

Photocatalytic deactivation of commercial TiO₂ samples during simultaneous photoreduction of Cr(VI) and photooxidation of salicylic acid

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Abstract

TiO₂ Degussa P25 and Hombikat UV-100 photocatalysts have been widely characterized. Certain structural and morphological differences have been found. Photocatalytic behaviour has been studied for Cr(VI) reduction and for salicylic acid oxidation, in photoreactions with single and mixed substrates. In the photoreaction with mixed substrates, higher conversion values have been found in comparison to those observed for single substrates. However, clear deactivation process can be noticed. This photocatalytic deactivation is higher for Degussa P25 photocatalyst than for Hombikat UV-100 and can be explained in terms of the surface features exhibited for both TiO₂ during the photoprocesses. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The photochemical degradation of pollutants using semi-conducting powders as catalysts is a subject of current interest [1]. This photocatalytic method is based on the reactive properties of electron–hole pairs generated in the semiconductor particles under illumination by light of energy greater than the semiconductor bandgap. These charge carriers can reach the particle surface and react with species in solution with suitable redox potentials [2,3]. This has been successfully applied to the degradation of organic pollutants [4–8]. Thus, the photocatalytic oxidation of organic compounds in aqueous suspensions of titanium oxide is a comparatively new method for the removal of impurities from water. Less attention has been paid to the catalytic elimination of inorganic compounds. Chromium(VI) is a very toxic pollutant which is present in a great variety of industrial wastes.

Many studies concern only the catalytic activity of titanium oxide with single substrates. There are few papers concerning decontamination of complex systems, which, however, are the actual situation of the real environmental pollution. Many waste streams may contain mixtures of hazardous organic and inorganic species. In fact, laboratory studies of these real mixtures are a complex problem to resolve. Fu et al. [9] reported the simultaneous degrada-

tion of 4-chlorophenol and Cr(VI) in a synergic oxidation–reduction reaction. The spontaneous reaction among these two toxic species under environmental conditions are negligible. But they reported an important increase in the photocatalytic degradation when they are present at the same time.

From the point of view of the photocatalysis theory both oxidation and reduction reactions can take place simultaneously by considering half redox semireactions with the electron–hole pairs photogenerated, avoiding this way the possibility of recombination of these pairs and, therefore, influenced synergically.

In the present paper, we present an interesting comparison study of two commercial TiO₂ for similar simultaneous photocatalytic oxidation–reduction reaction. In our case, we have used salicylic acid and Cr(VI) pollutant species. We have considered this binary system, since they are important industrial pollutant species and their mixture can be found in many waste streams.

2. Experimental section

2.1. Materials

Cr(VI) solution was prepared by using analytical grade K₂Cr₂O₇ (Aldrich, 99%) at acid pH about 1.5–2. H₂SO₄ was used to set the correct pH value. Salicylic acid (Aldrich,

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>99%) was prepared by dissolving the solid in deionized water. Both solutions having concentration of 4×10^{-4} M. For simultaneous degradation runs, solution was prepared by mixing the corresponding volume of each starting solution of single substrates. Therefore, the concentration of the new solution was in this case 2×10^{-4} M on each pollutant. The pH of the resulting solution was ca. 2. Degussa P25 and Hombikat UV100 (Sachtleben chemie) commercial titanium dioxide were employed as received.

All catalytic runs were performed in a Pyrex immersion well reactor. UV-illumination of the reaction solutions were carried out by using a medium pressure 400 W Hg lamp supplied by Applied Photophysics. Oxygen flow was employed in all cases as oxidant and simultaneously to produce a homogenous suspension of the catalyst in the solution. Before each experiment, the catalysts (1 g/l) were settled in suspension with the reagent mixture for 10 min.

The reagents concentrations were measured by means of UV–VIS spectroscopy, and using characteristic 348 and 290 nm bands for salicylic acid and Cr(VI), respectively. About 2 ml of suspension was removed and filtered (Milipore Millex25 0.45 μm membrane filter) previously to UV–VIS spectra.

2.2. Experimental

BET surface area measurements were carried out by N_2 adsorption at 77 K using a Micromeritics 2000 instrument. Pore volume were determined using the cumulative adsorption of nitrogen by the BJH method.

X-ray diffraction (XRD) patterns were obtained using a Siemens D-501 diffractometer with a Ni filter and graphite monochromator. The X-ray source was Cu $\text{K}\alpha$ radiation.

UV–VIS spectra were recorded in the diffuse reflectance mode (R) and transformed to a magnitude proportional to the extinction coefficient (K) through the Kubelka–Munk function, $F(R_\infty)$.

Scanning electron microscopy (SEM) was performed on gold-coated samples using a Jeol apparatus (model JSM-5400) and the dispersion of X-ray was measured with a Link Isis Model analyzer; a semi automatic image analyzer of magnetostrictive Kontron MOP-30 board was used to estimate the average weight size of aggregates and particles.

Infrared spectra were recorded in a FT-IR instrument (Nicolet 510). A resolution of 8 cm^{-1} was used with 256 scans averaged to obtain a spectrum from 4000 to 400 cm^{-1} . Samples were presented in pellets diluted in dried KBr for the analysis.

The XPS study was carried out on a Leybold–Heraeus LHS-10 spectrometer, working with a constant pass energy of 50 keV; Mg $\text{K}\alpha$ radiation was used for excitation ($h\nu = 1253.6 \text{ eV}$). A final pressure of 10^{-9} Torr was always attained before XPS recording. C(1s) signal (284.6 eV) was used as internal reference in all experiments.

3. Results and discussions

3.1. Structure and texture of catalysts

Specific surface areas of as received commercial titanium dioxide samples were determined by means of BET method. Adsorption–desorption isotherm plots of TiO_2 Degussa P25 and Hombikat UV-100 are shown in Fig. 1. In both cases, isotherms could be assigned to type II though a small hysteresis loop can be found. TiO_2 Hombikat presents an intermediate shape between types II and IV, with hysteresis loop of namely type H4 [10]. In Fig. 2, we represent the pore distribution for the two catalysts. From this plot, it can be seen a great difference in the pore texture of both oxides. Thus, Degussa P25 presents a small characteristic pore family in the range of 300–400 Å, with an average pore diameter of about 315 Å. TiO_2 Hombikat UV-100 does not present any defined porous system. From Fig. 2, it can be noticed that it presents pores in the whole range of pore size; the pore size distribution is in this case rather heterogeneous, being the average pore diameter in any case lower than 50 Å.

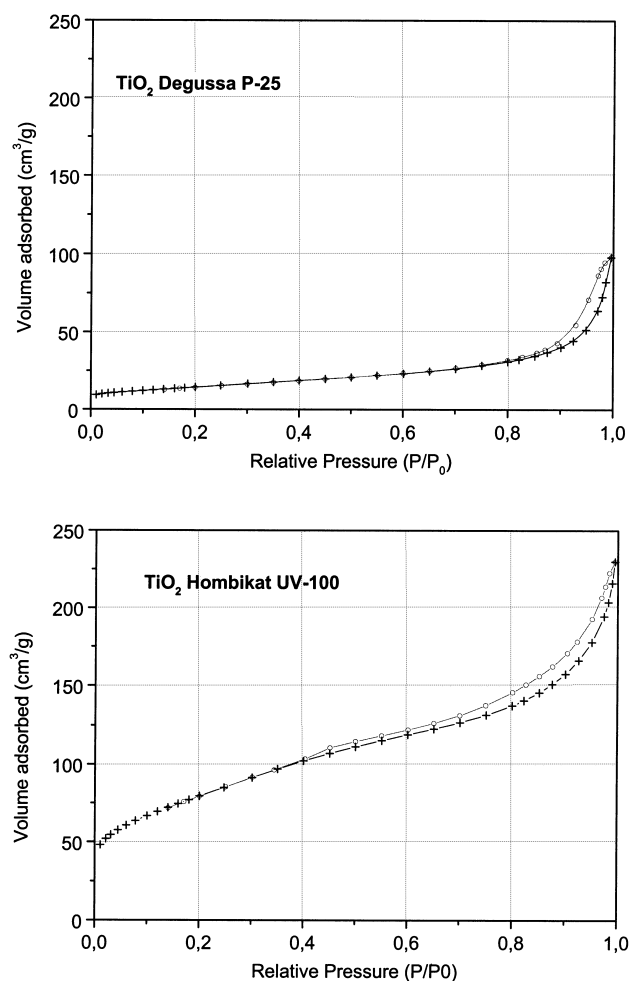


Fig. 1. N_2 Adsorption–desorption isotherms for TiO_2 Degussa P25 and Hombikat UV-100 catalysts.

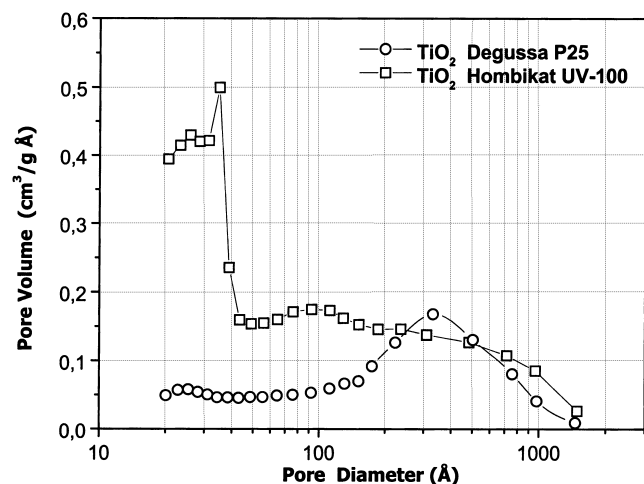


Fig. 2. Pore size distribution for TiO₂ Degussa P25 and Hombikat UV-100 catalysts.

Table 1 summarizes surface and pore size values for both catalysts. Worth of noting is the significantly higher value of the surface area for TiO₂ Hombikat UV-100 comparing to Degussa P25. Pore volume is also greater than that observed for Degussa P25, but the lower average pore diam-

Table 1
Surface characterization of catalysts

Catalyst	S_{BET} (m ² /g)	S_t (m ² /g)	V_p (cm ³ /g)	D_p (Å)
TiO ₂ Degussa P25	51.0	47.0	0.15	315
TiO ₂ Hombikat UV-100	289.0	282.0	0.34	35

eter indicates that Hombikat UV-100 particles are forming small and compact aggregates, giving high surface area. On the other hand, Degussa P25 can be thought to form rougher particles with a porous surface.

Fig. 3 shows SEM images for TiO₂ Degussa P25 and Hombikat UV-100. Morphology of Degussa sample is clearly different from Hombikat one. TiO₂ Degussa (Fig. 4a) presents a wrinkled surface. On the other hand, Hombikat (Fig. 4b) particles are mainly spherical, formed by small subparticles highly agglomerated. Therefore, the surface of these rounded particles is full of small very pores producing the higher specific surface area exhibited by Hombikat UV-100. This is consistent with the observations made from BET results.

Regarding to the structure, Fig. 4 shows diffractograms for Degussa P25 and Hombikat UV-100 titanium oxides. Degussa P25 shows well-defined diffraction peaks corres-

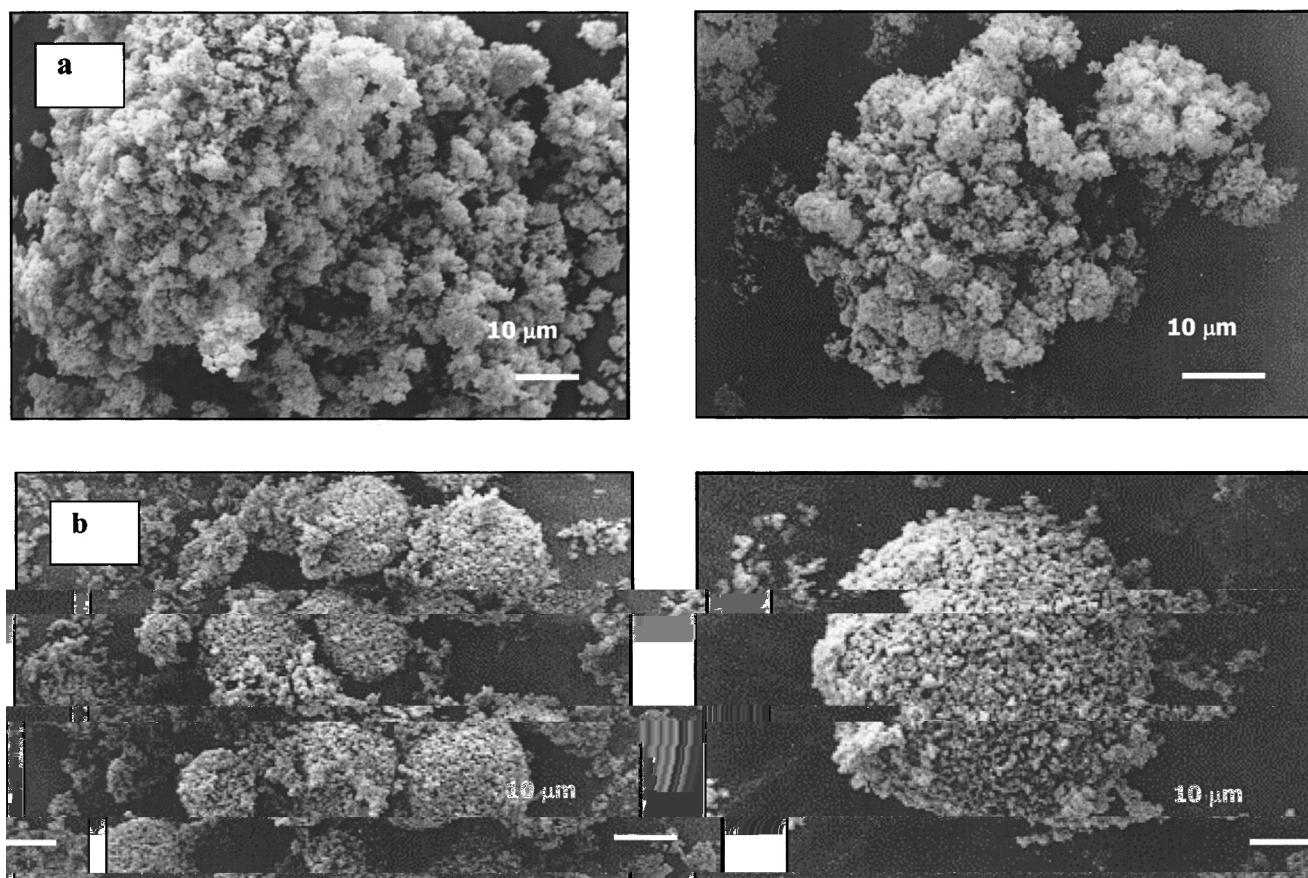


Fig. 3. SEM images for TiO₂: (a) Degussa P25; and (b) Hombikat UV-100.

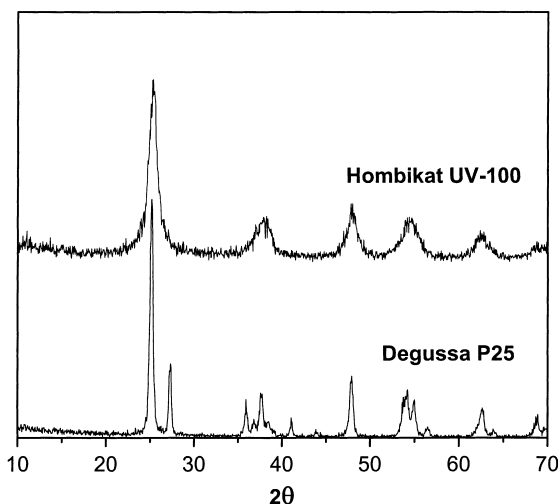


Fig. 4. XRD patterns for TiO₂: (a) Degussa P25; and (b) Hombikat UV-100 catalysts.

ponding to a phase mixture of anatase and rutile. The intensity ratio of the main diffraction peaks, (1 0 1) and (1 1 0) for anatase and rutile, respectively, is 80:20 approximately. On the other hand, TiO₂ Hombikat showed a rather amorphous diffraction pattern, with wider peaks, indicating less crystallinity. In this case, the only phase present is the anatase one. Mean crystallite sizes calculated from the Debye–Scherrer equation [11], using the main diffraction peak of anatase, are 20 and 7 nm for Degussa and Hombikat, respectively. These values clearly indicate the differences in the crystallinity degree of both titanium dioxides.

Diffuse reflectance spectroscopy gives information about the electronic absorption of the photocatalysts and, therefore, the bandgap energy of the semiconductor can be estimated. In Fig. 5, we show the UV–VIS diffuse reflectance spectra of Degussa and Hombikat TiO₂. In both cases, bandgap

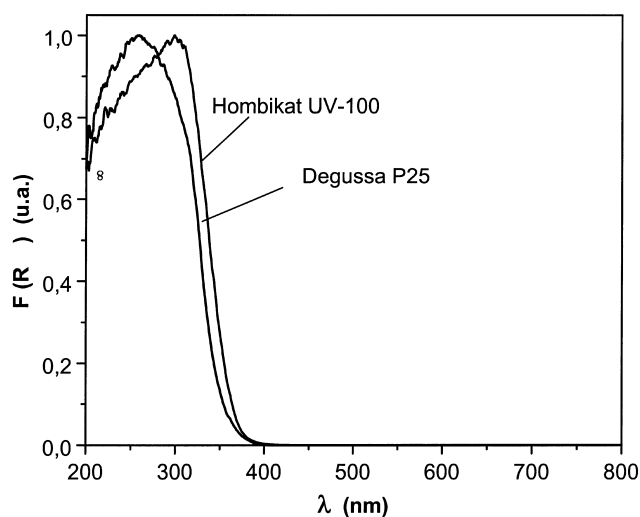


Fig. 5. Diffuse reflectance UV–VIS spectra for TiO₂ Degussa P25 and Hombikat UV-100 catalysts.

energy is approximately to 3.5 eV. Absorption is produced in both cases at wavelength lower than 400 nm. Degussa TiO₂ presents a wide absorption band centered at 300 nm, while Hombikat TiO₂ shows a small shift of this band toward higher wavelength, about 340 nm. However, bandgap values are very similar for both photocatalysts.

3.2. Photocatalytic properties

3.2.1. Reactions with single substrates: Cr(VI) or salicylic acid

TiO₂ Degussa P25 and Hombikat UV-100 were tested for either the photooxidation of salicylic acid or the photoreduction of Cr(VI) in the presence of oxygen flow in both cases. After 10 min in which the photocatalyst powders reach the equilibrium with the substrates to be photodegraded, we have irradiated the suspension for 7 h. Fig. 6 shows the conversion values for TiO₂ samples Degussa P25 and Hombikat UV-100 tested for these two reactions. As it can be noticed, the photooxidation of salicylic acid proceeds completely after the first 2 h, using TiO₂ Degussa P25, although need more illumination times to reach the complete mineralization for the Hombikat one (Fig. 6a). Conversion for the photooxidation process experiments a rapid increase just at the first illumination times. On the contrary, Cr(VI) photoreduction reaction seems to be a slowly process for the two types of photocatalyst. Thus, even at the end of the catalytic run the complete degradation is not reached yet (Fig. 6b). In fact, dissolved oxygen competes very strongly with Cr(VI) species for the photogenerated electrons, suggesting that its presence is detrimental to the reduction of Cr(VI) to Cr(III) as it has been reported [11].

3.2.2. Reactions with Cr(VI) and salicylic acid mixture

We have also studied the possible synergy effect of the simultaneous photooxidation–photoreduction of both pollutants. Since Cr(VI) and salicylic acid exhibited characteristic absorption bands, it is possible to follow the evolution of both species by UV–VIS spectroscopy. Catalytic runs with UV and in the absence of TiO₂ do not produce any change in the concentration of the species. Therefore, no contribution of a possible photoassisted redox reaction must be considered. There is no change in the UV–VIS spectra during illumination, so the formation of new species between Cr(VI) and salicylic acid is negligible.

In Fig. 7, we show the conversion values for Cr(VI) and salicylic acid photodegradation using TiO₂ Degussa P25 and Hombikat UV-100 as photocatalysts. The first feature that can be pointed out is that the simultaneous reaction is significantly much faster comparing with the single ones. Specially in the case of Cr(VI) reduction, this fact is rather important. Also worth of noting is that, when simultaneous photocatalytic reaction takes place, conversion for the Cr(VI) reduction is even higher than the conversion observed for salicylic acid oxidation. So we may say that the presence of the carboxylic acid enhance the photoreduction

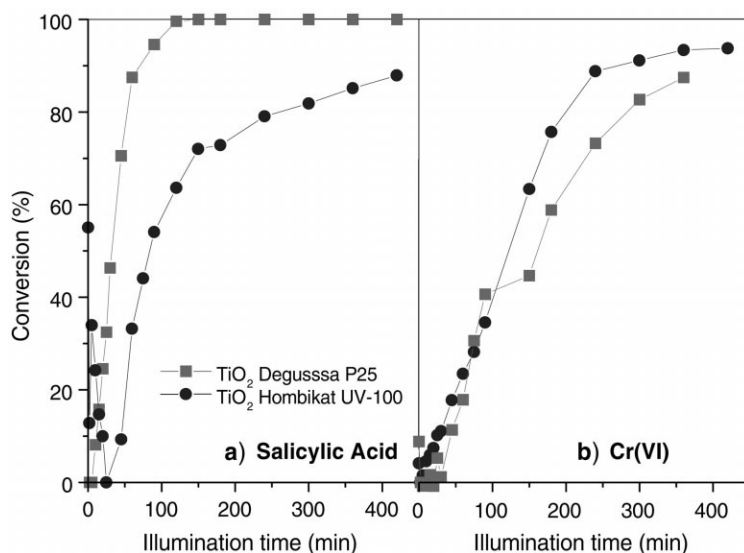


Fig. 6. Photocatalytic conversions for (a) salicylic acid oxidation; (b) Cr(VI) reduction single reactions.

process of Cr(VI). On the contrary, the presence of Cr(VI) clearly diminishes the photooxidation of salicylic acid. This observation is interesting, because recently Malato et al. [12] have reported an enhancement of the rate of solar photocatalytic mineralization of organic pollutants by inorganic oxidizing species such as $S_2O_8^{2-}$. It seems as the simultaneous reaction lead to an average conversion for both processes probably as a consequence of a competitive mechanism. Another important point is the fact that after 2 h of reaction the photodegradation conversion of both species seems to remain constant, indicating that the catalyst could be in some way deactivated. Similar results have been ob-

tained for TiO₂ Hombikat UV-100, but in this case, conversions after 2 h of irradiation are higher than those obtained for Degussa P25 in the same experimental conditions. Thus, the average conversion for both processes after 2 h is about 60% for Hombikat UV-100, being ~45% for Degussa P25.

At the end of 7 h of illumination, first cycle, we have continued the reaction with a new set of fresh catalyst. We have filtered the suspension in order to remove the used catalyst and replaced them with fresh ones in the same ratio of 1 g/l per liter of the remaining solution. In both cases, initial rate of conversion is very high and after three additional hours of reaction degradation of Cr(VI) and salicylic acid is almost

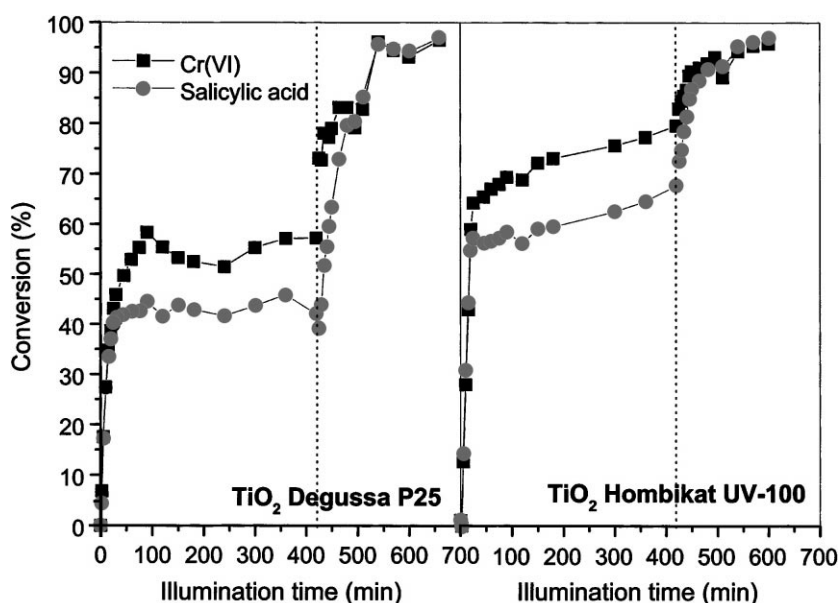


Fig. 7. Photocatalytic conversions for Cr(VI) reduction and salicylic acid oxidation simultaneous reactions.

Table 2
XPS results for TiO₂ catalysts after 7 h of reaction

Catalyst	Ti(2p)	O(1s)	Cr(2p)	Molar % Cr	Molar % C
TiO ₂ Degussa P25	458.8	530.5	577.9	14.4	31.4
TiO ₂ Hombikat UV-100	459.0	530.1	578.5	9.3	31.7

complete. So, the hypothesis of photocatalyst deactivation is confirmed. Surface deactivation is clearly more important in the case of Degussa P25 than for Hombikat UV-100. Table 2 summarizes the XPS results for the catalysts after the first cycle. Chromium content at the surface is clearly higher for TiO₂ Degussa P25 indicating that in this photocatalyst this species remains at the surface in a great extent than for Hombikat. Carbon content is for both catalysts the same, so the chromium should be the determining cause of the deactivation. For Degussa P25 photocatalyst, chromium ions trend to rest adsorbed at the surface, avoiding the salicylic adsorption. Fig. 8 shows XP spectra for Cr(2p) and C(1s) levels. Cr(2p) signal could be assigned mainly

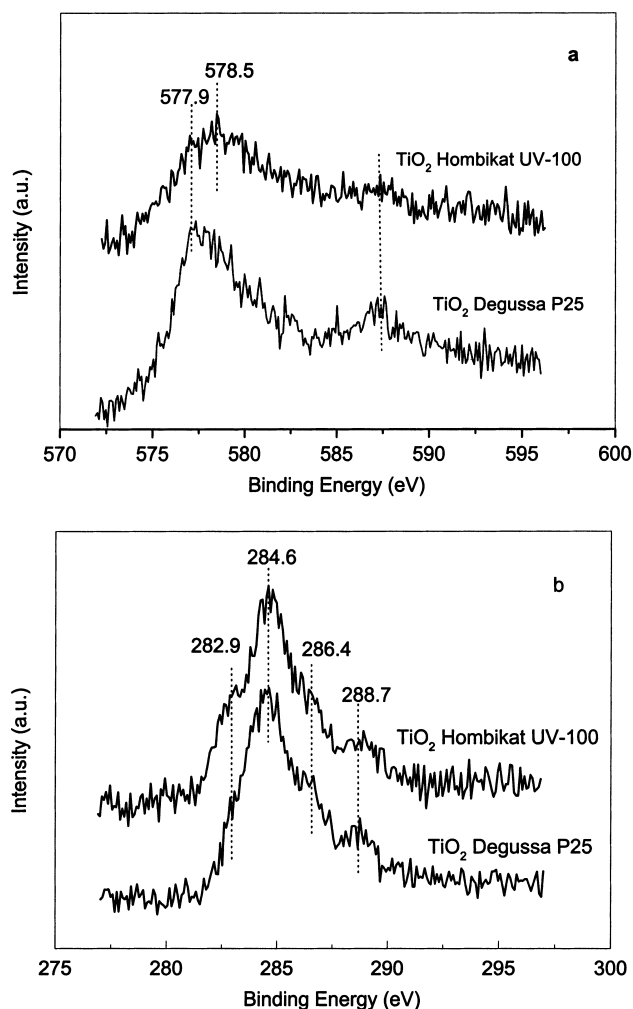


Fig. 8. XP spectra of (a) Cr(2p) and (b) C(1s) levels for TiO₂ Degussa P25 and Hombikat UV-100 catalysts.

to Cr(VI) species. Small contribution of Cr(III) can be expected specially for Degussa P25, however, is difficult to assure the presence of this species, since the small intensity of the XPS signal. From XPS results, it can be found different types of carbon species at the surface, indicating the presence of different carbonaceous species probably arising from photogenerated products during the salicylic acid degradation. In fact, the spectrum (Fig. 8) shows a C(1s) region in which peaks at 284.6, 286.4 and 288.7 eV can be distinguished and could be attributed to the carbon in the –CH₂–, –CH₂–O–CH₂–, and –CH₂OH functional groups, respectively, according to data from the literature [13].

4. Conclusions

Structural and morphological comparison of two commercial TiO₂ photocatalysts (Degussa P25 and Hombikat UV-100) reveals that both oxides present different crystalline structure as well as surface features. No significant differences can be found in the light absorptive properties. From the textural properties, the main difference to be considered should be the surface pore distribution and the morphological aspect of the particles, which are connected with the difference surfaces areas exhibited. Photocatalytic results for single reduction and oxidation reactions indicates almost similar behavior for both photocatalysts, being the Cr(VI) reduction the slower reaction. Almost total conversion can be reached for both processes at the end of illumination. On the contrary, when we consider simultaneous reduction–oxidation process, interesting conclusion could be pointed out. In both cases (for TiO₂ Degussa P25 and Hombikat UV-100), reactions proceed quicker than the single ones. However, after 7 h of illumination total conversion has not been reaching yet. A possible catalyst deactivation can be occurred in the simultaneous reaction. This deactivation is higher for TiO₂ Degussa P25 photocatalyst, for which after the first hour only 50% of pollutants have been eliminated. Hombikat UV-100 photocatalyst reaches also an almost constant conversion rates after the first hour of irradiation, but in this case conversion values are relatively higher. In the second cycle, by removing used catalysts, conversion values reach a rapid increase, as in the first cycle, reaching total elimination of Cr(VI) and salicylic acid after subsequent 2 h of illumination. XPS results indicates a high content of carbonaceous species as well as Cr(VI) species in the photocatalyst surface after the first cycle, suggesting that the deposition of both species at the surface of TiO₂ samples could be one of the origin for the losses of the photocatalyst activity.

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