

Enhancement of the photocatalytic activity of various TiO₂ materials by platinisation

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Abstract

In the present work, three commercially available TiO₂-catalysts, namely Degussa P25, Sachtleben Hombikat UV100 and Millennium TiONA PC50, were platinised by a photochemical impregnation method in two ratios of platinum deposits (0.5 and 1 wt.%). The physical characterisation of the new synthesised catalysts was carried out by measurements of the BET-surface area, the light absorption properties and the adsorption of the model compounds. The photocatalytic activities of these samples were determined using three different model compounds: EDTA, 4-chlorophenol (4-CP), and dichloroacetic acid (DCA). While in the case of EDTA its disappearance was studied, total mineralisation was measured for 4-CP and DCA. In all cases, the photocatalytic activity was found to increase with rising amounts of Pt, e.g., the photonic efficiency for DCA degradation increased from 12.2% for pure Hombikat UV100 to 32.1% for Hombikat UV100/0.5 wt.% Pt and to 42.7% for Hombikat UV100/1 wt.% Pt. Promising results were also achieved for the total mineralisation of 4-CP. The photonic efficiency rose from 0.82% using unmodified PC50 to 1.14% with PC50/0.5 wt.% Pt (zero-order kinetics assumed in all cases). Similar results were obtained with the other new synthesised catalyst samples and for the model compound EDTA. No immediate relationship between the photocatalytic activity of the catalyst samples and their physical properties (surface area, adsorption of pollutants, absorption of light) could be observed. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The improvement and the optimisation of TiO₂ as photocatalyst is one of the most important task for technical applications of heterogeneous photocatalysis in the future; therefore, in recent years, many investigations on the basic principles [1–3] and the enhancement of the photocatalytic activity have been undertaken [4].

The activity of a TiO₂ powder depends on its bulk and surface properties [5]. To improve the catalyst, two principle strategies have been applied. On one side, the procedures of synthesis of TiO₂ have been varied and optimised so that in last years a large number of new and highly active catalysts have been produced [6,7]. On the other side, the modification of pure TiO₂ has been investigated in a number of works. The studies include the combination with other semiconductors [5], the covering of the surface with dyes in order to extend the light absorption to the visible range

[8–10], and the doping and partially coating with noble and transition metals [11 and references therein]. A considerable increase of the photocatalytic activity have been reported, in particular, with platinum deposited on TiO₂ particles, especially for water splitting [12–15]. Generally, many studies show clearly that the efficiency of a photocatalyst for the degradation of organic and inorganic compounds is strongly dependent of their chemical nature [16]. Thus, the catalysts not only have to be optimised for their activity, but for a technical use, it must be investigated for which reactions or substrates are they most suitable. The strong influence of the substrate was also reported for platinised TiO₂. However, no systematic study is available in the literature to understand this behaviour.

In the present work, three different commercially available TiO₂ photocatalysts have been modified with two different amounts of platinum deposited on their surface. Usual methods for depositing platinum or other noble metals are thermal deposition and photoimpregnation [17,18]. As the last technique was reported in several cases to yield more active photocatalysts [19], the method was applied to platinise Degussa P25, Sachtleben Hombikat UV100 and Millennium

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TiONA PC50. For these three materials very different activities have been reported that are strongly dependent on the nature of the substrate to be transformed [20]. The aim of this work was to investigate the different photocatalytic behaviour and the influence of the deposition of increasing amounts of platinum, using three model compounds, namely dichloroacetic acid (DCA), 4-chlorophenol (4-CP) and EDTA, whose photocatalytic degradations have been studied by several workers [21–23]. A possible connection between the enhanced activity of the samples and two important kinetic parameters, surface adsorption of the substrate and absorption of light by the catalyst, was studied comparing the three basic materials. A possible relationship between the mechanism of the photocatalytic reaction over platinised TiO₂ samples and the physicochemical properties of the different photocatalysts is also discussed.

2. Experimental section

2.1. Preparation of catalysts

For the synthesis of the platinised TiO₂-catalysts a modification of the method described by Kraeutler and Bard [24] was applied. As basic materials, three commercially available TiO₂-catalysts, namely Degussa P25, Sachtleben Hombikat UV100 and Millennium TiONA PC50, kindly supplied by the manufacturing companies, were used. For each platinised sample, 4.5 g of TiO₂ were suspended, respectively, in 56.75 and 113.5 ml of a 2.04 mM hexachloroplatinic(IV) acid hexahydrate (Merck, 40 wt.% Pt) solution in bidistilled water, corresponding to amounts of 0.5 and 1 wt.% Pt to TiO₂. The solution was stirred for 1/2 h and irradiated with a 500 W mercury high-pressure immersion lamp (Heraeus TQ718 Z-4) for 2 h under constant stirring. The whole process was carried out under nitrogen, with the exception of PC50/1 wt.% Pt. Then, 4.5 g of hydroquinone (Merck) were added and the suspension stirred for 12 h more, most of the supernatant was discarded and the rest centrifuged at 4000 rpm for 60 min. The sample was washed twice with bidistilled water, centrifuged and dried at 120 °C for 24 h.

2.2. Experimental set-up

Photocatalytic runs were performed using a batch reactor based on the previously described ACP-reactor [25]. This reactor is made of UV-A transparent PMMA and consists of five separate 64 mm × 16 mm × 500 mm chambers in parallel. Thus, up to five degradation tests could be made during one experimental run. To prevent sedimentation and to supply a sufficient amount of oxygen, the chambers were bubbled from the bottom with air, employing an air pressure pump. A light field consisting of 16 horizontal and parallel UVA-light-tubes (Philips Cleo R-UVA 40 W) has been employed for irradiation. A light intensity of 23 W/m² ± 2.5%

has been determined with a UV meter device by Dr. Hoenle UV Technik using a UVA filter for the range from 320 to 400 nm.

The catalyst was applied in a concentration of 1 g/l; initial concentrations of DCA and 4-CP were 5 and 1 mmol/l, respectively, in a total reaction volume of 200 ml. The experiments were run at an initial pH of 3 and 9. After adjustments of pH with diluted HNO₃ or NaOH solutions, the suspensions were stirred in the dark for 1/2 h. PH was not controlled during the reactions. Samples were taken after 0, 20, 40, 60 and 120 min (for 4-CP additionally after 180 min) and analysed by TOC measurements, employing a Shimadzu TOC 5000.

The degradation of EDTA (Na₂EDTA, Merck) was performed using a different set-up. The employed photoreactor consisted of a thermostatted cylindrical cell ($V = 125$ ml) provided with a Teflon cap with a gas inlet, a sampler and a holder for a bandpass filter (Schott BG1; 270 nm < λ < 510 nm; maximum transmission (87%) at 360 nm). Irradiation was applied from the top using a high-pressure xenon arc lamp (Osram XBO, 150 W), provided with a Schott KG 5 filter to remove the IR fraction of the light. A photon flow per unit volume of $1.0 \pm 0.1 \times 10^{-5}$ Einstein/l/s was determined by actinometric measurements with the ferrioxalate method [26], using 10 ml of actinometric solution to keep the same conditions as in the experiments.

For the photocatalytic runs, 20 ml of an aqueous suspension of the catalyst (1 g/l), containing 5 mmol/l EDTA was prepared. The suspension was adjusted to pH 3 with diluted HClO₄ and stirred in the dark for 1/2 h to assure the adsorption equilibrium of EDTA. From this suspension, 10 ml were filled into the photoreactor and illuminated for 3 h under constant oxygen bubbling (volumetric flow rate = 1.4 ml/s) and without pH control. Samples were taken periodically for quantitative analysis and filtered through a 0.22 μ m Millipore filter. EDTA concentration was determined by spectrophotometric analysis with 2,4,6-tripyridyl-*s*-triazine (TPTZ) at 593 nm [27]. The UV-visible absorption measurements were performed employing a Shimadzu 210 A spectrophotometer. For each condition at least duplicated runs were carried out, averaging the results. The rate of total mineralisation was determined using a Shimadzu TOC 5000 A.

2.3. Determination of BET-surface areas and adsorption of model pollutant

BET-surface areas of the catalysts were determined by adsorption of N₂ using a Micromeritics FlowSorb II 2300 device.

The adsorption of DCA and 4-CP on the modified catalysts was measured at pH 3, 7 and 9. For the experiments, 60 mg of each catalyst have been added to 6 ml of a 5 mmol/l DCA solution, whereas 120 mg have been added to 6 ml of a 1 mmol/4-CP solution. The suspensions were shaken continuously for 24 h at ambient temperature. After this, the

catalyst was separated by centrifugation and the TOC of the clear solution was measured.

2.4. Measurement of diffuse reflectance of light

Diffuse reflectance spectra were measured with a Bruins instruments spectrophotometer, using an integrating sphere. For the measurements the samples were applied on glass carriers. BaSO₄ was taken as a standard.

3. Results

3.1. Measurements of BET-surfaces

The BET-surface areas of the unmodified TiO₂-powders were as stated by the providers: 50 m²/g for Degussa P25, 300 m²/g for Sachtleben Hombikat UV100 and 50 m²/g for Millennium PC50. The platinised catalyst samples showed no reduction or increase of specific surface area within the accuracy of measurement.

3.2. Adsorption of model pollutants

The adsorption of the model compound on the platinised samples was determined for DCA and 4-CP. Fig. 1 shows the absolute amounts of adsorbed compound per gram of catalyst at pH 3, 7 and 9. The adsorption of DCA increased with decreasing pH, with the exception of PC50 that shows at pH 3 nearly no adsorption and at pH 9 the highest one. Platinised UV100 exhibited the highest DCA adsorption, with a maximum for the 1 wt.% Pt sample (92 μmol DCA/g catalyst).

The adsorption of 4-CP on the different catalysts under the same experimental conditions as approx. eight to ten times less than that of DCA, as shown in the figure. Oppositely to the results of DCA, adsorption of 4-CP is larger at neutral or basic pH values. The strongest adsorption could be observed with the P25 samples, the 0.5 wt.% Pt sample exhibiting the maximum adsorption (10 μmol 4-CP/g catalyst).

3.3. Measurements of diffuse reflectance spectra

Comparison between the diffuse reflectance spectra of the unmodified and the platinised samples showed no differences in the UV range. In the visible range, a stronger absorption could be observed. From the optical point of view, that means that the samples are becoming darker with the increasing amount of platinum, ranging from pure white in the unmodified samples up to a very dark grey in P25/0.5 wt.% Pt. As an example, in Fig. 2a the diffuse reflectance spectra of the three UV100 samples are shown. It can be observed that the spectra remain almost unchanged after platinisation, with the exception of the strong decrease in reflectance from 400 nm up.

The different types of catalysts showed slight differences in reflectance. All samples showed nearly total reflectance

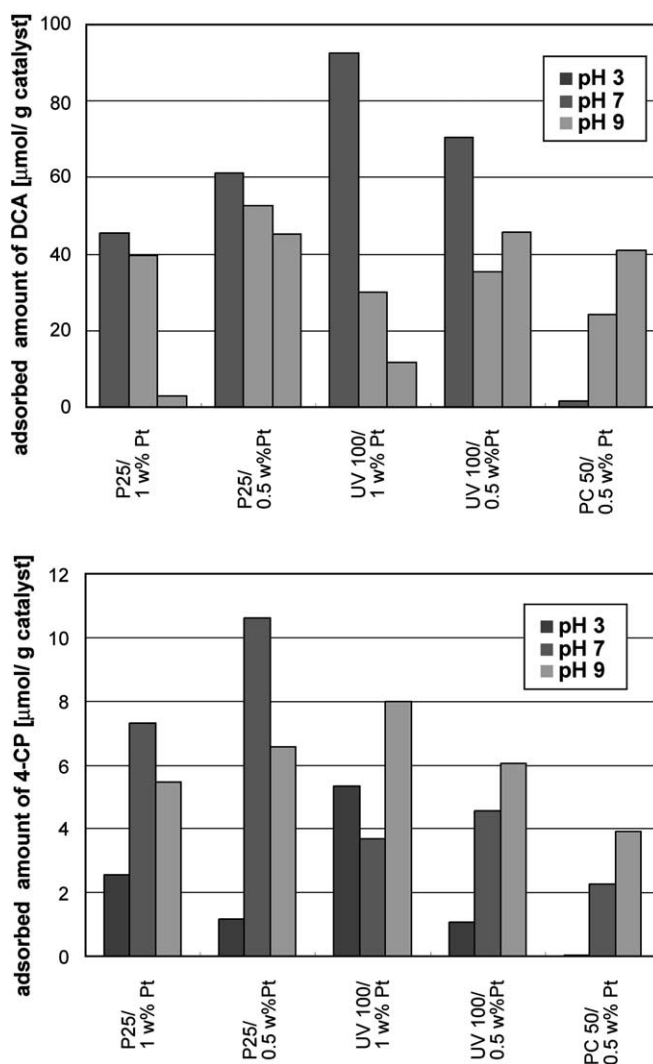


Fig. 1. Total amount of adsorbed DCA (upper) and 4-CP (lower) on different platinised TiO₂ materials.

in the visible and very low reflectance in the UV, as shown in Fig. 2b, but anyone exhibited a significant shift of the bandgap. While PC50 showed a very sharp transition, UV100 showed only a very slow change in reflectance. In the UV range, UV100 exhibited a lower reflectance than the other catalysts, i.e., ca. 7% against ca. 10% for P25 and PC50. The platinised samples gave similar results.

3.4. Degradation of model pollutants

The catalyst samples showed very different photocatalytic activities for the degradation of the model compounds. Platinisation resulted in all cases in an enhancement of the activity, but a dependence of the chemical nature of the organic pollutant could be observed.

After 2 h of illumination, DCA was degraded from an initial concentration of 120 ppm TOC to 2.3 ppm at pH 3 and 2.4 ppm at pH 9 employing the best photocatalyst, in this case, Hombikat UV100/0.5 wt.% Pt. As shown in Fig. 3,

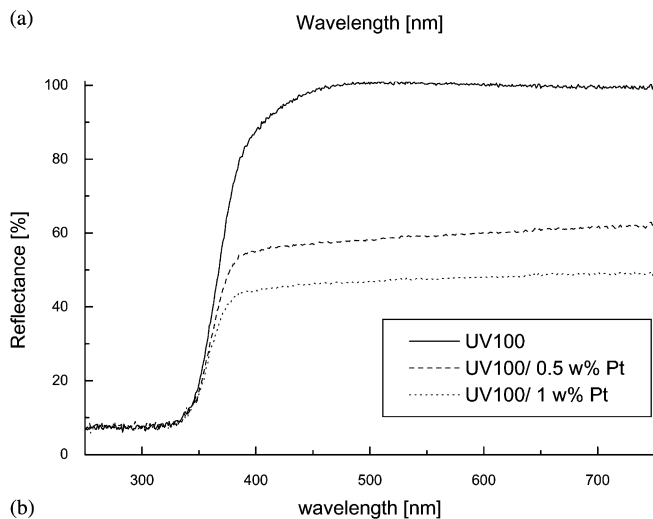
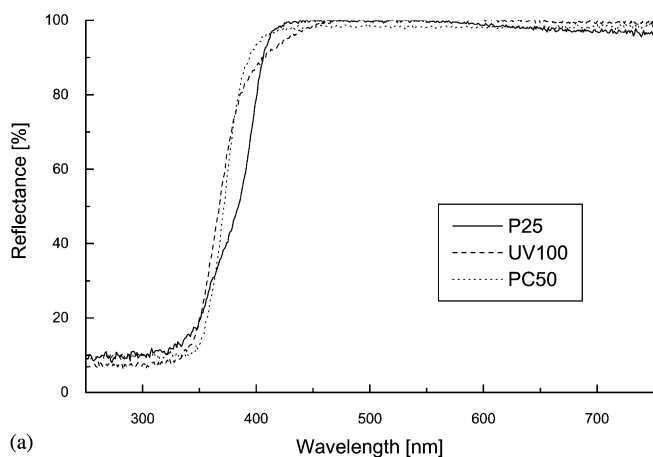


Fig. 2. (a) Diffuse reflectance spectra of unmodified P25, Hombikat UV100 and PC50, (b) comparison of the diffuse reflectance spectra of Hombikat UV100, unmodified and platinumised with 0.5 and 1 wt.% Pt.

increasing amounts of platinum increases the activity. P25 samples showed during the degradation experiments very strong sedimentation, causing that only a part of the total amount of catalyst was suspended, and that the correspond-

Table 1

Photonic efficiencies for the total mineralisation of DCA by platinumised and unmodified TiO₂ materials

Catalyst	ζ_0 (%) at pH 3	ζ_0 (%) at pH 9
P25/1 wt.% Pt	18.25	15.12
P25/0.5 wt.% Pt	21.22	8.29
P25	8.13	8.75
UV100/1 wt.% Pt	32.14	15.64
UV100/0.5 wt.% Pt	42.71	28.49
UV100	12.16	6.26
PC50/0.5 wt.% Pt	43.77	40.83
PC50	12.45	6.34

ing activities were lower than those of the other samples (see Fig. 3).

Based on these results, the initial photonic efficiencies ζ_0 for the total mineralisation of the model compound could be obtained.

$$\zeta_0 = \frac{\text{degraded molecules}}{\text{incident photons}}$$

and ζ_0 as shown in Table 1 could be calculated according to the following equation:

$$\zeta_0 = \frac{(-dC/dt)_{t=0}}{P_0}$$

where $(-dC/dt)_{t=0}$ is the initial reaction rate assuming a zero-order kinetics and P_0 the incident photonic flow per unit volume. The photonic efficiencies for DCA degradation are given in Table 1.

Similar results were obtained for the degradation of 4-CP. After 3 h of illumination, TOC was reduced from 72 to 30 ppm at pH 3 and to 32 ppm at pH 9, using the best photocatalyst PC50 with 0.5 wt.% Pt. As seen in Fig. 4, platinumisation increases significantly the activity for total mineralisation. As for DCA, increased amounts of platinum enhanced strongly the activity for 4-CP degradation.

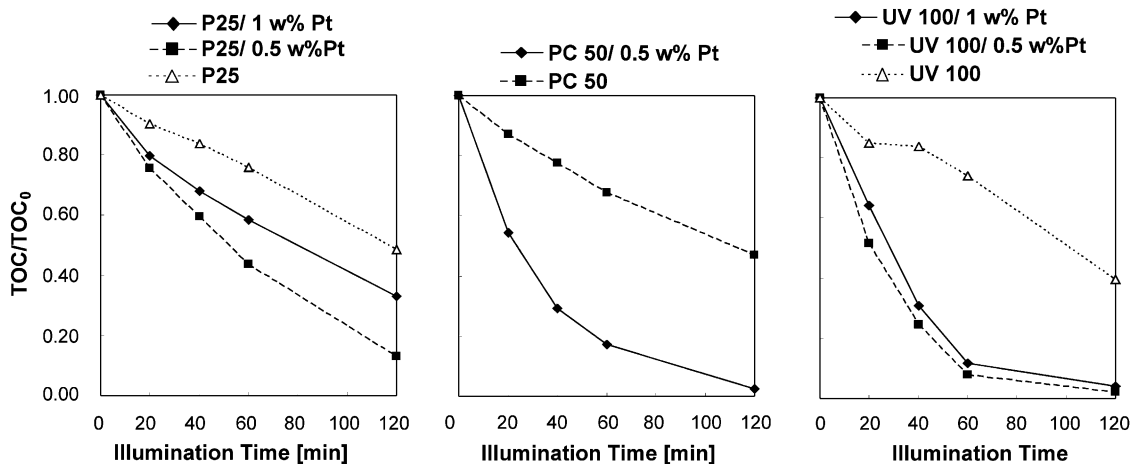


Fig. 3. Total mineralisation of DCA with platinumised TiO₂-catalysts in comparison to unmodified samples at pH 3.

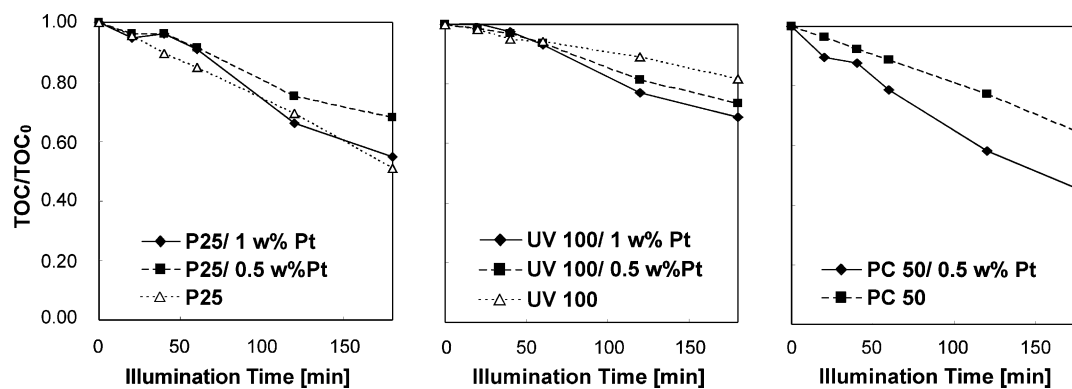


Fig. 4. Total mineralisation of 4-CP with platinised TiO₂-catalysts in comparison to unmodified samples at pH 3.

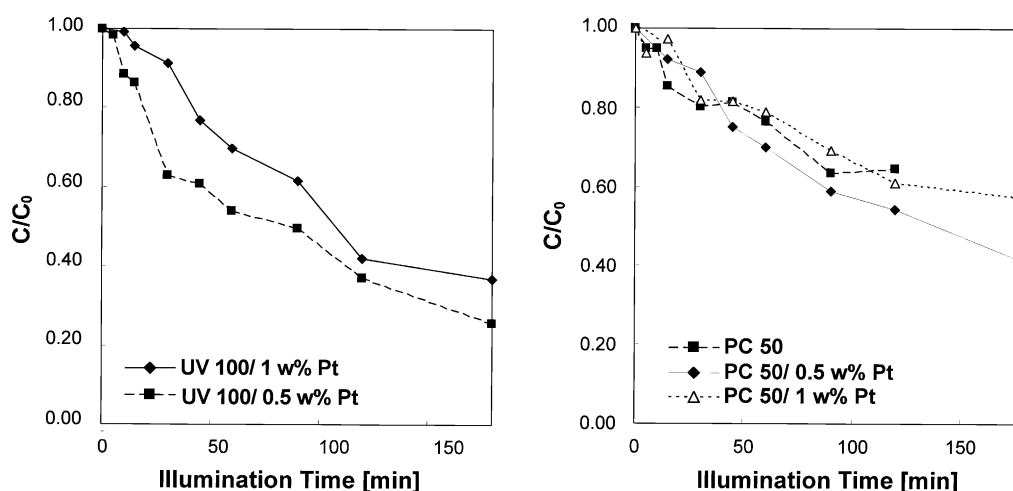


Fig. 5. Disappearance of EDTA with platinised TiO₂-catalysts in comparison to unmodified samples at pH 3.

Table 2
Photonic Efficiencies for the total mineralisation of 4-CP by platinised and unmodified TiO₂ materials

Catalyst	ζ_0 (%) at pH 3	ζ_0 (%) at pH 9
P25/1 wt.% Pt	0.87	0.86
P25/0.5 wt.% Pt	0.68	1.18
P25	1.10	–
UV100/1 wt.% Pt	0.67	0.81
UV100/0.5 wt.% Pt	0.56	0.72
UV100	0.40	–
PC50/0.5 wt.% Pt	1.14	0.98
PC50	0.82	–

Table 2 shows the relevant photonic efficiencies for total mineralisation.

Degradation experiments of EDTA with the platinised samples were only performed at pH 3. With UV100 and PC50, an increase of the rate of EDTA depletion (see Fig. 5) was observed, while for platinised P25 samples a decreased activity could be seen, which can be explained by the strong sedimentation of these materials as observed in DCA and

4-CP experiments. With all materials, the less platinised (0.5 wt.% Pt) samples were the most active.

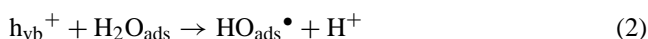
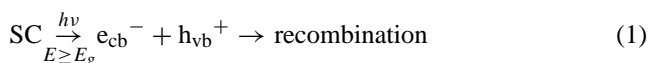
Although the used photocatalysts showed good results for the disappearance of EDTA, TOC results showed a low degree of mineralisation after 3 h, in accordance with previous results [22,23]. As the disappearance of the model compound was not investigated the photonic efficiencies are not given here.

4. Discussion

The results of the degradation experiments with the new prepared catalysts show that there are strong differences among the different TiO₂ materials, including the effect of platinisation. The photocatalytic activity of the unmodified TiO₂ materials can be related to their different physicochemical properties. As the samples have been prepared by different methods, they exhibit different degree of crystallinity and surface properties. For example, Hombikat UV100 has an approximately six times higher BET-surface area than P25

and PC50, implying that many more organic molecules can be adsorbed onto its surface. This was confirmed by DCA adsorption measurements (Fig. 2). As expected, the adsorption of the highly polar DCA molecule was higher than that of 4-CP. This result applies for all catalysts.

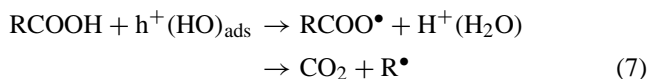
Hombikat UV100 consists of pure anatase, and its very small particles (5 nm) exhibit a very high porosity; therefore, the level of crystallinity of this material cannot be very high. PC50 shows larger particle sizes (20–30 nm), a very low porosity and thus a much lower surface area than UV100. P25 has nearly no pores, a surface area comparable to that of PC50, and consist of ca. 30% of the thermodynamically stable rutile modification. Consequently, the TiO₂-catalysts exhibit either a low crystallinity and a high surface area or the opposite. As the photocatalytic activity depends on the bulk and surface properties of TiO₂, some conclusions can be extracted. It can be proposed that a high crystallinity enhances mainly the lifetime of electron–hole pairs in the semiconductor, whereas a high surface area increases the adsorption of the pollutant on the catalyst. The generally accepted first steps in photocatalytic processes are



where SC stands for semiconductor and D and A for donors and acceptors, respectively.

Reaction (5) is indicated to occur with the reagents adsorbed on the surface, but it can take place also in the bulk of the solution (see later).

For carboxylic acids such as DCA or EDTA, the anodic process leads to rapid CO₂ liberation and the formation of the corresponding decomposition products. The anodic process can be viewed as the attack by holes or hydroxyl radicals forming initially a carboxylate radical, which readily decomposes irreversibly liberating CO₂



In the presence of molecular oxygen, the cathodic process will be the O₂ reduction by conduction band electrons, which can also result in the formation of hydroxyl radicals, also contributing to the degradation of the carboxylic acid:

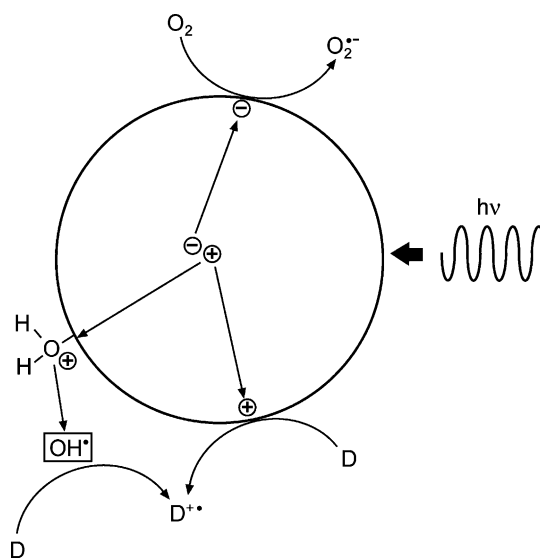
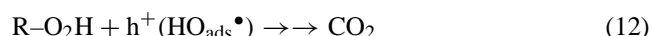
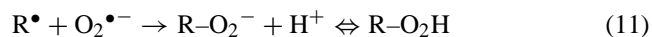


Fig. 6. Basic mechanisms of the photocatalytic oxidation at semiconductors: direct oxidation of adsorbed organic molecule; oxidation of H₂O molecules and formation of hydroxyl radicals.

More probable than this multi-electron transfer process is the direct reaction of O₂^{•-} with organic pollutants forming peroxides (reaction 11), which results subsequently in total oxidation.



Oxidation by holes (reaction 4) is favoured for molecules that adsorb easily on the photocatalyst. On the other hand, HO[•] are able either to react in the interface or to diffuse away from the semiconductor particle (reaction 5), thereby reacting with organic molecules in solution (Fig. 6). Which one of these mechanisms is mainly taking place seems to depend strongly on the nature and properties of the TiO₂-catalyst. This is also affected by the chemical properties of the pollutant and, consequently, some conclusions on the reaction pathway can be extracted from the behaviour of a model compound with the different materials. The rate of oxidation by holes or by HO[•] on the surface will be strongly influenced by the adsorption, but, if reaction occurs by HO[•] in solution, molecules that hardly or not at all adsorb on the TiO₂ surface can be also oxidised.

Adsorption on the highly polar TiO₂ surface is mainly favoured for polar molecules like DCA or EDTA, so that a high surface area should enhance the photodegradation. This occurred in the case of Hombikat UV100, which exhibited very good results, especially for DCA mineralisation. Also for the disappearance of EDTA unmodified Hombikat UV100 shows the highest activity compared to P25 and PC50 (Fig. 5).

The much less polar 4-CP will present a much lower adsorption density, and then the photodegradation of this com-

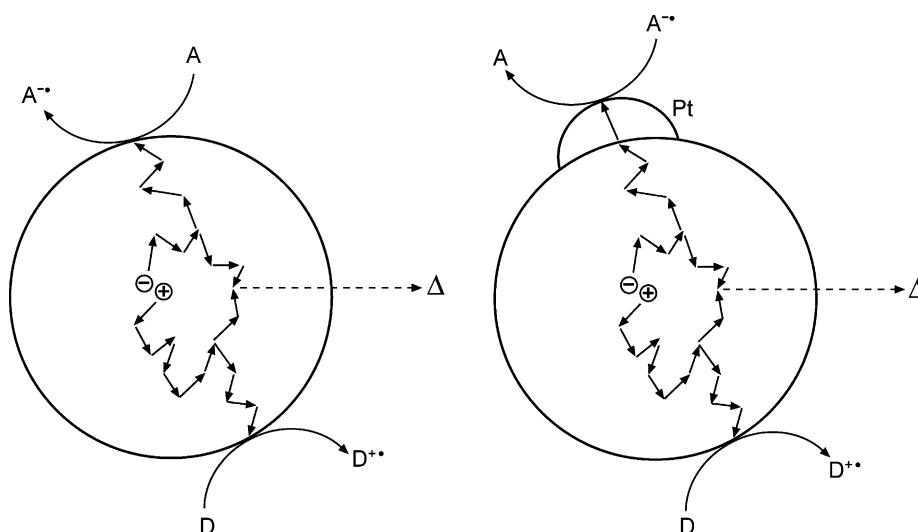


Fig. 7. The fate of electron–hole pairs in unmodified and platinumised semiconductors: diffusion of the charge carriers to the surface, recombination will lead to production of heat before trapping at the surface by acceptors and donors.

pond will be more dependent of the production of HO^\bullet radicals and their reaction in the bulk of the solution. As in aqueous solution there are always water molecules adsorbed on the surface of the photocatalyst, the rate of the formation of HO^\bullet radicals will be independent of the BET-surface area, and only dependent on the number of electron–hole pairs. However, electron–hole pairs must also have average lifetimes long enough to diffuse to the surface. This can be helped by strong irradiation intensity or by a strong absorption of photons, both factors increasing the number of charge carriers. On the other hand, the lifetime of electron–hole pairs can be affected also by the number of recombination centres in the bulk of the semiconductor, such as impurities or structural defects in the crystal phase, a high number of them increasing the probability of recombination [1] (Fig. 7).

Therefore, a highly crystalline photocatalyst and/or a high absorption of light will produce a high number of HO^\bullet , explaining the high efficiencies of P25 and PC50, which are relatively independent of the nature of the substrate to be oxidised.

On the other hand, platinisation increased the photocatalytic efficiency in all cases, no matter were the type of catalyst and the type of substrate. The slightly enhanced adsorption of DCA and 4-CP on the platinumised samples (probably the same effect can be observed the case of EDTA) is not sufficient to explain the strongly enhanced activity. Results of diffuse reflectance spectra of platinumised samples show neither an increase of absorption in the UV region nor a shift in the band gap. Based on results of diffuse reflectance spectra, an enhanced absorption in the UV region or a shift in the

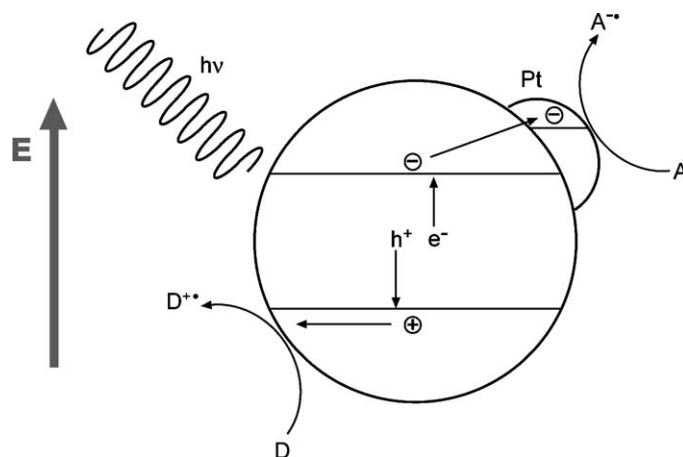


Fig. 8. Trapping of electrons from the semiconductor conduction band by platinum islands due to the Schottky barrier at the metal–semiconductor interface and thus reduced recombination of charge carriers.

band gap due to platinisation can be excluded. Therefore, an enhancement of the photoactivity by these effects must also be excluded.

Deposits of platinum and other noble metals enhance the separation of the electron–hole pairs in a semiconductor. Platinum islands are very effective traps for the electrons due to the formation of a Schottky barrier at the metal–semiconductor contact [5] (Fig. 8). As previously described [12], the enhancing effect of the platinisation can be very well explained by the increase of the rate of the cathodic reaction 8. Generally, in oxidative photocatalytic reactions in the presence of molecular oxygen, the reductive cathodic process of reduction by cb electrons forming superoxide radical appears to be the limiting step. Pt islands can be beneficial by reducing the overpotential for transfer of electrons to molecular oxygen and all the subsequent oxidative reactions. This effect will apply to direct oxidation of the organic compounds by holes as well as to reactions with HO• (either adsorbed or in the solution bulk), i.e., to the three substrates analysed in this work (Fig. 6).

Summarising, the main enhancing effect of the platinisation seems to be a higher rate of production of oxidising species, holes or HO• radicals. These effects are independent of the adsorption and directly proportional to the number of charge carriers produced in the bulk and diffusing to the surface. Based on this, the high reactivity of P25 and PC50 samples for 4-CP could be explained because these two catalysts seem to exhibit a high production rate of oxidising species, especially HO• radicals, which are further enhanced by platinisation. Hombikat UV100 shows very good results for DCA and EDTA, which are much more polar and will adsorb much stronger.

It has been frequently reported [13] that there is an optimum amount of platinum to increase the photocatalytic efficiency of a semiconductor. Our results indicate that this optimum is dependent of the nature of the pollutant. Both, DCA and 4-CP, could be degraded with the highest efficiencies using 1 wt.% Pt samples, while with EDTA the optimum quantity of platinum is 0.5 wt.%. As these results were general for all catalysts, the differences can be attributed to the different chemical nature of the compound and to the reaction pathway. To verify this assumption, deeper investigations on the initial photocatalytic step and on the elucidation of intermediates in the presence of platinised catalysts must be undertaken.

5. Conclusions

In the present work, an enhancement of the photocatalytic activity of TiO₂ materials by deposition of platinum have been achieved. This has been observed for the degradation of three different model compounds. The efficiencies strongly vary with the type of employed catalyst. These differences can be explained in part considering the two possible alternative photocatalytic mechanisms, i.e., direct oxidation by

holes or by HO• radicals. The direct oxidation seems to apply mainly to high surface catalysts like Hombikat UV100, which shows a high activity for very polar substances. For P25 and PC50, presenting a much lower surface area, an enhanced formation of HO• radicals could be suggested, the adsorption of the substrate onto the catalyst surface having a lower influence. This would explain the good efficiency of these two materials for less polar compounds like 4-CP.

Deposits of platinum on the surface would enhance the separation of charge carriers in the bulk of the photocatalyst, due to the formation of a Schottky barrier, thereby increasing the lifetime of electron–hole pairs and the rate of the limiting cathodic step, i.e., reduction of O₂ by conduction band electrons. Based on results of diffuse reflectance spectra, an enhanced absorption in the UV region or a shift in the band gap due to platinisation can be excluded. As there is no relationship between the enhancement of the photocatalytic activity and the adsorption data for the different compounds here analysed, it could be assumed that platinisation is mainly increasing separation of electrons and holes, the formation of HO• radicals, and the rate of oxygen reduction, which is the limiting step of the oxidation reactions. On the other hand under conditions where the production of charge carriers is not the limiting factor of the reaction it could be expected that platinised photocatalysts will show a dependence of their physical properties. This would be achieved in experiments using high intensities of UV light and only very low concentrations of pollutant.

In addition, an optimum amount of platinum must be found. Results for EDTA show that this optimum will be influenced by the pollutant itself, but this must be confirmed and explained by investigation on the reaction pathways and identification of the intermediates.

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