductor particles because of different diffusion lengths of the carriers of different sorts. The ratio of the charge carrier concentrations is determined by the value of the absorption coefficient. At sufficiently high concentrations of carriers, the difference in diffusion length creates an electric field between carriers of opposite signs to compensate for the different spatial distributions of the carriers (the so-called ambipolar diffusion). Thus, the effective diffusion length of electrons and holes becomes the same. However, if the concentration of carriers is much lower than the concentration of defects in the solids (most typical of "real" photocatalysts under moderate photoexcitation), then the spatial distribution of the electric field in the solid will be dictated by the spatial distribution of the defects. In such a case, the effect of ambipolar diffusion becomes negligible. The carriers' concentration profiles are determined by the distributions of photogenerated charge carriers and by the rates of recombination of these carriers through the defects. Thus, the difference between the surface concentrations of electrons and holes is caused by the photophysical events occurring in the solids. Surface chemical reactions create new (chemical) pathways of so-called surface recombination (surface decay) of charge carriers that will certainly affect the efficiency of the surface electronic processes. In particular, it can lead to changes in the surface charge. Germane to this discussion, an ideal photocatalytic process can be considered as an external recombination cycle with respect to the surface charge carriers that cause complete electronic relaxation of the photoexcited solid through chemical transformations of molecules at the surface. However, real photocatalytic reactions are complex and consist of several steps of chemical transformations. That is, the relaxation process is completed after a few (not just a single one) elementary chemical reactions involving both surface charge carriers and molecules of reagents and intermediates formed during the primary and secondary chemical reactions. It should also be noted that the (apparent) photocatalytic reaction may be accompanied by noncatalytic reactions such as photostimulated adsorption of molecules and ions (e.g., one may expect to observe adsorption of chloride anions formed during the 4-chlorophenol degradation) to compensate for the surface charge. In addition, solvent molecules can also play a role in establishing a new charge distribution during heterogeneous photoreactions. Clearly, a complete photocatalytic process is a very complex issue. In the present study, we focused on the initial steps of the photodegradation of 4-chlorophenol and monitored the formation of primary intermediates during the initial period of the photocatalytic process when the charge distribution,

as believed, still remains similar to that of isolated particles. In fact, the significant influence of secondary chemical steps involving intermediates formed in primary reactions was observed only after 10–15 min of irradiation. Attention was also focused on how the initial charge carriers'

distribution governs the direction of the primary reactions. Despite the knowledge base available, a fuller understanding of the complete cycle of the photocatalytic process will require additional experimental and theoretical studies.