

Heterogeneous photocatalytic reactions comparing TiO₂ and Pt/TiO₂

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Abstract

Two commercial samples, namely Degussa P-25 and Sachtleben Hombikat UV 100, and platinized modifications of these samples have been tested comparatively as photocatalysts for EDTA oxidation and for Cr(VI) reduction in the absence and in the presence of EDTA. Platinized photocatalysts were prepared by photoimpregnation of H₂PtCl₆ on TiO₂ by prolonged irradiation in the presence of methanol. Only slight differences in efficiency were found between both pure commercial forms, except for the Cr(VI) reduction in the presence of EDTA, where Hombikat UV 100 samples were more active. Platinized Hombikat UV 100 was found to be less active for Cr(VI) reduction in water. The concentration of dissolved molecular oxygen was crucial for EDTA oxidation and had no influence on Cr(VI) reduction. From kinetic profiles, initial photonic efficiencies (ζ) and conversion degrees have been calculated. Platinization did not improve Cr(VI) reduction but increased the initial photonic efficiency for EDTA oxidation. However, after prolonged irradiation, the conversion of EDTA was lower employing platinized samples instead of pure samples. The effect of platinum on titania was analyzed on the basis of proposed mechanisms. © 2002 Published by Elsevier Science B.V.

Keywords: Heterogeneous photocatalysis; TiO₂; Platinized TiO₂; EDTA; Cr(VI)

1. Introduction

The improvement of the photocatalytic activity of TiO₂ is one of the most important aspects of heterogeneous photocatalysis. The activity of TiO₂ depends generally on intrinsic bulk and surface properties of the samples as well as on the nature of the photocatalytic reaction [1]. Attempts to increase the TiO₂ efficiency have been made by doping and coating with transition or noble metals [2], by modification with other semiconductors or by covering the surface with dyes to increase the optical absorption in the visible range [3]. In particular, the addition of platinum to TiO₂ particles has been shown to enhance particularly the photocatalytic production of molecular hydrogen from H₂O splitting [4,5]; in other reactions, the efficiency seems to be highly dependent of the nature of the substrate to be transformed [6–8].

The usual methods for modification of TiO₂ with platinum or other noble metals are thermal impregnation and photodeposition (see e.g. [9–11] and references therein) and, in most of the reported cases, the latter technique yields more active photocatalysts [5,12]. The photodeposition process involves the reduction of metal ions by conduction band electrons, the anodic process being the oxidation of water by valence band holes [13]. Oxidisable additives (sacrificial electron donors) such as acetate, formaldehyde, methanol, or 2-propanol are generally added to improve the rate of photodeposition [9].

Cr(VI) and EDTA are environmentally important pollutants in waters. EDTA is a contaminant of industrial and domestic wastewaters, owing to its extensive use in detergents, fertilizers, herbicides, etc. It is also used in cleaning mixtures of boilers and components of nuclear reactors, and it is a common sacrificial agent in photoelectrochemical systems. EDTA is not easily biodegradable [14], scarcely degradable by chlorine, and its elimination has been attempted with activated carbon filters, ozonation and UV/H₂O₂ (see [15] and references therein), with variable results. The mechanisms associated to the photocatalytic EDTA degradation have not been yet completely elucidated [16–19]. Cr(VI) is a toxic, carcinogenic and mobile contaminant originating from in-

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dustrial processes such as electroplating, pigment production, leather tanning, or paint manufacture. Its concentration in drinking waters has been regulated in many countries. By reduction to Cr(III), the Cr(VI) toxicity is decreased, and precipitation in alkaline medium allows its easy separation from the waters. The photocatalytic reduction of Cr(VI) with different semiconductors has been widely studied (see [9] and references therein). The Cr(VI)/EDTA mixed system is of interest because the addition of an electron donor facilitates the heterogeneous photocatalytic Cr(VI) reduction [20,21]. In addition, this system can be taken as model for real wastewaters where oxidants and reductants are frequently present together. In previous papers, some of us have reported aspects of the heterogeneous photocatalytic reactions of EDTA oxidation and Cr(VI) reduction in the absence and in the presence of EDTA using TiO₂ Degussa P-25 (P-25) and other semiconductors as photocatalysts [22–27].

In this work, comparative photocatalytic studies on the same systems over P-25, Hombikat UV 100 (UV 100) and the respective platinized samples prepared in the laboratory are presented. The efficiency of the titania samples related to the nature of the particular photocatalytic reaction is discussed.

2. Experimental section

Degussa P-25 and Sachtleben Hombikat UV 100 were commercial samples, gently supplied by the manufacturers and used as provided. Platinized catalysts have been prepared by photoimpregnation according to the following technique. To an aqueous suspension of TiO₂ (5 g dm⁻³) a calculated volume of 1 mM aqueous solution of hexachloroplatinic(IV) acid hexahydrate (Merck, 40% Pt) was added, followed by the addition of methanol (at a 500:1 methanol to H₂PtCl₆ molar ratio). The suspension was irradiated with a 500 W mercury high-pressure immersion lamp (Heraeus TQ718 Z-4) for 6 h under vigorous stirring. After irradiation, the samples were washed twice with water, centrifuged, dried at moderate temperature (60–70 °C) for 16 h and carefully grinded. Two samples, i.e., a 0.5 wt.% Pt containing Degussa P-25 (Pt/P-25) and a 0.2 wt.% Pt containing Hombikat (Pt/UV 100) were chosen for the photocatalytic experiments. The platinum content of the samples was determined by ICP/MS analysis, using a FISONS Plasma Quad II+ instrument. Specific surface areas of the samples (*S*_{BET}) were obtained with an automatic system (Micromeritics FlowSorb II 2300) with nitrogen gas as adsorbate at the liquid nitrogen temperature.

Na₂EDTA and K₂Cr₂O₇ (Carlo Erba) were of quality grade and used as provided. All other reagents were at least of reagent grade and used without further purification. Water was double distilled in a quartz apparatus. Diluted HClO₄ was used for pH adjustments.

Photocatalytic irradiations were performed using a high-pressure xenon arc lamp (Osram XBO, 150 W). The

photocatalytic runs were carried out in a thermostatted cylindrical cell (125 cm³ of capacity) irradiated from the top. The cell was provided with a Teflon cap with a gas inlet, a sampler and a holder for a bandpass filter (Schott BG 1, thickness 3 mm; 270 nm < λ < 510 nm; maximum transmission (87%) at 360 nm). The IR fraction of the incident light was removed by another suitable filter (Schott KG 5).

Actinometric measurements were performed by the ferrioxalate method [28], using 10 cm³ of actinometric solution to keep the same conditions as in the photocatalytic experiments. A photon flow per unit volume of $1.0 \times 10^{-5} \pm 0.1 \times 10^{-5}$ einstein dm⁻³ s⁻¹ was calculated.

UV–visible absorption measurements were performed employing a Shimadzu 210A spectrophotometer. For all photocatalytic runs, a fresh solution (10 cm³) of the substrate at a known concentration was adjusted to pH 3, and the catalyst was suspended at a 1.0 g dm⁻³ concentration. Prior to irradiation, suspensions were kept in the dark and magnetically stirred at 25 °C for a time sufficient to assure substrate–surface equilibrium. The concentration of the substrate after equilibration was taken as the initial concentration (*C*₀) to account for the dark adsorption and to evaluate only changes due to irradiation.

Irradiation for a fixed period of time was performed at 25 °C under magnetic stirring. Samples were periodically withdrawn for quantitative analysis and filtered through a 0.22 μm Millipore filter. At least, duplicated runs were carried out for each condition, averaging the results.

The oxidative degradation of EDTA was performed at an initial concentration of 3.0 mmol dm⁻³ with molecular oxygen bubbling (water-saturated, volumetric flux: 1.4 cm³ s⁻¹). Suspensions were stirred in the dark for 30 min before irradiation. EDTA concentration was evaluated by spectrophotometric analysis with 2,4,6-tripyridyl-s-triazine (TPTZ) at 593 nm [29]. No EDTA degradation was observed in the absence of the photocatalyst.

For Cr(VI) experiments, 0.4 mmol dm⁻³ K₂Cr₂O₇ solutions were used and the suspensions were stirred for 25 min before irradiation. Experiments were performed with the cell open to air or under nitrogen bubbling (2.0 cm³ s⁻¹). Changes in Cr(VI) concentration were followed by UV spectrophotometry at 349 nm [30]. Similar experiments were repeated in the presence of 1.0 mmol dm⁻³ EDTA.

In order to study the photostability of the Pt/TiO₂ materials, the presence of platinum in the filtered solution after irradiation was evaluated by a spectrophotometric method [31].

3. Results

3.1. Properties of the photocatalysts

Table 1 shows some differential properties of photocatalyst samples. It is interesting to note that the *S*_{BET} areas are ca. 5 times higher for UV 100 samples compared with P-25

Table 1
Some properties of the photocatalyst samples

	Sample	
	Hombikat UV 100	Degussa P-25
Phases	Anatase	Anatase 80%, rutile 20%
BET ($\text{m}^2 \text{g}^{-1}$)	290, 268 ^a	49, 45 ^a
Porosity	Mesopores, $\phi = 5.6 \text{ nm}$	Non-porous
Primary crystal size (nm)	≈ 6	≈ 30

^a After platinization.

samples and that platinization decreases somewhat the specific surface area. Evaluation of other differential properties of the samples by physicochemical techniques (SEM, DRX, etc.) are in progress.

3.2. Photocatalytic reactions

Figs. 1–3 show the results of the photocatalytic experiments employing the four catalysts in the model systems. In the case of EDTA degradation (Fig. 1), the presence of molecular oxygen was found to be crucial for the degradation because in its absence, and as expected, the degradation

was very slow. An increase of pH from 3 to ca. 5–6 at the end of the irradiation (120 min) was observed in all cases. Concentration vs. time profiles exhibit a linear behavior with pure samples, with no significant differences between P-25 and UV 100. In contrast, it can be observed that platinized samples showed higher rates at the early stages of the reaction, but a deceleration occurred at longer irradiation times. This deceleration might be attributed to catalyst deactivation by photocorrosion (Pt dissolution). To test this hypothesis, Pt was evaluated by spectrophotometry, but no Pt was detected in solution.

In the Cr(VI) system in the absence of any electron-donor (Fig. 2), all profiles exhibit a non-linear decelerative behavior. Only small differences in efficiency were found for the different photocatalyst samples, except for Pt/UV 100, which showed a considerably lower activity. Similar results for the photocatalytic Cr(VI) conversion were obtained either in air or under N_2 atmosphere. In this system, only small changes in pH (ca. 0.5 units) were found after 120 min irradiation in all cases. Under no circumstance did platinization of the catalyst result in an enhancement of the Cr(VI) reduction efficiency. No Pt was detected in solution after irradiation.

In the presence of EDTA (Fig. 3), a significant increase of the rate of the photocatalytic Cr(VI) reduction was observed,

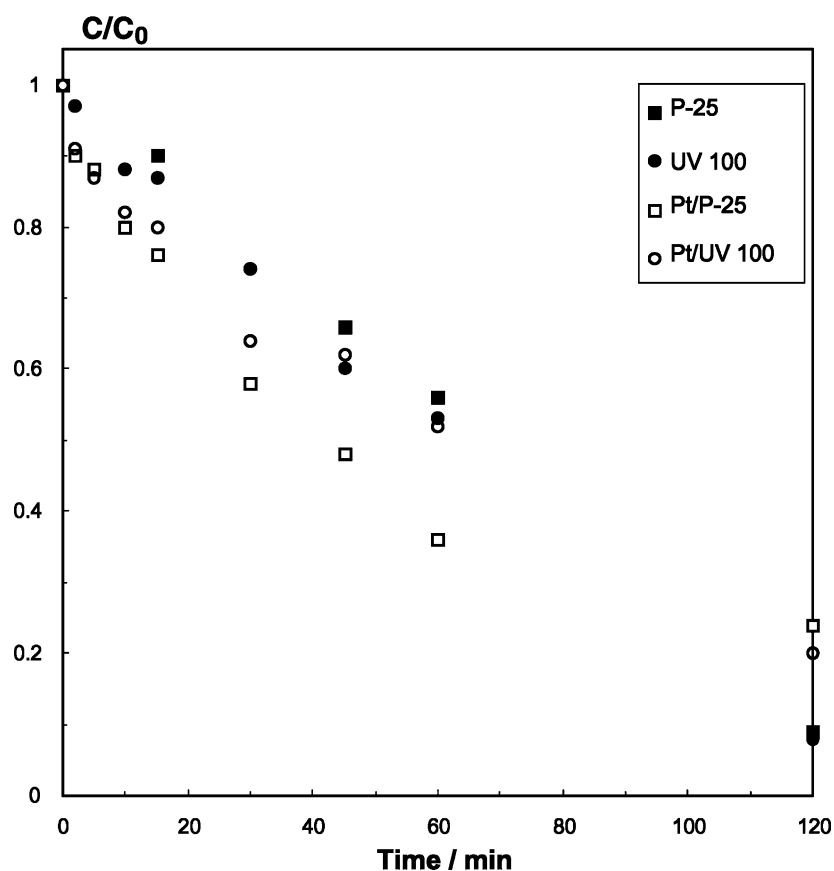


Fig. 1. Normalized concentration vs. time for EDTA oxidation over different catalysts. Conditions: $[\text{EDTA}] = 3.0 \text{ mmol dm}^{-3}$; pH 3; $[\text{catalyst}] = 1 \text{ g dm}^{-3}$; $T = 25^\circ \text{C}$; O_2 bubbling; $P_0 = 1.0 \times 10^{-5} \text{ einstein dm}^{-3} \text{ s}^{-1}$; $270 \text{ nm} < \lambda < 510 \text{ nm}$.

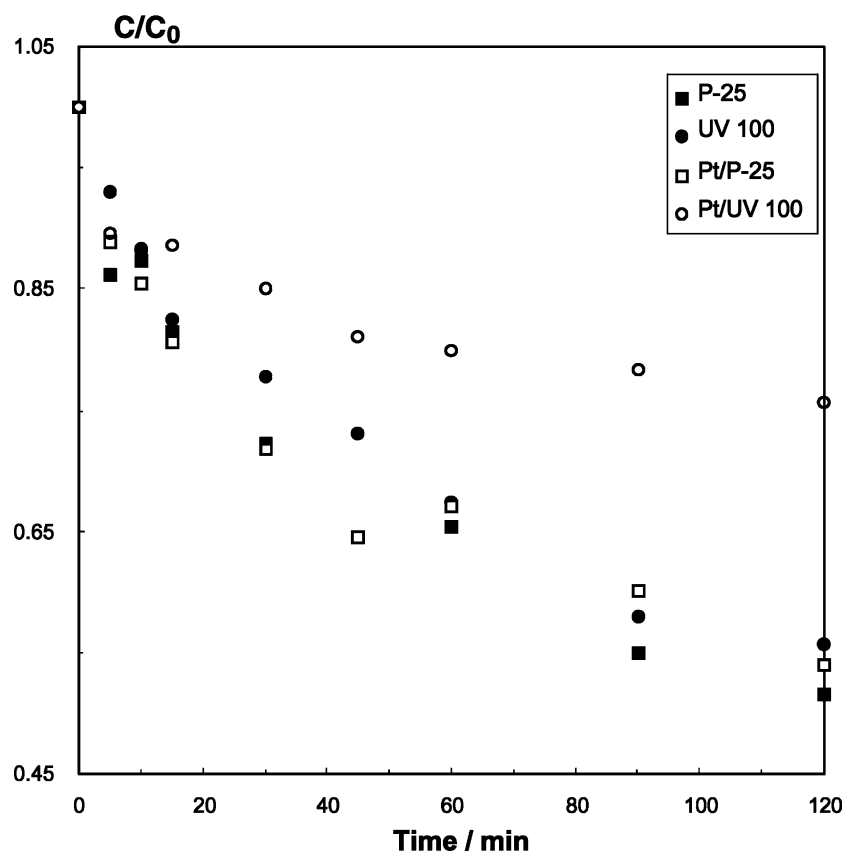


Fig. 2. Normalized concentration vs. time for Cr(VI) reduction over different catalysts. Conditions: $[\text{K}_2\text{Cr}_2\text{O}_7] = 0.4 \text{ mmol dm}^{-3}$; $[\text{catalyst}] = 1 \text{ g dm}^{-3}$; pH 3; $T = 25^\circ\text{C}$; open to air; $P_0 = 1.0 \times 10^{-5} \text{ einstein dm}^{-3} \text{ s}^{-1}$; $270 \text{ nm} < \lambda < 510 \text{ nm}$. Similar results were obtained under nitrogen.

again with similar results in air and under N_2 atmosphere. In this system, both pure and platinized UV 100 samples were found to be the most active photocatalysts, achieving a complete Cr(VI) conversion in less than 50 min. At the end of the irradiation, important changes in pH were noted from 3 to ca. 6–7.

Initial photonic efficiencies ($\zeta\%$) have been calculated for all the systems according to:

$$\zeta = \frac{(-dC/dt)_{t=0}}{P_0} \times 100 \quad (1)$$

where $(-dC/dt)_{t=0}$ is the initial reaction rate and P_0 the incident photonic flow per unit volume. The respective results are presented in Table 2. Although photonic efficiencies are affected by rather large errors due to the imprecision of the analytical measurements at the initial stages of the reaction, especially for the Cr(VI) system under the absence of EDTA, this parameter allows the comparison of the intrinsic activity of all samples under similar conditions (substrate and oxide concentration, geometry, incident light intensity), independent of any deactivation, inhibition or other secondary effect that may occur at prolonged irradiation times. According to these results, it can be concluded that there are no significant differences in initial photonic efficiencies between P-25 and UV 100 for all photocatalytic systems studied here. There is

no variation in efficiency for Cr(VI) reduction when the reaction is performed under nitrogen or in air, but ca. fivefold increase of ζ is observed when EDTA is present. Higher initial photonic efficiencies (around 3–4 times) were calculated from the results shown in Fig. 1 for the EDTA oxidation over platinized TiO_2 in comparison with those values obtained for the pure samples. In contrast, platinization did not alter ζ for the Cr(VI) reduction, except for a slightly lower value obtained in the case of Pt/UV 100 in the absence of EDTA.

On the other hand, the degree of substrate conversion after fixed periods of irradiation is presented in Table 3.

Table 2
Initial photonic efficiencies for the different catalysts in the studied systems ($\zeta\%$)

Photocatalyst	EDTA oxidation (under O_2)	Cr(VI) reduction		Cr(VI) reduction with EDTA (air or N_2)
		Air	N_2	
P-25	3.6	1.2	1.5	5.2
UV 100	3.7	1.1	1.1	4.6
Pt/P-25	12	1.4	1.4	5.9
Pt/UV 100	16	0.7	0.6	5.0

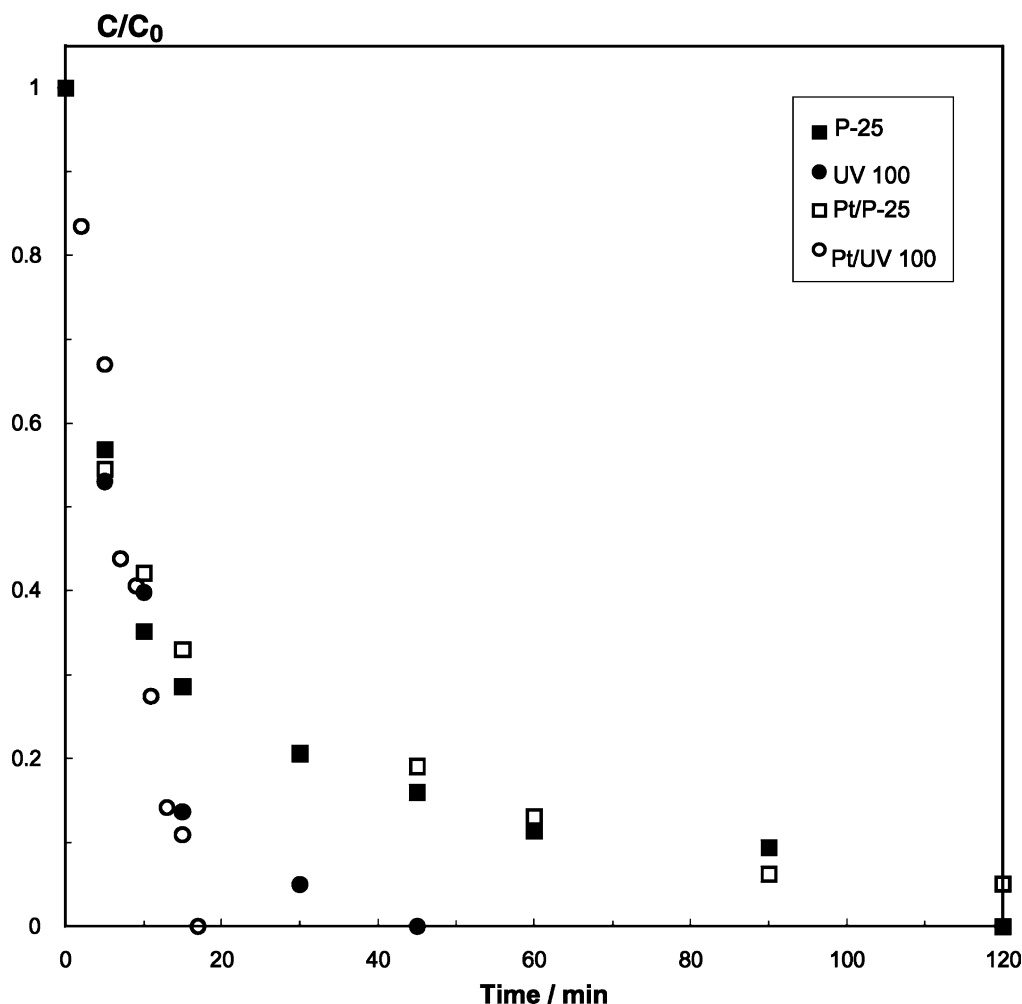


Fig. 3. Normalized concentration vs. time for Cr(VI) reduction in the presence of EDTA over different catalysts. Conditions: $[\text{K}_2\text{Cr}_2\text{O}_7] = 0.4 \text{ mmol dm}^{-3}$; $[\text{EDTA}] = 1.0 \text{ mmol dm}^{-3}$; $[\text{catalyst}] = 1.0 \text{ g dm}^{-3}$; pH 3; $T = 25^\circ\text{C}$; $P_0 = 1.0 \times 10^{-5} \text{ einstein dm}^{-3} \text{ s}^{-1}$; $270 \text{ nm} < \lambda < 510 \text{ nm}$. Similar results were obtained under nitrogen.

These data, crucial for real applications, show that final conversions were lower for EDTA oxidation over platinized samples in comparison with those obtained for the pure catalysts, in spite of higher ζ values in the former case. Only negligible differences among the samples were observed for the Cr(VI) reduction in the absence of EDTA (either aerated or deaerated), with the exception of Pt/UV 100, which showed the smallest extent of conversion. In the presence

of EDTA, Cr(VI) was totally reduced within 2 h with all the employed catalysts, but UV 100 samples presented the highest conversion (15 min for total conversion with Pt/UV 100 and 45 min with UV 100, respectively).

The amount of Pt (0.2 or 0.5 wt.%) in the samples did not seem to influence the activity. Similar results have been observed in other photocatalytic systems up to 1 wt.% platinum loading [5,7,12].

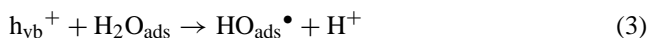
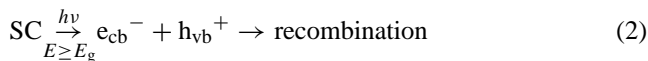
Table 3
Substrate conversion after 60 and 120 min irradiation time

Photocatalyst	EDTA oxidation (under O_2) 120 min (%)	Cr(VI) reduction 120 min		Cr(VI) reduction with EDTA (air or N_2)	
		Air (%)	N_2 (%)	120 min (%)	60 min (%)
P-25	91	48	51	100	89
UV 100	92	44	42	100	100
Pt/P-25	76	46	45	95	87
Pt/UV 100	80	22	23	100	100

4. Discussion

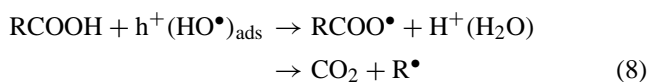
4.1. Proposed mechanisms

The generally accepted first steps in photocatalytic processes are:



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

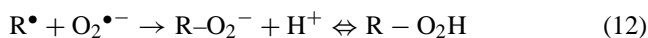
For oligocarboxylic acids such as EDTA, the anodic process leads to rapid CO₂ liberation and the formation of the corresponding decomposition products. The anodic process can be viewed as the attack by holes or hydroxyl radicals forming initially a carboxylate radical, which readily decomposes irreversibly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



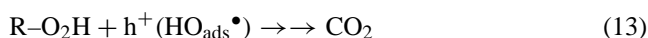
In the presence of molecular oxygen, the cathodic process will be the O₂ reduction by conduction band electrons, which in principle can also result in the formation of hydroxyl radicals, which would then also contribute to the EDTA degradation:



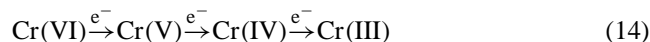
However, such multistep electron transfer processes are rather unlikely in particulate photocatalytic systems where the absorption of a subsequent photon by the same photocatalyst particle will only take place with a delay of several microseconds under ordinary irradiation conditions [32]. Much more likely is the subsequent reaction of O₂^{•−} formed in reaction (9) with R[•] (formed in reaction (8)) [33]:



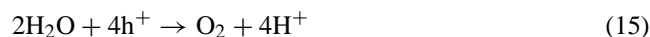
Subsequent oxidation of the peroxides formed in (12) will then result in the complete oxidation of the pollutant molecule:



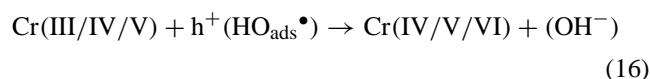
Cr(VI) reduction occurs probably via three subsequent one-electron transfer processes [9,22]:



The anodic process could in principle be the final oxidation of water by holes, with the final oxidation to oxygen:



However, as soon as reduced chromium species will be present on the surface of the photocatalytic particle, its competitive oxidation via:



will be a very likely alternative to the rarely observed formation of molecular oxygen from water. Electron shuttle mechanisms similar to the sequence (14), (16) have been reported previously in the case of Fe(III)/Fe(II) [34] and hydroquinone/benzoquinone [35] always resulting in an undesired electron/hole recombination and thus a reduced photonic efficiency (cf. Fig. 2). The non-linear kinetic behavior, i.e., deceleration, can be attributed also to the inhibitory adsorption of Cr(III) produced by reduction [22,23].

Cr(VI) reduction in the presence of EDTA occurs by cooperative action of reactions (8) and (14), with reaction (14) competing effectively with reaction (16). Therefore, the electron shuttle mechanism can be suppressed, resulting in a faster Cr(VI) reduction (see [9] and references therein).

4.2. Initial photonic efficiencies and final conversions

When comparing the pure photocatalysts, our results indicate almost identical initial efficiencies for Degussa P-25 and Sachtleben Hombikat UV 100 in the three systems tested (Table 2), in spite of the varying differential properties presented in Table 1. The initial efficiency of a photocatalyst, as already mentioned, will generally be dependent on the bulk and surface properties of the material, arising from the preparation technique, on the chemical history of the sample and on the nature of the photocatalytic reaction. In the case of P-25 (the most widely used photocatalyst) and UV 100, different results have been obtained depending on the substrate to be transformed. For example, higher photonic efficiencies have been found for the model pollutant dichloroacetic acid (DCA) oxidation with UV 100 but for 4-chlorophenol the discrepancies with P-25 were relatively small [6,7]. Even the amount of the catalyst can be very important, i.e., it has been observed during the photocatalytic degradation of DCA that while P-25 reaches its maximum efficiency already at a concentration of 0.5 g dm^{−3}, the rate of DCA oxidation in the presence of UV 100 still increases even beyond 10 g dm^{−3} [6,7,36].

To explain the effect of platinum on titania, the model depicted in Fig. 4 must be considered. When platinum

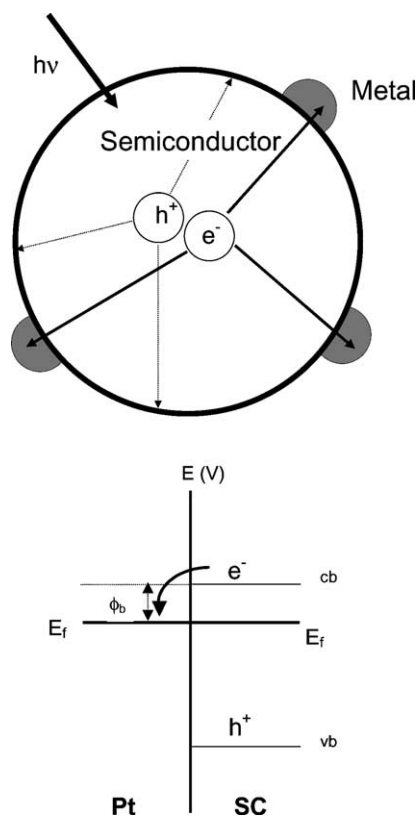


Fig. 4. Schematic diagram for a Pt-modified semiconductor showing the flow of cb electrons from the SC to the metal. ϕ_b , Schottky barrier.

islands are deposited on the surface of a semiconductor particle, a Schottky barrier (ϕ_b) between the metal and the SC is formed, while both metal and semiconductor Fermi levels equilibrate. Upon irradiation, the cb electrons flow from the SC to the metal, i.e. to a Pt site. Thus, the Schottky barrier acts as an efficient electron trap that decreases the recombination rate [4]. It has, e.g., been found that platinization enhances the rate of the photocatalytic cyanide oxidation [8] as well as the initial photonic efficiency for DCA oxidation [6,7]. However, it has almost no effect on the 4-chlorophenol degradation compared with pure TiO₂ [6,7]. According to the mechanisms proposed above and the examples given in the literature, an interpretation of the effect of platinization in each system studied here can be postulated, which is depicted in Fig. 5.

Let us first examine the case of EDTA (Fig. 5a). Valence band holes may directly oxidize water (Eqs. (3) and (4)) or the organic compound (Eq. (8)), the latter process being favored due to its irreversibility and a less positive one-electron redox potential. When molecular oxygen is present, the reductive process, i.e. its reduction by cb electrons (Eq. (9)) appears to be the limiting reaction. For this reason, the amount of oxygen dissolved in this system is crucial, and Pt can be beneficial by reducing the overpotential for electron transfer to molecular oxygen, at least in the early stages of the process. A similar argument was proposed to explain the different activities of TiO₂ and Pt/TiO₂ for the oxidation

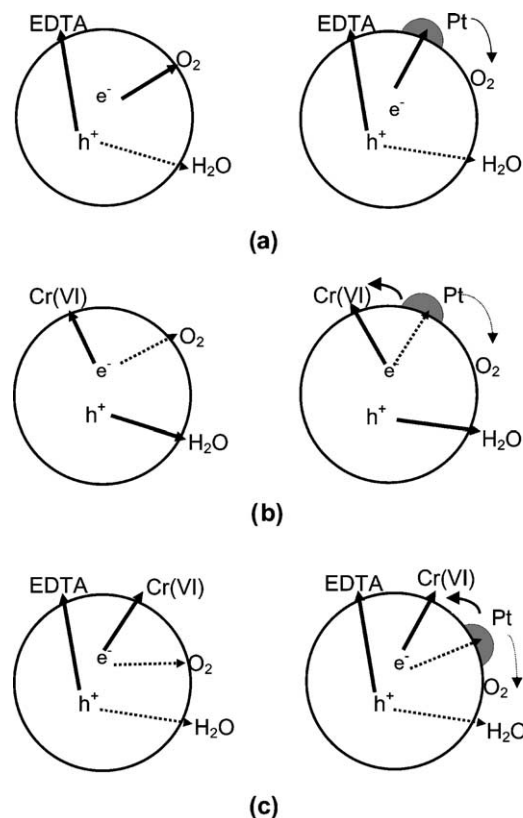


Fig. 5. Influence of platinum in the different photocatalytic systems: (a) EDTA oxidation; (b) Cr(VI) reduction; (c) Cr(VI) reduction in the presence of EDTA.

of Pb(II) [9,37]. In addition, reaction (9) will finally also lead to the formation of HO[•], which in turn contribute to enhance EDTA oxidation. Molecular oxygen probably also acts as a reagent for the intermediate radicals formed according to Eq. (8). An analogous example is the enhancing effect of platinization observed in the photocatalytic water reduction to hydrogen over rutile in the presence of EDTA, an otherwise thermodynamically rather unfavorable process [5]. In this case, it has been proposed that the accumulation of conduction band electrons at a Pt site, improved by the irreversible nature of the EDTA oxidation, may contribute towards the shift in V_{fb} , reducing the overpotential for H₂ formation and rendering hydrogen reduction thermodynamically more favorable. In conclusion, platinization of titania should help EDTA oxidation, which is, in fact, in good agreement with our observations, at the initial stages of the reaction (cf. Fig. 1). However, at longer irradiation times, the reaction is decelerated. As deactivation of the catalyst by photocorrosion (Pt dissolution) was experimentally not supported, this deceleration may arise from inhibitory products or reaction intermediates competing with EDTA for SC sites; these species can be different from those formed over pure photocatalysts. Experiments to detect intermediate products in the photocatalytic EDTA oxidation are underway. As pH increases with reaction time, the formation of HCO₃⁻ or CO₃²⁻ and their known hole scavenging action [38] should

be also taken into account. Photocorrosion of the catalyst without dissolution, i.e. changes on the textural properties by irradiation, cannot be excluded either.

In the case of Cr(VI) reduction (Fig. 5b), a similar beneficial effect of Pt would be expected, if one considers that Pt reduces the overpotential for electron transfer from the conduction band to molecular oxygen and assumes that $O_2^{\bullet-}$ might be a mediator for the reduction of Cr(VI). In contrast, a competition between molecular oxygen and a transition metal of appropriate redox potential for the cb electrons has been proposed. This competition is also being discussed in the case of Cr(VI), with dissimilar results in the literature [9]. The results of this work show no detrimental effect of the presence of molecular oxygen. Therefore, O_2 can neither be considered a mediator nor a competitive species. Oxidation of water by holes (Eq. (15)), a kinetically sluggish process, may be proposed here as the rate limiting reaction [9]. Therefore, the direct and rapid reduction of the metal cation by cb or Pt trapped electrons [22] can be expected, which explains the similar efficiency of all samples in this system. The low activity of the Pt/UV 100 sample in this reaction remains unclear and may be due to detrimental surface properties which must be investigated.

When EDTA is added (Fig. 5c), Cr(VI) reduction is greatly accelerated with no special differences between pure and platinized samples. Again, no effect of molecular oxygen on the overall reaction has been found and, consequently, no influence of platinization is observed. In this case, Hombikat UV 100 samples (pure and platinized) are found to be very efficient photocatalysts, which may be attributed to the surface properties of the SC related to the special features of the reaction mechanism operative in this mixed system (in study).

In conclusion, platinization does not improve the activity of titania in the systems here studied. Even when an initial higher efficiency is observed (EDTA oxidation), Pt becomes detrimental in the latter stages of the reaction. Only a final remark must be done: photodeposition of platinum can result in different oxidation states (Pt, $Pt(OH)_2$, PtO_2), depending on the conditions of deposition [9]. Additional studies such as the complete characterization of the present samples, including important photocatalytic parameters, e.g., textural properties, isoelectric points (IEPs), or oxidation state of Pt, are in progress. Also, the preparation and characterization of platinized titania by other techniques and the evaluation of the photocatalytic activity with the chemical substrates here investigated and other species will be attempted. However, for technological applications, a compromise between an increased efficiency and the increased cost by Pt addition should always be considered.

5. Conclusions

Pure Degussa P-25 and Sachtleben Hombikat UV 100 photocatalysts have been found similarly effective for the

Cr(VI) reduction and the degradative EDTA oxidation in water. Cr(VI) reduction is greatly enhanced by the presence of EDTA; in this last system, a very high activity is obtained using Hombikat UV 100 samples. Platinization does not seem to improve the performance of the photocatalysts in the present systems. In the Cr(VI) reduction (with or without EDTA), no effect of platinum has been observed, and was explained by a rapid electron transfer of the cb or Pt trapped electrons to chromium, without the participation of molecular oxygen. In the degradative EDTA oxidation, platinum islands provoke an increase of the initial photonic efficiency most likely by a decrease of the overpotential for O_2 reduction (the rate limiting reaction step); however, a deceleration of the oxidation compared to pure samples occurs after prolonged irradiation, probably due to inhibition by products.

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