

Recombination rate of photogenerated charges versus surface area: Opposing effects of TiO₂ sintering temperature on photocatalytic removal of phenol, anisole, and pyridine in water

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Abstract

The sintering temperature is an important parameter in many TiO₂ synthesis processes. Increasing this temperature (1) reduces the number of defect sites and, accordingly, the rate of electron–hole recombination, which improves photocatalytic rates and (2) decreases particle surface area, which a priori may be expected to reduce photocatalytic rates. We have studied the photocatalytic removal in water of the title probe molecules over a series of Millennium Chemicals TiO₂ prepared at increasing sintering temperatures in the order: PC500, PC105, PC50, and PC10. For phenol and anisole, reaction rates increase with increasing sintering temperature. For pyridine, the trend is opposite for PC500, PC105, and PC50, but PC10 outperforms all three. Therefore, the net effect of sintering temperature depends on the pollutant to be removed even for structurally closely related pollutants and is likely the result of an essentially surface-based reaction mechanism for pyridine versus a near-surface solution-phase mechanism for phenol and anisole. Hypotheses are presented regarding the higher activity of PC10 even for pyridine removal and the differences between phenol and anisole removal rates.

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1. Introduction

Degradation of organic pollutants using UV-irradiated TiO₂ is a widely studied method for the purification of water [1–3]. Whereas nearly all organic chemicals can be mineralized by TiO₂ photocatalysis, the reaction rates tend to be low relative to certain competing technologies. This owes to relatively low quantum efficiencies [4,5] (for a discussion of this terminology in photocatalysis see, for example, Ref. [6]): typical values are below 1% [5]. As a result, photocatalysis has not found widespread commercialization in water purification, but has been limited to niche applications [7].

Consequently, there is continually a great deal of research focused on producing higher activity TiO₂. Decreasing the recombination rate of photogenerated charges is essential since

these charges are the basis of the photocatalytic activity. This can be achieved by diminishing the density of surface defects. At the same time, it is important to prepare TiO₂ samples with a high surface area because the basic photocatalytic events occur at the surface or, possibly, in the water layers very close to it [8,9]. A number of synthesis techniques have been developed. Many of them begin with a low-temperature formation of TiO₂, followed by a high-temperature sintering step. The low-temperature step frequently results in amorphous or poorly crystallized titania with a high surface area. The chief purpose of sintering is to produce well-formed crystals. However, many desirable or undesirable changes, with respect to the photocatalytic activity, occur in the photocatalyst during the sintering process, with complex effects that depend on the sintering temperature and duration. Here, we shall focus on two important effects of sintering: decreasing the concentration of crystal defects and increasing the average particle size, i.e. lowering the surface area.

As the sintering temperature is increased, the photocatalyst becomes better crystallized and the number of defects is reduced. This results in a decreased rate of recombination of photogenerated electrons and holes, as can be measured by various

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time-resolved techniques [10–14]. This clearly improves photocatalytic activity. Sintering also causes the collapse of small pores and the fusion of small crystallites into larger agglomerates, thereby decreasing surface area. This should, in principle, have a negative effect on photocatalytic activity by reducing the adsorbed amounts of the reactants.

Our interest was to examine the competition between decreased recombination rate of photogenerated charges and decreased surface area as the sintering temperature is increased, and the resulting net effect on photocatalytic removal rates of some organics in water. An earlier study [15] on TiO₂ films fired at different temperatures found relatively little variation in the range from room temperature to 873 K, but a slight optimum at 773 K, with respect to the aqueous removal of a single compound: formic acid. We selected as probe compounds three aromatic molecules of similar size but with different functionalities: phenol (hydroxybenzene), anisole (methoxybenzene), and pyridine. The purpose was to vary the electron density on the ring, the order being: phenol > anisole ≫ pyridine, with a view to changing the reactivity with the photogenerated holes and •OH radicals [1–3]. Also, the hydroxylic H atom of phenol is susceptible to abstraction by an •OH radical more easily than the methylic H atoms of anisole. Phenol has often been used as a test compound in photocatalysis; the photocatalytic removal rate of anisole relative to *para*-substituted anisoles has been reported [16]; studies regarding the intermediate products of the photocatalytic degradation of anisole [17] or pyridine [18] have also been published.

The TiO₂ photocatalysts studied are a series produced by Millennium Chemicals and denoted PC500, PC105, PC50, and PC10, in order of increasing sintering temperature. These TiO₂ specimens offer the advantage of originating from the same source, which makes the comparisons more sound. Their commercial availability is also of interest as it facilitates further comparisons across different laboratories. Each aforementioned compound was reacted over each photocatalyst, and below we present the photocatalytic results and assess their implications.

2. Materials and methods

2.1. Chemicals

TiO₂ was produced by Millennium Chemicals. The company unfortunately does not reveal the sintering temperatures, except that they increase from PC500 (from which the others are derived) to PC10. The surface areas were previously measured [19] and are indicated in Table 1, along with other textural characteristics provided by Millennium Chemicals. All are 100% anatase according to the manufacturer. All organics were from Aldrich, of 99% or better purity, and used without further purification.

2.2. Adsorption measurements

The dark adsorption of the three organics to each of the catalysts was measured as follows. To a 25-mL amber bottle

Table 1
Characteristics of Millennium Chemicals titania

Name	BET surface area (m ² g ⁻¹)	Mean pore diameter (nm)	Particle size (nm)
PC10	10	24.1	65–75
PC50	54	20.1	20–30
PC105	85–95	15.3	15–25
PC500	317	6.1	5–10

wrapped in aluminum foil, 200 mg of TiO₂ was added, followed by 10 mL of water containing 150 μmol L⁻¹ phenol, anisole, or pyridine, yielding a catalyst loading of 20 g L⁻¹. The bottle was sealed and the slurry stirred for 18 h. After 15 min of settling, the slurry was sampled. The initial solution, kept under identical conditions (except for TiO₂ addition), was also sampled.

2.3. Photocatalytic removal of test compounds

Photocatalytic reactions were carried out in a custom Pyrex cylindrical cell with a volume of about 80 mL. The optical bottom window had an area of ca. 11 cm². A Phillips HPK-125 W high-pressure mercury lamp irradiated the slurry through this optical window, with the light first passing through a circulating water cuvette that included a filter that removed wavelengths shorter than 340 nm. The irradiation intensity incident on the bottom of the reactor was measured as 39.5 mW cm⁻² with a UDT 21 A Powermeter. The cell was loaded with 44 mg TiO₂, followed by the addition of 20 mL of water containing phenol, anisole, or pyridine at 150 μmol L⁻¹. Before irradiation, the slurry was mixed in darkness for 3 h to allow equilibration at the surface. Samples were taken after dark equilibration and after 5, 15, 30, 60, 120, and 180 min of irradiation. The initial solution was also analyzed.

2.4. Sampling

Sampling involved drawing 400 μL into a plastic 1-mL syringe (Codan), then filtering (Millex-HV, 0.45 μm pores, 4 mm) into a 2-mL amber glass vial. Subsequently, 100 μL of internal standard (100 ppmv butan-1-ol) was added with a 100-μL glass syringe (Hamilton). The exact amounts of sample and internal standard were determined gravimetrically.

2.5. Analysis

All samples were analyzed by GC using a Chrompack CP-Sil 5CB column (30 m × 0.53 mm × 5 μm). N₂ flowed through the column, and the detector was FID using an H₂/air flame. The temperature program was 343 K for 2 min, followed by a ramp of 10 K min⁻¹ up to 413 K. Butan-1-ol, pyridine, anisole, and phenol eluted at 3.0, 4.5, 7.0, and 8.1 min, respectively. The relative response factors were determined using five injections of a standard mixture.

3. Results and discussion

3.1. Dark adsorption

The affinity of the TiO_2 surface for a given molecule can have a large effect on the degradation kinetics of the molecule. In comparing the kinetics for different molecules, then, it is important to determine whether there are significant differences in the amount of each molecule that adsorbs to the catalyst surface. We therefore measured the dark adsorption of each of the probe molecules.

For phenol, anisole, and pyridine, measurements carried out in the dark with elevated TiO_2 loadings (20 g L^{-1}) and the same concentration ($150 \mu\text{mol L}^{-1}$) of the test compound showed no detectable adsorption. According to the detection limits of our GC measurements, the lowest detectable amount of adsorption, in $\mu\text{mol g}^{-1} \text{ TiO}_2$, would have been 0.6 for phenol, 1.5 for anisole, and 0.2 for pyridine, based on twice the standard deviation of concentration measurements. These measurements clearly confirm that the TiO_2 surface coverage is dominated by water molecules. Despite the lack of observed adsorption, we presume that a weak fraction of the probe molecules is in contact with the TiO_2 surface at any time, and that differences in this fraction and residence time at the surface may contribute, together with the chemical structure of the pollutant, to the differing importance of catalyst surface area for different probe molecules.

3.2. Photocatalytic kinetics

Photocatalytic removal experiments were conducted using every combination of phenol, anisole, or pyridine and each of the four TiO_2 samples in aqueous suspension. The photocatalyst loading was always the same on a mass basis, namely 2.2 g L^{-1} . The degradation results are presented in Figs. 1–3. For quantitative comparison of the removal kinetics across all compounds and photocatalysts, the initial pseudo-first-order reaction rate of

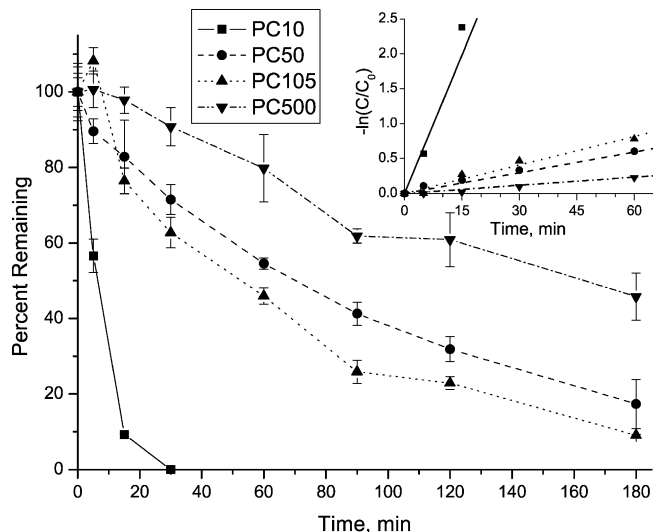


Fig. 2. Photocatalytic degradation of anisole. *Inset*: Fitting of initial kinetic constant, k_0 .

each reaction was normalized to that over PC10 and plotted in Fig. 4. Initial rates (based on the first 60 min), k_0 , have been used to focus on rates of elimination of the parent compound and to minimize effects of competition with the removal of intermediate products.

3.2.1. Phenol removal

The relative performance of the different photocatalysts varies greatly for different probe molecules. In the case of phenol (Fig. 1), reaction rates increase in the order $\text{PC500} < \text{PC105} < \text{PC50} < \text{PC10}$, that is, in order of increasing sintering temperature. This means that PC10 significantly outperforms PC500 despite having 30-fold less surface area (Table 1). These results show that, for removal of phenol, the decrease in the electron–hole recombination rate outweighs the decrease in surface area resulting from the sintering temperature.

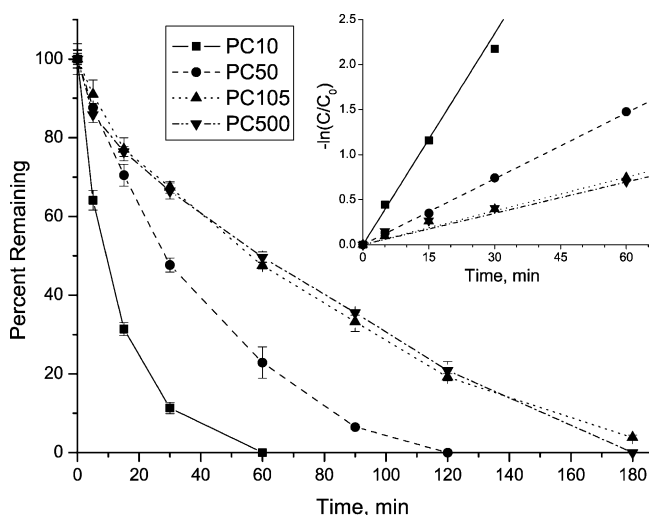


Fig. 1. Photocatalytic degradation of phenol. *Inset*: Fitting of initial kinetic constant, k_0 .

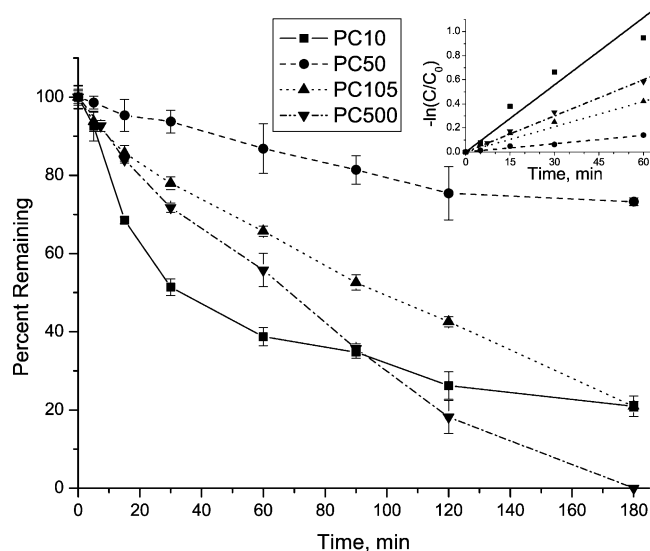


Fig. 3. Photocatalytic degradation of pyridine. *Inset*: Fitting of initial kinetic constant, k_0 .

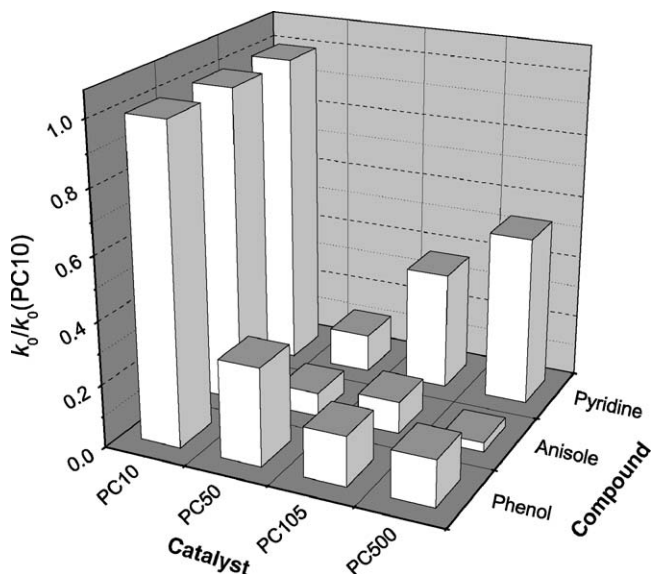


Fig. 4. Pseudo-first-order initial rate constants based on the first 60 min of reaction, normalized to the rates for PC10.

3.2.2. Anisole removal

For anisole (Fig. 2), the trend is nearly the same as for phenol; that is, generally, the change in crystal defect concentration is again the dominant effect of sintering upon the photocatalytic removal rate. The reaction rates of anisole are lower than those of phenol over PC500 and PC50, in agreement with a removal occurring through electrophilic attack. However, PC105 narrowly outperforms PC50, so that removal rates for phenol and anisole over PC105 are almost equal (Figs. 1 and 2).

This latter phenomenon might be related to another effect of sintering: the decrease in the UV-induced lability of TiO₂ surface O atoms. It has been shown by measurements of the isotopic exchange between UV-irradiated Ti¹⁶O₂ and gaseous ¹⁸O₂ at room temperature that, in the series of these Millennium samples, the greatest drop in the lability of surface O atoms occurs between PC105 and PC50 [19]. A question arises regarding how this difference in lability of surface O atoms could affect the removal rate of anisole more than that of phenol. The structural difference between the two compounds being the substituent, we consider here the abstraction of an H atom.

Abstraction from the phenol OH group gives the phenoxy radical, which does not react with O₂ (based on gas-phase measurements [20,21]). The most probable reaction of the phenoxy radical is to abstract an H atom from another phenol molecule, to no net effect. Since the concentration of phenoxy radicals would be very low at any time, the probability of two phenoxy radicals reacting with each other is presumably low. Therefore, the mostly likely radical termination step for the phenoxy radical is the abstraction of an H atom from an HO₂• radical, completing what is effectively a multi-step recombination of electron and hole, resulting in no net chemical change. The protonated HO₂• radical, which has a pK_a of 4.84, would be at a significant concentration in our experiments, since the pH of the suspensions differed by at most one pH unit from this value.

The photocatalytic degradation of anisole in water has been found to produce phenyl formate, which has been proposed to derive from the Ph–O–CH₂• radical through the complex Russell mechanism [22] which involves O₂ addition followed by reaction with an HO₂• radical and elimination of O₂ and H₂O [17]. However, this mechanism would not account for the different ranking of PC105 and PC50 in the cases of phenol and anisole removals since, unlike the mechanism we suggest, it does not directly involve a surface species. Consequently, we tentatively suggest that the formation of phenyl formate from the Ph–O–CH₂O₂• radical via HO₂• elimination might involve, as in the case of oxygen isotopic exchange, the participation of a labile surface O atom (of which the density is higher on PC105 than on PC50) forming a five-membered ring as an intermediate (see Fig. 5). The resulting O vacancy would be replenished by dissociation of adsorbed O₂ or more likely superoxide. Although oxygen isotope exchange experiments have not been performed for TiO₂ aqueous suspensions, a correlation between the rates of oxygen isotopic exchange in the gas phase with the removal rates of aromatics in the aqueous phase has been observed [9]. This lends some support to the mechanism suggested here.

3.2.3. Pyridine removal

The photocatalytic results are quite different for pyridine (Fig. 3), with initial reaction rates following the order PC50 < PC105 < PC500 < PC10. For catalysts PC50, PC105, and PC500, the order of reaction rates is opposite that for phenol, as these rates increase with decreasing sintering temperature. Rather than adhere to this trend, PC10 gives the highest initial reaction rates, as with phenol and anisole removal. Generally, then, surface area (Table 1) is more important than recombination rate for the removal of pyridine, but PC10 is special among this series of photocatalysts (for an interpretation, vide infra).

Previous studies [23,24] have shown that benzo[*b*]pyridine (quinoline), a molecule containing a pyridine moiety, photocatalytically reacts over TiO₂ predominantly via formation of a radical cation centered on the pyridine ring. This implies direct electron transfer to TiO₂, which in turn suggests close contact with the TiO₂ surface. Pyridine can be expected to react according to a similar mechanism. This would account for the importance of catalyst surface area (Table 1) in the photocatalytic removal kinetics of pyridine.

3.3. Near-surface solution-phase versus surface-based reaction events

The different responses of the probe compounds to changes in the catalyst induced by sintering substantiate earlier results from our laboratory [9], showing that removal rates of 4-chlorophenol (4-CP), 4-chlorobenzoic acid (4-CBA), and dichloroacetic acid (DCAA) differed greatly in their responses to partial obstruction of the titania surface by SiO₂ used to better affix TiO₂ powders onto a thin fiberglass material. The results were interpreted by suggesting that 4-CP could react at some distance from the TiO₂ surface, whereas DCAA required direct contact with the titania, and 4-CBA exhibited intermediate behavior depending on whether the initial attack of the photoproducted active species

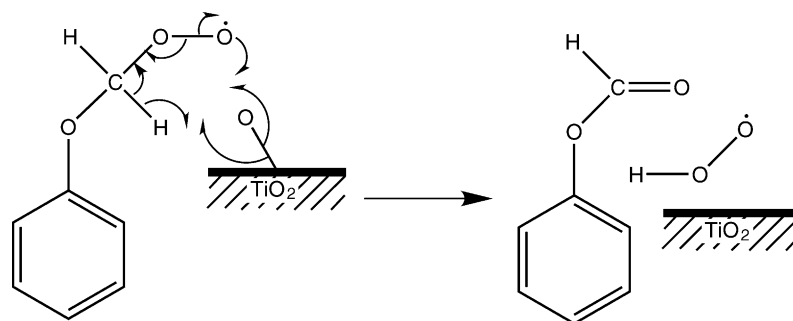


Fig. 5. Proposed reaction for the generation of phenyl formate via a modified Russell mechanism [22].

occurs on the carboxylic group or on the aromatic nucleus. Likewise, the relative unimportance of surface area for phenol and anisole removal would imply that these molecules can react in the water layers close to the TiO_2 surface, whereas reaction at the surface itself is more important for pyridine. If $\bullet\text{OH}$ can diffuse some distance away from the TiO_2 surface (a matter of ongoing debate [1,8,9,19,25–27]), it would reduce the importance of adsorption of phenol and anisole, and de-emphasize surface area as a reaction parameter.

Note that aliphatic carboxylic acids are expected to be formed in the course of the photocatalytic treatment and to represent the main part of the remaining total organic carbon in the final stages of the treatment. Like DCAA, aliphatic carboxylic acids are photocatalytically decarboxylated by direct electron transfer (hole capture), which implies a close contact with the surface [9]. Therefore, the pronounced decrease in the pyridine removal rate at irradiation times >60 min for the lowest surface area sample, i.e. PC10, can be attributed to competitive adsorption between pyridine and the aliphatic carboxylic acids (and, possibly, amides [18]) formed from pyridine.

3.4. Reflections on the activity of the highest-temperature sintered TiO_2 (PC10)

It remains to explain the exceptional behavior of PC10. For all compounds tested, PC10 appears to have a specific activity so high that it more than offsets the reduction in reaction rate due to reduced surface area (Table 1; Fig. 4). Since PC10 is sintered at the highest temperature among the photocatalyst series, it is possible that partial conversion of the TiO_2 from the anatase phase to the rutile phase occurred. The manufacturer reports that all catalysts in the series are 100% anatase, but trace amounts of rutile in anatase are extremely difficult to detect by X-ray diffraction; moreover, the expansion of the absorption tail of PC10 to the visible spectral range [19], with respect to the other Millennium samples, may be regarded as an indication of the presence of rutile. Mixed-phase TiO_2 photocatalysts have been reported to have significantly higher activity than single-phase TiO_2 , which has been interpreted as due to electronic interactions between the anatase and rutile phases [28] and to highly active sites formed at the phase interfaces [29]. These phenomena may impart an especially high activity to PC10 aside from the gradual improvement in crystallinity with sintering temperature. The higher absorption of PC10 relative to the other samples at

365 nm [19] (the principal wavelength entering the reactor given the lamp and the optical filter used) is also a factor in increasing removal rates, but it cannot entirely account for the increases observed (Figs. 1–4).

Also complicating the effect of sintering temperature on removal kinetics is surface hydroxylation. TiO_2 particles are surrounded by several layers of well-organized, tightly adsorbed water [30]. The water is bound via hydrogen bonding to TiO_2 surface hydroxyl groups, whose density depends on the sintering temperature. Therefore, photocatalysts sintered at higher temperatures can be expected to have thinner layers of tightly bound water [30]. This would in turn facilitate the penetration of organic solutes through the immobile water layers to the catalyst surface. This effect of the removal of surface hydroxyl groups thus tends to improve photocatalytic activity for molecules that must react at the TiO_2 surface and to offset the reduction in photocatalytic activity due to decreased surface area. This could be particularly important for pyridine, for which surface reactions are apparently more important than for phenol or anisole. The reduced thickness of surface-bound water layers could also make it easier for anisole to approach the TiO_2 surface, since anisole is the least soluble of the three probe molecules, which is consistent with a lower capability to hydrogen bond with water. This hypothesis would explain why the PC10-photocatalyzed removal of anisole is more efficient than that of phenol (Figs. 1 and 2), even though the opposite would be expected from the lower electron density on the anisole ring than on the phenol ring.

4. Conclusions

We have examined the net effect of the sintering temperature during TiO_2 photocatalyst preparation upon removal rates of organics in water. Three probe compounds were used. For removal of phenol, reaction rates increase with increasing sintering temperature, indicating that the improved crystallinity and reduced recombination rate caused by the decreased concentration of structural defects outweigh the reduced surface area due to sintering. For anisole, the trend is generally the same. Pyridine follows the opposite trend for PC50, PC105, and PC500: removal rates increase with decreasing sintering temperature and therefore with increasing surface area. However, PC10 gives the most rapid removal of pyridine despite having the highest sintering temperature and lowest surface area.

We attribute the differences in activity trends to different reaction mechanisms for the three probe aromatic molecules. Phenol and anisole would be able to react with $\bullet\text{OH}$ in near-surface solution layers, whereas pyridine would mainly react on the TiO_2 surface, emphasizing the importance of surface area. Aside from increased absorption of the UV irradiation employed, factors that may explain the exceptional performance of PC10 include trace amounts of rutile formed at its high sintering temperature [28,29], and thinner surface-bound water layers [30] due to a lower surface hydroxyl content that allow easier approach of the organic pollutant to the TiO_2 surface.

It must be stressed that although we have principally considered two effects of increasing the sintering temperature, namely a decreased recombination rate and decreased surface area, and made some reference to surface oxygen lability and surface hydroxylation, there are numerous additional effects of the sintering temperature that may contribute to the observed photocatalytic rates. Among these properties changed by sintering are the hydroxyl radical generation rate, electron transfer rates, properties and concentration of active sites, the point of zero charge, and mass transport owing to changes in the pore structure. More work is necessary before the contributions of all of these effects of sintering on photocatalytic activity can be fully understood.

It is clear from our results that the net effect of sintering temperature depends on the pollutant to be removed. One should not expect to find a single sintering temperature that is optimal for a wide range of compounds. Rather, the preparation process should be optimized for the intended target pollutants whenever possible. Alternatively, the use of two photocatalytic reactors in series might be envisaged. The first one would contain TiO_2 efficient for organics whose removal does not demand a close contact with the surface; the second one would contain TiO_2 suited to the elimination of organics, such as aliphatic carboxylic acids [9], that are mainly attacked at the surface.

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