Photosensitization of Crystalline and Amorphous Titanium Dioxide by Platinum(IV) Chloride Surface Complexes

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Abstract: Anatase, rutile, and amorphous titania powders were surface-modified by grinding with $PtCl_4$ and $H_2[PtCl_6]$. Only the anatase modification afforded hybrid photocatalysts capable of degradation of 4-chlorophenol (4-CP) with visible light, with sufficient stability towards decomplexation. Grinding with $K_2[PtCl_4]$ produced materials of only low photocatalytic activity. Most efficient photocatalysts contained up to 2 wt% of Pt^{IV}. At higher surface loading the excess fraction of the complex is desorbed into the aqueous solution. Scavenging experiments with benzoic acid and tetranitromethane revealed that hydroxyl radicals are produced by the primary reduction of oxygen by conduction band electrons generated through electron injection from a postulated surface platinum(III) complex. It is proposed that the latter is formed from a charge-transfer ligand-to-metal (CTLM) excited state through homolysis of the Pt–Cl bond. Accordingly, the primary oxidation of 4-CP may occur by adsorbed chlorine atoms, the intermediary existence of which was demonstrated by scavenging experiments with phenol.

Keywords: amorphous materials · photochemistry · platinum · sol–gel processes · titanium

Introduction

Semiconductor photocatalysis of chemical reactions by titania has progressed from basic research and reached technical applications like solar purification of air and water from organic and inorganic pollutants.[1] Although titania absorbs only about 3% of solar light, this is high enough to induce reasonable photodegradation rates of these compounds, present only in trace amounts. However, for this and other applications a more efficient utilization of solar light is desirable. Accordingly, many efforts have been made to sensitize titania for visible light induced photocatalytic reactions. Recently we have used $Na_2[PtCl_6]$ and other metal chlorides like $AuCl_3$ and $RhCl_3$ to prepare *amorphous* microporous titania (AMM-Ti) modified in the bulk.[2–4] These hybrid photocatalysts catalyzed the photomineralization of 4-chlorophenol (4-CP) with visible light. Apparent disappearance quantum yields reached 1.3×10^{-3} at 546 nm and increased to 4.5×10^{-3} at 366 nm. The most active photocatalysts contained 3% Pt^{IV}. Photoelectrochemical experiments proved the semiconductor nature of the powders; the action spectrum of the photocurrent extended down to about 600 nm.[4] These novel materials were prepared by a sol–gel procedure affording high specific surface areas of 160–200 $m^2 g^{-1}$. According to extended X-ray absorption fine structure (EXAFS) results, isolated $PtCl_4$ molecules are homogeneously distributed in an almost exclusively amorphous matrix of titania.

It was postulated that the photocatalytic activity of Pt^{IV}/AMM-Ti in the visible originates from local excitation of the platinum(IV) chloride chromophore affording an adsorbed chlorine atom and Pt^{III} as an intermediate species. Charge separation was assumed to proceed through electron injection from Pt^{III} into the conduction band of titania, followed by reduction of oxygen, while the surface-trapped chlorine atom may oxidize 4-CP to the radical cation. Degradation of the latter should follow the mechanism as proposed for unmodified titania.[5–7] This mechanistic proposal was based, inter alia, on analogy with the photochemistry of chlorocopper(II)[8] and chloroplatinum(IV) complexes in aqueous solution. The broad CTLM bands extending from the UV to the visible region overlap with ligand field bands at approximately 350 nm and are characteristic for $[PtCl_x(H_2O)_{6-x}]^{4-x}$ ($x = 4-6$) species.[9, 10] $[PtCl_6]^{2-}$ in aqueous solutions exposed both to UV or visible light irradiation undergoes photoaquation. The reaction is initiated by photodissociation of a chlorine atom [Eq. (1)], followed by chain reactions.

$$[Pt^{IV}Cl_6]^{2-} \xrightarrow{h\nu} [Pt^{III}Cl_5]^{2-} + Cl \quad (1)$$

Chloride substitution takes place with quantum yields of 13.4 to 0.87 in the wide range of irradiation wavelength from 270 to

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450 nm.[10] The corresponding thermal reaction requires several days for completion.[11]

Although the proposed mechanism for these amorphous titania photocatalysts, doped in the bulk, seemed reasonable, it raised some important questions. For instance, unexpectedly no reduction of $PtCl_4$ to elemental platinum occurred during the photodegradation, a reaction well known for unmodified titania irradiated in the presence of reducing agents like citrate, acetate, or methanol.[12, 13] This process finds application in metallic platinum deposition on TiO_2 surfaces, but also can be useful for platinum recovery from diluted solutions of Pt^{IV}. Furthermore, it was unknown whether an amorphous titania phase and volume doping are necessary to obtain the visible light activity or whether crystalline phases and surface doping would accomplish the same. In the following we therefore report on the photocatalytic activity of the two crystalline modifications, anatase (P25) and rutile (TiO_2-R), and one amorphous phase, (TiO_2-a), all surface-doped with platinum(IV) chloride complexes. Mechanistic experiments in the presence of scavengers for electrons and OH radicals provide basic information on the initial stages of the photodegradation.

Results and Discussion

Preparation and stability of surface-modified titania: Surface-modified photocatalysts were prepared by grinding the two crystalline titania powders P25 and TiO_2-R and the amorphous TiO_2-a with various amounts of $PtCl_4$ and $H_2[PtCl_6]$. The specific surface area of $50\,m^2g^{-1}$ of unmodified P25 increases to $65\,m^2g^{-1}$ for 1% $PtCl_4$/P25. According to transmission electron micrography, the morphology closely resembles that of P25 as indicated by the presence of 0.2 to 1 micrometer aggregates, composed of small particles with an average diameter of 20 nm.[14] The diffuse reflectance spectrum of 3% $PtCl_4$/P25 is shown in Figure 1. Compared to the spectrum of P25 a long tail-absorption extends into the visible region, as also observable in the spectrum of solid $PtCl_4$. Since surface modification of P25 with $K_2[PtCl_4]$ resulted in a material at least 50% less active in 4-CP degradation ($\lambda >$ 455 nm) than the analogous $PtCl_4$/P25 catalyst, we conclude that the oxidation state of the photoactive platinum species is +IV, in accordance with the previously reported bulk-doped Pt^{IV}/AMM-Ti photocatalyst.

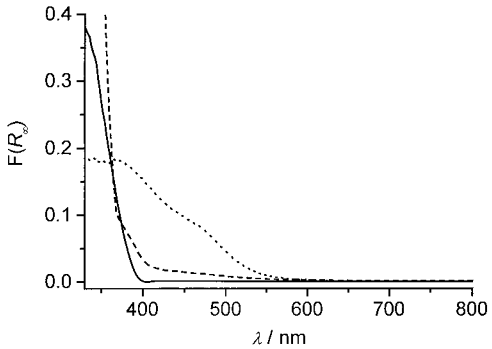


Figure 1. Diffuse reflectance spectra of 3% $PtCl_4$/P25 (dashed line), P25 (solid line), and $PtCl_4$ (dotted line).

Abstract in German: *Verreiben von Anatas, Rutil und amorphem Titandioxid mit* $PtCl_4$ *und* $H_2[PtCl_6]$ *ergibt oberflächenmodifizierte Hybridphotokatalysatoren. Diese sind nur im Falle der Anatasmodifikationen stabil genug, um einen effizienten Abbau von 4-Chlorphenol mit sichtbarem Licht zu ermöglichen. Die aktivsten Katalysatoren besitzen bis zu 2 wt%* Pt^{IV}*, bei höherer Beladung wird der überschüssige Komplex in die wäßrige Lösung desorbiert. Als Mechanismus der photoinduzierten Ladungstrennung wird vorgeschlagen, daß Lichtabsorption des Oberflächenplatin(IV)komplexes über einen Charge-Transfer-Ligand-to-Metal (CTLM)-Zustand zur Homolyse der Pt–Cl-Bindung führt. Das dabei gebildete Chloratom oxidiert 4-Chlorphenol, während die gleichzeitig entstandene Platin(III)zwischenstufe ein Elektron in das Leitungsband von Titandioxid injiziert. Letzteres reduziert anschließend Sauerstoff zu Superoxid, welches schließlich zur Bildung von OH-Radikalen führt. Abfangversuche mit Benzoesäure, Tetranitromethan bzw. Phenol bestätigen das Auftreten dieser intermediären Radikale bzw. Chloratome.*

To investigate the stability of the modified samples with respect to desorption of the platinum component, aqueous suspensions were stirred in the dark for five days. Formation of $[PtCl_x(H_2O)_{6-x}]^{4-x}$ ($x = 4-6$) complexes was monitored by measuring the strong absorbance at 259 nm. In order to have predominantly the $[PtCl_6]^{2-}$ complex present, as indicated by the absorption spectrum, the filtrates were acidified with HCl (2M) before measurement. For P25 materials with Pt^{IV} contents below or equal to 2% only less than 1% of the total platinum amount appeared in solution, while 11 and 50% were found for 1% $PtCl_4/TiO_2$-R and 1% $PtCl_4/TiO_2$-a, respectively. The good stability in the former case suggests that chemisorption has taken place during or after grinding, most likely by formation of Ti–O–Pt bonds. This type of bonding was also postulated for $[Pt^I(bpy)]$ complexes (bpy = 2,2′-bipyridine).[15] When $H_2[PtCl_6]$ was employed, the resulting materials suffered stronger desorption than $PtCl_4$-modified P25, suggesting a smaller fraction of chemisorbed complexes. It is expected, that chloride substitution by surface $[Ti]-O^-$ [16] in $[PtCl_6]^{2-}$ should be slower than water substitution in $[PtCl_x(H_2O)_{6-x}]^{4-x}$ ($x = 4$, 5), the species generated from $PtCl_4$.[17] The results are also consistent with the reactivity of platinum(IV) chlorides in thermal[11] and photoaquation[10] reactions. The amount of chemisorbed complexes can be increased upon irradiation with visible light as demonstrated for 1% $H_2[PtCl_6]$/P25. The initial amount of dissolved platinum complex present in an aqueous suspension decreased from about 4.5% to below 3% after irradiation with $\lambda > 400$ nm for 30 min.

Photodegradation of 4-chlorophenol: Figure 2 displays the photodegradation curves of 4-CP for four typical catalysts upon irradiation with visible light ($\lambda_{irr} > 455$ nm) in the presence of air. Whereas the rutile and amorphous titania based samples, 1% $PtCl_4/TiO_2$-R and 1% $PtCl_4/TiO_2$-a, were almost inactive, the anatase-containing powders $PtCl_4$/P25 and $H_2[PtCl_6]$/P25 induced initial decomposition rates even

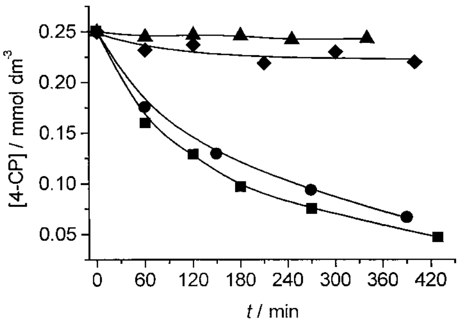


Figure 2. Photodegradation of 4-CP catalyzed by various $[PtCl_x]^{4-x}/TiO_2$-modified materials upon irradiation at $\lambda_{irr} > 455$ nm. ■ 1% $PtCl_4$/P25, ● 1% $H_2[PtCl_6]$/P25, ◆ 3% $PtCl_4/TiO_2$-a, ▲ 1% $PtCl_4/TiO_2$-R.

50–60% higher than those observed for amorphous bulk-doped Pt^{IV}/AMM-Ti under the same experimental conditions.[2, 3] Similar to the latter, mineralization occurred as indicated by formation of carbon dioxide and hydrochloric acid; accordingly the pH value changed from approximately 7 to 2.7. The catalytic nature with respect to platinum chloride follows from the apparent turnover number of 10 as calculated for a single run from the amount of 4-CP degraded, divided by the amount of platinum present in 1% $PtCl_4$/P25. Making the reasonable assumption that for mineralization of one 4-CP molecule more than one photocatalytic cycle is required, the true turnover number should be much higher. When after complete disappearance of 4-CP a new 4-CP portion was added to the suspension up to the same initial concentration, the rate decreased by about 60%. The lower rate may be due to a loss of catalyst through multiple sample withdrawing and catalyst deactivation.

The influence of the platinum content on the reaction rate of surface-doped P25 was investigated with a series of *n*% $PtCl_4$/P25 catalysts ($n = 0.5, 1.0, 1.5, 2.0, 2.5, 3.0$). The rate of degradation of 4-CP increased with increasing platinum content up to about 3 wt% (Figure 3). However, this is an apparent value, since a considerable part is due to the known homogeneous reaction of the dissolved platinum complex[4] formed by desorption (Figure 3). Accordingly the semiconductor-catalyzed reaction exhibits the maximum rate when the platinum(IV) content is about 2 wt%.

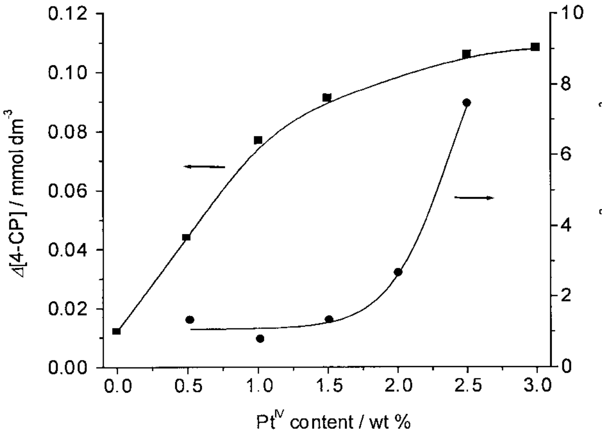


Figure 3. Amount of 4-CP decomposed after irradiation with visible light for 6.5 h (■) and desorption of Pt^{IV} complexes after five days in the dark (●) as function of increasing surface loading; 0–3% $PtCl_4$/P25.

Surprisingly, no photoreduction of Pt^{IV} to Pt^0 was observable under the experimental conditions mentioned above, irrespective of whether visible or UV light ($\lambda_{irr} > 335$ nm) was employed. This differs significantly from UV irradiation of unmodified TiO_2 in the presence of aqueous $[PtCl_6]^{2-}$ which produces Pt^0 even in the absence of any reducing agent.[18–20] Reduction to Pt^{II} seems also unlikely, since in the presence of air, adsorbed $[PtCl_4]^{2-}$ is easily oxidized to the Pt^{IV} complex.[21] Only when 4-CP was replaced by methanol in high concentration (50 vol%) was elemental platinum formed upon UV or long-term visible irradiation, according to a well-known reaction.[13] The resulting gray powder induced an initial rate of degradation of 4-CP about 70% lower than that of untreated 1% $PtCl_4$/P25.

Figure 4 shows results of photooxidation of 4-CP in sunlight in various systems based on $PtCl_4/TiO_2$ materials. The highest rate of 4-CP degradation was observed in the case of undoped P25 even though it is active only in UV light. This phenomenon will be discussed later.

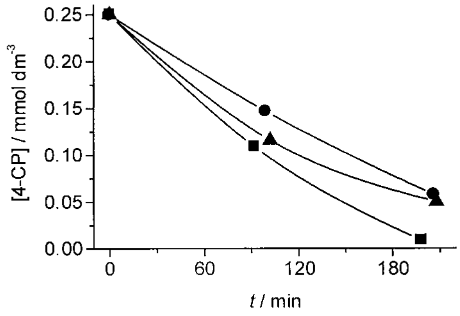
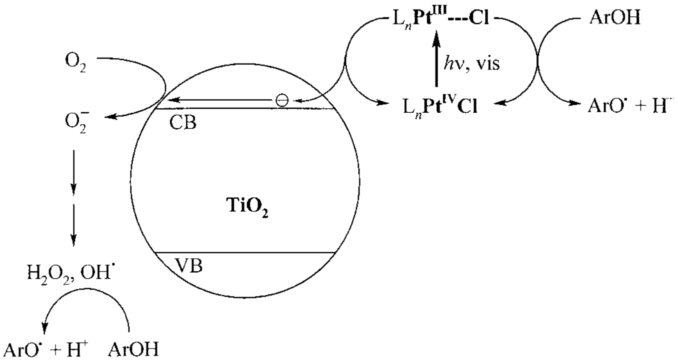


Figure 4. 4-CP degradation upon solar irradiation of ● 1% $PtCl_4$/P25, ▲ 3% $PtCl_4$/P25, ■ P25 suspensions.

Mechanism: Since the photodegradation of 4-CP catalyzed by crystalline surface-doped P25 completely corresponds to the results observed for the bulk-doped amorphous titania Pt^{IV}/AMM-Ti, the same mechanism may operate in both reactions. It was proposed that visible light CTLM excitation of the platinum(IV) chloride surface complex affords a Pt^{III} species and a weakly bound chlorine atom.[2–4] Chloroplatinum(III) complexes have been generated in homogeneous solution through photolysis of $[PtCl_6]^{2-}$[22, 23] and at the surface of P25 powders through oxidation of $K_2[PtCl_4]$ by valence band holes or OH radicals.[24] For the latter case an average lifetime of a few microseconds was evaluated from diffuse reflectance flash photolysis. For the present system it is assumed that subsequent electron injection from Pt^{III} into the conduction band of titania regenerates Pt^{IV}. This mechanistic pathway is termed *indirect* sensitization. It is supported by the fact that modification of the bulk-doped amorphous titania by $PtBr_4$ afforded less active photocatalysts.[3] However, the alternative, *direct* electron transfer sensitization by electron injection from the excited surface platinum complex without preceding Pt–Cl cleavage cannot be excluded at the present. It would correspond to the well-established sensitization by bipyridyl complexes of Ru^{II} and Fe^{II}. In this case electron injection occurs from a CTML excited state.[25–28] Although an analogous mechanistic pathway cannot be ruled out, it seems rather unlikely since the CTLM states of chloroplatinum(IV) complexes in solution are known to undergo bond cleavage rather than electron transfer. Furthermore, unlike ruthenium and iron, the resulting higher oxidation state, in this case Pt^V, is known only from complexes with more electronegative ligands, like in $[PtF_6]^-$.[29] Irrespective of the detailed mechanism, the electron injected into the titania conduction band is expected to reduce oxygen to superoxide, which in turn is transformed into hydrogen peroxide and OH radicals (Scheme 1).[30–34] This mechanistic proposal is corroborated by experiments in the presence of scavengers for OH radicals and electrons. Thus, when the standard photodegradation ($\lambda > 400$ nm, 1 % $PtCl_4$/P25) was performed in the presence of benzoic acid (10^{-2} M), substantial amounts of salicylic acid were detected. Although this suggests that the OH radicals are formed through the proposed O_2 reduction pathway, it does not exclude an oxidative pathway via an hitherto unknown strongly oxidizing surface platinum complex. To answer this question and to have a more simple system, 4-CP was omitted in the further experiments. As depicted in Figure 5, upon irradiation with visible light salicylic acid formation was observed only when oxygen was the electron scavenger. When the latter was tetranitromethane (10^{-2} M) only trace amounts of salicylic acid were detectable, and the relatively stable yellow $C(NO_2)_3^-$ anion was identified through its typical absorbance at 350 nm.[35–37] In contrast, a fast formation of salicylic acid occurred when the latter experiment was conducted with UV light ($\lambda > 335$ nm). In this case light absorption by the titania matrix generates valence band holes which oxidize water or surface hydroxyl groups to the OH radical, whereas the conduction band electrons still reduce tetranitromethane. These experiments clearly demonstrate that upon excitation with visible light the OH radical is formed by the *reductive* pathway. Furthermore, the unexpected observation that in the solar degradation experiments undoped P25 induced a slightly faster reaction than the two modified samples (Figure 4), may be now rationalized. Upon UV excitation additional OH radicals are formed by water oxidation through light absorption of the titania matrix. This effect should be more efficient in unmodified P25, since no platinum surface complex can act as a light filter as in modified P25. Thus, the beneficial role of the modified surface in the visible spectral region apparently does not counterbalance its negative influence in the UV.



Scheme 1. Proposed mechanism of TiO_2 sensitization by $[\mathrm{Pt^{IV}Cl}_x]^{4-x}$ complexes. CB and VB denote conduction and valence band edge, respectively.

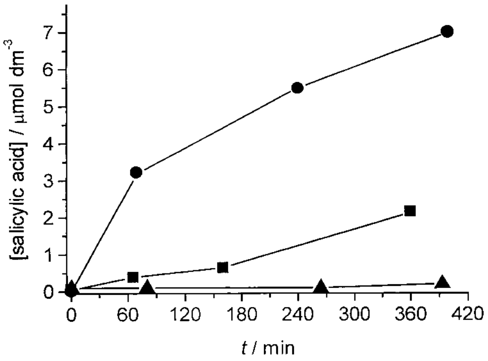


Figure 5. Formation of salicylic acid upon irradiation of 1 % $PtCl_4$/P25 in aerated suspension in the presence of benzoic acid ($\lambda_{irr} > 400$ nm, ■); in Ar-saturated suspension in the presence of $C(NO_2)_4$ ($\lambda_{irr} > 400$ nm, ▲ and $\lambda_{irr} > 335$ nm, ●). For details see text.

When sensitization of titania proceeds through the indirect electron transfer mechanism, some of the chlorine atoms are expected to undergo addition to the substrate. To test for this possibility, phenol was used instead of 4-CP in the standard irradiation experiment employing visible light ($\lambda > 455$ nm). In this reaction at least 3 % of the total Cl content was converted to CP, proving the existence of intermediary chlorine atoms (Figure 6). This side reaction may explain the partial deactivation of the photocatalyst observed upon multiple use. Free chlorine atoms are slightly weaker oxidants than OH radicals ($E^\circ_{\mathrm{Cl/Cl^-}} = 2.6$ V,[38a] $E^\circ_{\mathrm{OH/OH^-}} = 2.8$ V[38b]) and therefore should oxidize phenol[9, 39] and 4-CP but not water or surface hydroxyl groups. Thus, in agreement with the scavenging experiments we propose as a working hypothesis that upon excitation with visible light with the hybrid photocatalyst, 4-CP is oxidized to the corresponding phenoxyl radical and a proton by intermediate chlorine atoms, generated by homolytic Pt–Cl bond cleavage in the CTLM state of a chloroplatinum(IV) surface complex and by OH radicals originating from the reduction of oxygen (Scheme 1). Further

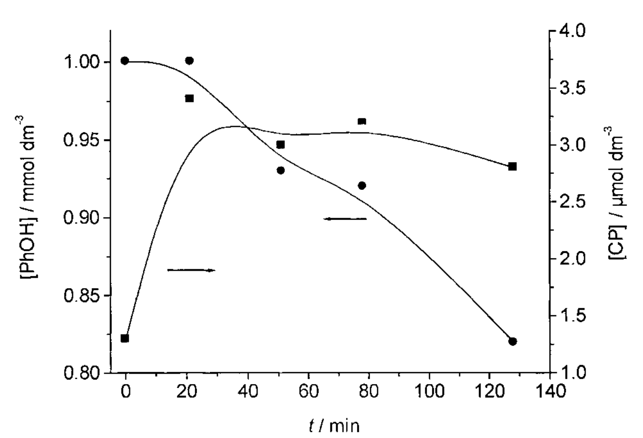


Figure 6. Phenol degradation (●) and 4-CP formation (■) at 1 % $PtCl_4$/P25 ($\lambda_{irr} > 455$ nm). $[Pt]_{total} = 25$ µM, $[Cl]_{total} = 100$ µM.

oxidation proceeds via hydroquinone, benzoquinone, and additional intermediates finally to CO_2, H_2O, and HCl.[3, 4, 6, 34, 40]

The results summarized in Figure 2 for photodegradation with visible light demonstrate the strong influence of the titania modification. Only anatase afforded photocatalysts of satisfying activity, whereas the rutile and amorphous phase based materials were almost inactive. Accordingly, calcination of TiO_2-a at 300 – 350 °C produced an anatase-containing material, which after surface modification showed activity similar to that of the modified P25 photocatalyst. This distinct difference in the degradation with visible light may be partially due to the smaller fraction of chemisorbed platinum complexes present at the rutile and amorphous phase surface. Furthermore, the much higher activity of anatase relative to rutile resembles the difference generally observed for these two crystal modifications in photooxidation processes driven by UV light. It was assumed that faster recombination of electron-hole pairs in the case of rutile, due to its poorer adsorption properties for O_2, is responsible for the lower photocatalytic activity.[41] A further reason could be the higher electron mobility of anatase as compared to rutile.[42–44] The latter difference can also rationalize the much higher activity of the surface-modified anatase materials upon excitation with visible light, when it is postulated that electron injection and oxygen reduction proceed at different surface sites. In this case recombination of the injected electron with the chlorine atom competes with electron trapping at the oxygen adsorption site. In the modified rutile materials electron trapping may be too slow to compete with recombination.

Experimental Section

Materials: 4-Chlorophenol (4-CP, Fluka) was purified by distillation at low pressure. The fraction boiling at 355 K ($p = 5$ Torr) was collected. Triply distilled water was used during all manipulations. The modified TiO_2 powders 1 % $K_2[PtCl_4]/TiO_2$, x % $PtCl_4/TiO_2$, and x % $H_2[PtCl_6]/TiO_2$ were prepared by grinding various amounts of $K_2[PtCl_4]$ (Merck), $PtCl_4$ (Degussa), or $H_2[PtCl_6]$ (Fluka), respectively, in an agate mortar with Degussa P25 (ca. 70 % anatase, 30 % rutile), TiO_2-R (Aldrich, rutile); the procedure was reproducible within ± 10 % as indicated by the corresponding photodegradation rates of 4-CP. The amorphous TiO_2-a, which was prepared by a sol – gel procedure described elsewhere,[3] was also ground with $PtCl_4$. As proven by X-ray diffraction analysis anatase can be also formed from TiO_2-a by heating at 620 K for 17 h under air. The platinum contents (given in wt % of Pt) of 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 wt % were calculated under the assumption of complete adsorption.

Irradiation of 1 % $PtCl_4$/P25 ($0.5\,g\,L^{-1}$) in methanol/water (1:1 *v*/*v*) with UV light ($\lambda > 320$ nm) resulted in reduction of Pt^{IV} to Pt^0 and significant darkening of the catalyst. In visible light ($\lambda > 455$ nm) this process was observed only after long irradiation times (ca. 20 h).

Instruments: Diffuse reflectance spectra of the solids were recorded on a Shimadzu UV-3101PC UV/Vis-NIR scanning spectrophotometer equipped with a diffuse reflectance accessory. Samples were spread onto an Al_2O_3 plate, the background reflectance of which was measured prior to measurement. Reflectance was converted by the instrument software to $F(R_\infty)$ values according to the Kubelka – Munk theory. Electronic absorption spectra were recorded on the same apparatus, fluorescence spectra on a Perkin Elmer LS 50B luminescence spectrometer. An HPLC (Kroma-System 2000 controller, Kontron 320 autosampler with 430A photodiode array detector) was used to determine concentrations of 4-CP. A reverse-phase C-18 column (Kontron, Spherisorb 5 ODS 2) and water – methanol eluent (40/60, v/v) were employed. Absorbances at 280 and 220 nm were measured for the detection of 4-CP and phenol, respectively. Specific surface areas have been determined with a Gemini 2370 instrument according to Brunauer – Emmett – Teller theory.

Photodegradation procedure and product analysis: The photocatalytic degradation of 4-CP was carried out in a jacketed cylindrical 15 mL quartz cuvette attached to an optical train. Irradiation was performed with an Osram XBO 150 W xenon arc lamp (I_o (400 – 520 nm) = 2×10^{-6} Einstein $s^{-1}\,cm^{-2}$) installed in a light-condensing lamp housing (PTI, A1010S). Appropriate cut-off filters were placed in front of the cuvette. Running water was circulated through the jacket to ensure constant temperature of the reaction mixture, which was stirred magnetically.

In the standard experiment, a pure or modified TiO_2 suspension (14 mL, $0.5\,g\,L^{-1}$) containing 4-CP ($2.5 \times 10^{-4}\,mol\,L^{-1}$) was sonicated for 15 min and then transferred to the cuvette. During an illumination run, the reaction solution (approximately 1.0 mL) was sampled at given time intervals. The samples were filtered through a Millipore membrane filter (0.22 μm) and then subjected to HPLC analysis.

For carbon dioxide determination a IR gas cuvette (10 cm) was inserted into the system in such way that circulation of the reaction atmosphere through the quartz and IR cuvettes was enabled with help of a small gas pump (Crouzet SK0251). The CO_2 concentration was determined through the strong absorption at 2362 cm^{-1}. The initial 4-CP concentration was ten times larger than in the standard photodegradation experiment. In the case of 1 % $PtCl_4$/P25 ($0.5\,g\,L^{-1}$) approximately 45 μmol CO_2 (> 22 % of theoretical amount) was found after 29 h of irradiation with visible light (> 455 nm) and a further > 80 μmol (> 38 %) after 7 h of UV irradiation (> 320 nm).

Solar illuminations were carried out simultaneously on a May afternoon in Erlangen (49.5° N Lat.). The catalysts ($0.5\,g\,L^{-1}$) were suspended in 4-CP solution (40 mL, $2.5 \times 10^{-4}\,mol\,L^{-1}$) in Pyrex glass reactors with magnetic stirring. HPLC analysis was performed as described above.

Scavenging of OH radicals: Benzoic acid (10^{-2} M) was added to the standard photodegradation experiment. Samples were withdrawn as described above and salicylic acid was detected through the strong fluorescence signal at 400 – 420 nm when excited at 300 nm;[45] shape and maximum of emission was identical with an authentic sample. When necessary, argon was bubbled for 40 min prior and during irradiation. Experiments in the absence of 4-CP were conducted analogously. When $C(NO_2)_4$ (10^{-2} M) was used as an electron scavenger, after filtration the nonionic substances were extracted with CH_2Cl_2 and the solvent was evaporated. The residue was dissolved in water and subjected to quantitative analysis by fluorescence spectroscopy. Formation of $C(NO_2)_3^-$ anion was proved by UV spectroscopy at 350 nm.[35–37] Salicylic acid was also found as the result of a much slower thermal oxidation of benzoic acid with H_2O_2 in aqueous solution.

Scavenging of Cl atoms: Phenol (10^{-3} M) was used instead of 4-CP in the standard irradiation experiment, and disappearance of phenol and formation of CP were monitored by HPLC as described above.

Pt^{IV}-desorption experiments: Aqueous suspensions of x % $PtCl_4/TiO_2$ and 1 % $H_2[PtCl_6]/TiO_2$ (5 mg in 2.5 mL of water) were sonicated for 15 min and then kept in the dark for five days. After filtration through the Millipore filter, the filtrate (1.8 mL) was added to HCl (0.6 mL, 2 M). The resulting solution was left for another six days for thermal equilibration. Thereafter the absorbance at 259 nm was compared with that of standard solutions of $PtCl_4$ in HCl (0.5 M); the extinction coefficient at 259 nm was determined as $11.8 \times 10^3\,mol^{-1}\,dm^3\,cm^{-1}$ as compared to 400 $mol^{-1}\,dm^3\,cm^{-1}$ found for the corresponding Pt^{II} complex.

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