Reconsideration to the deactivation of TiO₂ catalyst during simultaneous photocatalytic reduction of Cr(VI) and oxidation of salicylic acid

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ABSTRACT

Photocatalytic reduction/oxidation and deactivation of TiO₂ photocatalyst was investigated in the systems composed of Cr(VI) and salicylic acid. The selection of analysis method of Cr(IV) was very important to the monitoring of the photocatalytic process. It was found that as previously reported, serious deactivation of TiO₂ catalyst in the simultaneous photo-reduction of Cr(VI) and oxidation of salicylic acid was incorrectly observed if the Cr(VI) level was analyzed by directly monitoring the absorbance at characteristic 348 nm band of Cr(VI), because it seriously suffers from the interferences of the intermediates generated from the degradation of salicylic acid. By using an appropriate method to determine the Cr(VI) concentration, it was observed that all the added Cr(VI) could be reduced, not showing marked deactivation of the photocatalyst. A long time photocatalytic reduction of Cr(VI) under UV illumination induced the deposition of Cr(III) species on the surface of TiO₂ particles, which could cause a mild deactivation of the photocatalyst. However, the accompanied oxidation of salicylic acid was demonstrated to depress the deactivation effect of the deposited Cr(III) species on the photocatalytic activity of the TiO₂ photocatalyst.

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1. Introduction

TiO₂ photocatalysis has been intensively investigated for its application to the environmental decontamination covering the oxidation of organic compounds and the reduction of metal ions [1–7]. This technology is based on the photo-induced highly reactive electron/hole (e^-–h^+) pairs on TiO₂ under illumination by light of energy greater than its bandgap. Holes and various oxygen-containing radical species (e.g., •OH, O_2^-•, HO_2•) play an important role in the photocatalytic oxidation of organic pollutants, while photo-generated electrons are critical to the photocatalytic reduction of heavy metal ions.

Photocatalytic reduction of heavy metal ions can be combined with other effective separation method to yield a practical technology for removing toxic metals from wastewaters. Thus, increasing attention has been recently paid to the photocatalytic reduction of inorganic contaminants. Among the heavy metal ions, Cr(VI) is one of that attracting the most attention, because it is a toxic, carcinogenic and mobile contaminant originating from various industrial processes such as electroplating, pigment production, and leather

tanning. The preferred treatment is to reduce Cr(VI) to less harmful Cr(III), which can be precipitated in neutral or alkaline solutions as Cr(OH)₃. Therefore, the photocatalytic reduction of carcinogenic and mobile Cr(VI) to less harmful and immobile Cr(III) has been well-reported [4,5].

When Cr(VI) alone is photocatalytic reduced, the reduction of Cr(VI) to Cr(III) proceeds only slowly. If the reduction is paired with the photocatalytic oxidation of some organic compounds, the reduction of Cr(VI) should be promoted significantly in theory, because of the enhanced charge separation of photo-induced hole/electron pairs by the simultaneous reduction/oxidation reactions. Moreover, hazardous organic and inorganic compounds usually co-exist in streams of practical wastewaters, and the simultaneous photocatalytic treatment of organic and inorganic pollutants will show profits in both economics and technology. Schrank et al. reported that both the photo-reduction of Cr(VI) and photodegradation of dye processed more rapidly in their mixture system than in the single component system [8]. Sun et al. reported the synergistic effects in the simultaneous conversion of 4-chlorophenol and Cr(VI) in TiO₂ suspensions under visible-light illumination [9]. Similar phenomena were observed by other research groups [10–12]. Recently, we also investigated the photocatalytic reduction of Cr(VI) over different TiO₂ photocatalysts and the effects of dissolved organic species [13]. We have found that the photocatalytic reduction of Cr(VI) was dependent on both

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of specific surface area and crystalline structure of the photocatalyst in the absence of any organic compounds, but was dominated by the specific surface area of the photocatalyst in the presence of organic compounds because of the synergistic effect between the photocatalytic reduction of Cr(IV) and the photocatalytic oxidation of organic compounds.

However, the enhanced photocatalytic reaction may be retarded gradually during the simultaneous photocatalytic reduction of Cr(VI) and oxidation of organic pollutants, due to poisoning of TiO_2. Chio and co-workers observed that both dye and Cr(VI) could be photocatalytic converted completely, but the total organic carbon (TOC) in the mixture remained constant after 1 h illumination [10]. Papadam et al. reported that the photocatalyst deactivation occurred over the reused TiO_2, and the Cr(VI) conversion was decreased by 13% in the third run in comparison with the first run [14]. Both the above-mentioned works hypothesized that complexes may be formed between the by-products of the dye degradation and chromic species, which deactivate the photocatalyst [10,14]. Nevertheless, a different observation was reported by Colón et al., who found that after 2 h irradiation the concentrations of both Cr(VI) and salicylic acid, which were directly measured at their characteristic bands on a UV–vis spectrophotometer (348 nm for Cr(VI), 290 nm for salicylic acid), seemed to keep constant (corresponding to a conversion of ca. 50%) [15,16]. Considering the characteristic 348 nm and/or 290 nm bands can be easily interfered by some aromatic intermediates generated during the photocatalytic treatment, we suspect that the different observations in the salicylic acid/Cr(VI)/TiO_2 system comes from an inappropriate selection of the Cr(VI) and salicylic acid determination methods on the basis of some preliminary experiments in our laboratory. Therefore, the deactivation of TiO_2 photocatalyst is further investigated in the co-exist of Cr(VI) and salicylic acid by using two different analytical methods of the Cr(VI) determination. The diphenylcarbazide colorimetric method (GB 7466-87, Standards of China) as a better analysis method for the determination of Cr(VI) is used to ensure the exactness of the monitoring of the Cr(VI) concentration and Cr(VI) conversion during the simultaneous photocatalytic treatment. By using this method, it is confirmed that the deactivation of TiO_2 photocatalysts is fairly weak during the simultaneous photocatalytic treatment of Cr(VI) and salicylic acid. Subsequently, UV–vis diffuse reflectance spectroscopy (UVDRS) and X-ray photoelectron spectroscopy (XPS) are used to gain insight into the reason for the slight deactivation of TiO_2 during the simultaneous photocatalytic treatment of Cr(VI) and organic compounds.

2. Experimental

TiO_2 powders (Degussa P25, ca. 80% anatase, 20% rutile; BET area, ca. $50\,m^2\,g^{-1}$) were used as received. All other chemicals were of analytical reagent grade and used without further purification. Distilled water was used throughout. Cr(VI) stock solution ($0.02\,mol\,L^{-1}$) was prepared by dissolving $K_2Cr_2O_7$ into distilled water. To prepare the chromogenic agent for the Cr(VI) determination, diphenylcarbazide (0.1 g) was dissolved into 50 mL of alcohol, and then 200 mL of 10% (v/v) H_2SO_4 aqueous solution ($1.84\,mol\,L^{-1}$) was added slowly into the above-mentioned diphenylcarbazide solution. The chromogenic agent was prepared freshly every week and stored in the dark at 5 °C prior to its use. The pH of solutions was adjusted by using diluted aqueous H_2SO_4 or NaOH solutions.

Photocatalytic experiments were performed at room temperature (25 ± 2 °C) in a 150-mL reactor. In each experiment, a load of 0.10 g TiO_2 was suspended into 100 mL aqueous solutions containing $0.2\,mmol\,L^{-1}$ Cr(VI) and/or $0.2\,mmol\,L^{-1}$ organic compounds, followed by adjusting pH to pH 2.0 with H_2SO_4 solutions. A 20-W UV lamp with a maximum emission at 253.7 nm was positioned about 5 cm above the photo-reactor. Prior to irradiation, the suspensions were first sonicated for 60 s, and then magnetically stirred in the dark for ca. 30 min to ensure the establishment of adsorption–desorption equilibrium of the concerned chemical substances on the surface of TiO_2. The reaction mixture was maintained in suspension by using a magnetic stirrer during the experiment.

At given time intervals, 2 mL aliquots were sampled, immediately centrifuged at 14,000 rpm for 15 min, and then filtered through a 0.22-μm pore size filter to remove the TiO_2 particles. The filtrates were collected and analyzed. The degradation of salicylic acid was quantified by HPLC (JASCO, PU-2089) equipped with a Hiqsil C18 ODS column (4.6 mm × 150 mm) and a UV detector (JASCO, UV-2075). The detection wavelength was 289 nm, and the mobile phase was 35% methanol and 65% KH_2PO_4 ($0.01\,mol\,L^{-1}$) at $1.0\,mL\,min^{-1}$. The concentration of Cr(VI) was determined by two methods. One was the direct measurement of the absorbance at its characteristic 348 nm band, and the other was the measurement of the absorbance at 540 nm according to the diphenylcarbazide colorimetric method (GB 7466-87, Standards of China). In the diphenylcarbazide colorimetric method, 0.5 mL of filtered sample was pipetted into a 10-mL colorimetric tube, mixed rapidly with 1.5 mL chromogenic agent, and then diluted to 5 mL with distilled water. After a reaction time of 5 min, the UV–vis absorption was measured on a Varian Cary 50 spectrophotometer.

Control experiments were carried out in the TiO_2 suspension without UV illumination and in the TiO_2-free solution under UV illumination. It was found that the changes in the concentration of concerned compounds (Cr(VI) and salicylic acid) was negligible. For example, a 120-min treatment in the presence of TiO_2 without UV illumination produced a conversion of less than 0.9% for Cr(VI), and a 120-min UV irradiation converted only 0.2% of the added Cr(VI) in TiO_2-free solution photocatalyst. Thus, the adsorption, and the direct photolysis and chemical reduction of Cr(VI) will not make considerable contributions to the variations of concerned compounds observed during our photocatalytic experiments.

The surface atomic compositions of the used TiO_2 photocatalysts were determined by X-ray photoelectron spectroscopy (XSAM 800, KROTOS) using the Mg Kα line ($h\nu = 1253.6$ eV) as an excitation source. The pressure in the XPS analysis chamber was maintained at 10^{-9} mbar. The binding energies of all peaks were referenced to the C (1s) line (285.0 eV). The UV–vis diffuse reflectance spectra (UV–vis DRS) in the wavelength range of 200–800 nm were recorded on a Shimadzu UV-2550 spectrophotometer, with $BaSO_4$ powders as a standard.

3. Results and discussions

3.1. Effects of the analysis method of Cr(VI) on the rate and extent of its photo-reduction

By using two different methods of Cr(VI) determination, kinetic data were obtained for the photocatalytic conversion of Cr(VI) in the presence of salicylic acid and phenol. As shown in Fig. 1, when the concentration of Cr(VI) is determined by directly monitoring the absorbance at characteristic 348 nm band of Cr(VI), the conversions of Cr(VI) in the presence of salicylic acid or phenol are increased with illumination time (curves 1′ and 2′). However, even the illumination is performed as long as 390 min, the conversion of Cr(VI) in the presence of salicylic acid is only 66.5%. This observation is very similar to that reported by Colón et al. [15,16], who attributed it to the deactivation of the photocatalyst. These authors proposed that the deactivation of TiO_2 due to the accumulation of metal complexes arising from the aromatics intermediates on active sites. If it is so, the deactivation should be observed similarly in the photocatalytic system of Cr(VI) and phenol mixture,
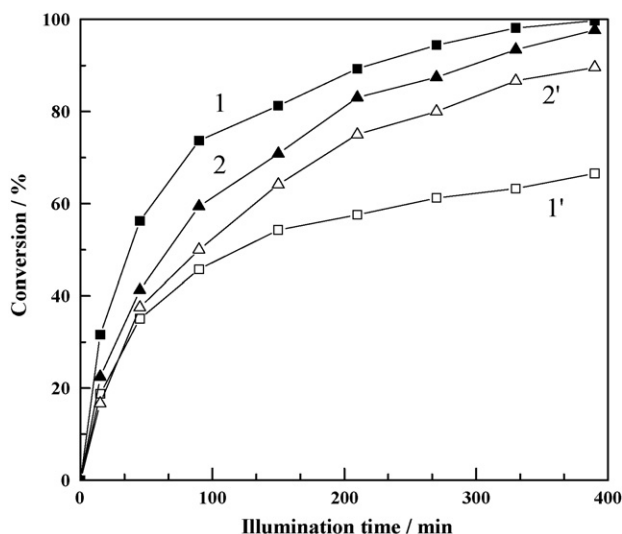
Fig. 1. Photocatalytic conversion of Cr(VI) in the presence of (1, 1′) salicylic acid and (2, 2′) phenol. Concentrations of Cr(VI) were determined by monitoring (1′, 2′) the absorbance at 348 nm and (1, 2) the absorbance at 540 nm via the diphenylcarbazide colorimetric method.

because of the generation of similar intermediate dihydroxybenzenes. However, the conversion of Cr(VI) was increased to about 90% in the presence of phenol (curve 2′), that is, the deactivation of TiO$_2$ is, if any, much depressed by using phenol. In fact, if salicylic acid was substituted with many other organic substances, the so-called deactivation of the photocatalyst tended to be completely depressed. It is interesting to declare the reasons for such differences, and we suspect that the determination method of Cr(VI) with the aid of determining the absorbance at 348 nm is proper or not.

We measured the UV–vis absorption spectra of Cr(VI), salicylic acid, and their mixture in aqueous solutions. As shown in Fig. 2a, the characteristic absorption band of Cr(VI) at 348 nm (curve 1) is well separated from that of salicylic acid at 298 nm (curve 2), and the absorption spectrum of their mixture (curve 3) is exactly the sum of their alone spectra. This often demonstrate that the determination of Cr(VI) can be performed by directly determining the absorbance at 348 nm, which was the analytical method in Colón's work [15,16]. However, we monitored the absorption spectra of the mixture solution during the photocatalytic process. A sub-peak was observed at ca. 335 nm in the absorption spectrum of the mixture solution under UV illumination for a period of time (curves 4 and 5). The appearance of the sub-peak is able to be attributed to the absorption of some generated intermediates due to the photocatalytic degradation of salicylic acid. The generated intermediates seem to be much more difficult to be degraded than salicylic acid, and the absorption of the intermediates at 335 nm apparently increased the absorption of Cr(VI) at 348 nm. Therefore, when the Cr(VI) concentration is determined by directly monitoring the absorbance at 348 nm, the remained Cr(VI) concentration must be over-estimated, and the conversion of Cr(VI) is under-estimated. This will lead to the so-called deactivation of the photocatalyst as mentioned above. When phenol was used instead of salicylic acid, the absorption spectra of single compounds and the illuminated mixture solution were similarly obtained as shown in Fig. 2b. Because the generated intermediates show absorption only at wavelengths less than 300 nm (curves 4 and 5 in Fig. 2b), the absorption of the characteristic of Cr(VI) is only slightly interfered by the possible absorption of the generated intermediates. Thus, a greater conversion of Cr(VI) is achieved, which is consistent with the observation in Fig. 1 (curve 2′). This can lead to a conclusion

that the reported serious deactivation of the TiO$_2$ photocatalysts observed is substantially attributed to the selection of a inappropriate method for the determination of Cr(VI) concentration. If the absorption of Cr(VI) at 348 nm is not interfered by the generated intermediates during the photocatalytic process, such a deactivation of the photocatalyst is not observable. This is the case of the Cr(VI)/phenol system, and an almost complete conversion of Cr(VI) was also reported for the Cr(VI)/dye system [10].

To overcome the interference of the generated intermediates from the photocatalytic oxidation of organic compounds on the Cr(VI) determination, the remained concentration of Cr(VI) can be determined by using the diphenylcarbazide colorimetric method (GB 7466-87, Standards of China), which is based on the fact that Cr(VI) reacts with diphenylcarbazide to produce a colored product with an absorption maxima at 540 nm, being far from the absorption peaks of the possible intermediates as shown in the insets of Fig. 2. In this way, the kinetic data for the photocatalytic conversion of Cr(VI) in the presence of salicylic acid and phenol as shown in Fig. 1 (curves 1 and 2). By comparing curve 1 with curve 1′ and curve 2 with curve 2′, it is easily seen that the presence of salicylic acid does not induce the deactivation of TiO$_2$ catalysts.
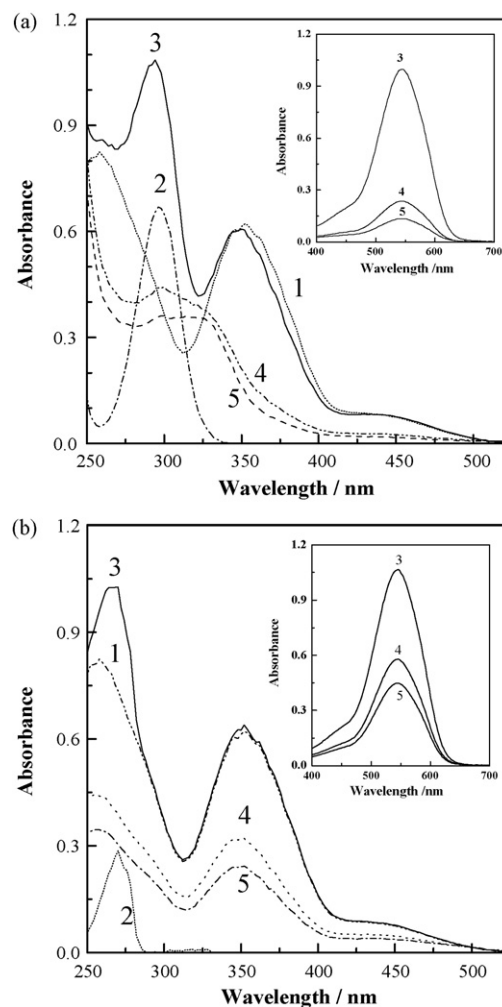

Fig. 2. (a) UV–vis absorption spectra of (1) Cr(VI), (2) salicylic acid, (3) Cr(VI) + salicylic acid before illumination, and the solution of (3) after being UV irradiated for (4) 150 min and (5) 210 min. (b) UV–vis absorption spectra of the systems similar to that in (a) but phenol is used instead of salicylic acid. Each of the initial concentrations of Cr(VI), salicylic acid and phenol was 0.2 mmol L^{-1}. The insets show the spectra of the mixture solution obtained in the diphenylcarbazide colorimetric system for determination of Cr(VI).
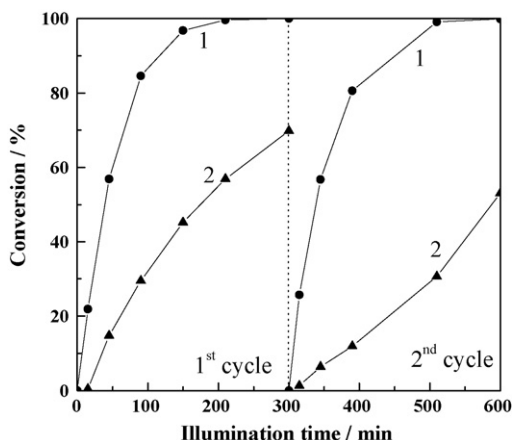
Fig. 3. Photocatalytic conversions of (1) salicylic acid and (2) Cr(VI) in single systems.

Table 1
Half-time of Cr(VI) and salicylic acid in the single and binary photocatalytic systems.

	$t_{1/2}$ (min)	
	1st cycle	2nd cycle
Cr(VI)		
Single system	174.9	287.6
Binary system	37.0	146.6
Salicylic acid		
Single system	39.3	38.6
Binary system	16.5	79.0

cates that the deactivation of the photocatalyst during a long time of service, if any, is very slight. Relative to the oxidation of organic compound, the reduction of Cr(VI) seems to induce a mild deactivation of the photocatalyst.

The time required for one-half of a specified compound to be converted ($t_{1/2}$) may be used to represent the kinetic characteristics of the photocatalytic reduction/oxidation reactions, because the removal of substrates did not follow a simple and single kinetics reaction. Table 1 compares the values of half-time $t_{1/2}$ for the conversion of two substrates in the first and second cycles. For the single systems, the $t_{1/2}$ value for the oxidation of salicylic acid was measured as 39.3 min and 38.6 min for the first and second cycles, respectively, implying that the catalyst remained fully its activity after an UV illumination of at least 5 h. A moderate deactivation of the photocatalytst was observed in the photo-reduction of Cr(VI), because increased the value of $t_{1/2}$ was increased from 174.9 min in the first cycle to 287.6 min in the second cycle. It was noted that the white TiO$_2$ particles turned light greenish after the first cycle of Cr(VI) photo-reduction, possibly due to the Cr(III) deposition on the surface of TiO$_2$ particles.

Next, the photocatalytic experiments were similarly carried out in binary systems, i.e., in the mixture solution of Cr(VI) and salicylic acid, and the kinetic data and the obtained $t_{1/2}$ values for each substrates were given in Fig. 4 and Table 1, respectively. As shown in Fig. 4, the conversion achieves almost to 100% for both Cr(VI) and salicylic acid. It is known that the photodegradation of organic compound consumes photo-induced holes and/or •OH radicals, promoting the photo-generated electron–hole separation and then increasing the total photoefficiency [8–16]. As expected, the paired photocatalytic reduction of Cr(VI) and the oxidation of salicylic acid in the binary system significantly enhanced the reduction/oxidation of the substrates each other. The values of $t_{1/2}$ for the reduction of Cr(VI) and the oxidation of salicylic acid in the

3.2. Photocatalytic reactions with single and binary systems

In general, any catalyst will suffer from deactivation to an extent during its service. Because the correctness of the previously reported conclusion about the deactivation of TiO$_2$ photocatalyst in the presence of Cr(VI) and salicylic acid is seriously influenced by the inappropriate selection of the analysis method, it is necessary to re-investigate the possible deactivation of the photocatalysts in the related photocatalytic systems. Hereafter, the Cr(VI) concentration is determined by using the diphenylcarbazide colorimetric method, and the degradation of salicylic acid is quantified by using HPLC.

Firstly, the photocatalytic reduction of Cr(VI) was carried out in Cr(VI) solution, and the photocatalytic oxidation of salicylic acid was conducted in the presence of salicylic acid alone, where the solution system is referred to as single systems. As shown in Fig. 3, the conversion of salicylic acid achieves almost 100% after a 210-min illumination (curve 1), whereas the photocatalytic reduction of Cr(VI) is much slower and only 70% of Cr(VI) is reduced even after being illuminated for 300 min. The slow photocatalytic reduction of Cr(VI) in the absence of organic compounds is not due to the deactivation of the photocatalyst, but because the net photocatalytic reaction in a completely inorganic aqueous solution is the three-electron-reduction of Cr(VI) to Cr(III) with oxidation of water to oxygen, which is a kinetically slow four-electron process [8]. After the first cycle of photo-oxidation/reduction was performed under UV illumination of 5 h, the same amount of the specified substrate (0.2 mmol L^{-1}) was added again into the reaction suspension, and the second cycle of the experiment was further carried out. By comparing the kinetic data in the second cycle with the first cycle in Fig. 3, only a very slightly slower conversion rate was observed for the degradation of salicylic acid in the second cycle, which indi-
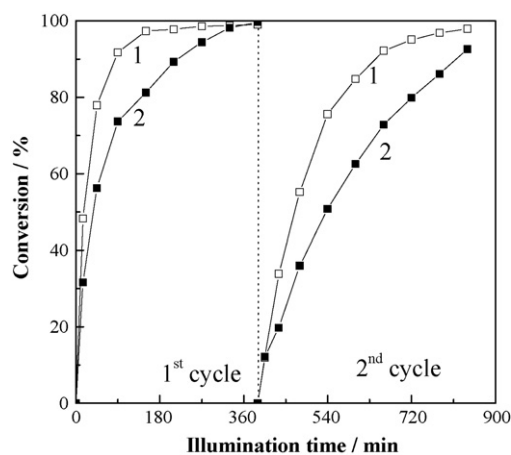

Fig. 4. Photocatalytic conversions of (1) salicylic acid and (2) Cr(VI) in their mixture solution.

first cycle were decreased from 174.9 min and 39.3 min in the single systems to 37.0 min and 16.5 min in the binary system, respectively. After a long time of illumination, the conversion rate of either Cr(VI) or salicylic acid is somewhat decreased in the second cycle in comparison with that in the first cycle (Fig. 4), and the $t_{1/2}$ values for the reduction of Cr(VI) and the oxidation of salicylic acid is increased from 37.0 min and 16.5 min in the first cycle to 146.6 min and 79.0 min in the second cycle, respectively. Thus, there is a slight deactivation of the photocatalyst in the mixture solution of Cr(VI) and salicylic acid. Such deactivation is possibly due to aggregation, deposition of Cr(III) and/or formation of Cr-complexes on the surface of TiO_2 particles [10,14–16]. Colón et al. emphasized that the formation of Cr-complexes or Cr(VI) deposition is the major reason for the observed deactivation of photocatalyst [15,16].

Under the specified experimental conditions at pH 2.0, the TiO_2 surface is electropositive, which favors the adsorption of Cr(VI) anions ($Cr_2O_7^{2-}$) via the electrostatic interaction and then its reduction to Cr(III) on TiO_2 surface. In the mixture solution of Cr(VI) and salicylic acid, the coupled oxidation of the organic compound consumes photo-generated holes efficiently, resulting in blocking the electron–hole recombination and accelerating the Cr(VI) reduction. Although Colón et al. reported that the deactivation of the photocatalyst is attributed to the formation of Cr-complexes or Cr(VI) deposition [15,16], our experimental data clearly shows that in the second cycle, the $t_{1/2}$ value for Cr(VI) reduction is 287.6 min in the absence of salicylic acid, being greater than that (146.6 min) in the presence of salicylic acid. This indicates that the presence of salicylic acid can depress the deactivation of TiO_2 photocatalyst.

3.3. Deposition of Cr(III) species and its effect on the photocatalytic activity of TiO_2

As discussed above, the TiO_2 photocatalysts does not suffer any deactivation process for the first cycle in both single and binary systems, and the decreased photocatalytic activity of TiO_2 was observed only in systems containing Cr(VI) for the second cycle. Therefore, chromium species may deactivate the photocatalysts.

To confirm the deposition of any Cr-containing species on the surface of TiO_2 photocatalysts, the used TiO_2 catalysts were separated by filtering and vacuum dried at 50 °C after the photocatalytic reaction, followed by XPS and UV–vis DRS measurements. The used TiO_2 catalysts in the single and binary systems were briefly referred to as S-TiO_2 and B-TiO_2, respectively. As a control, the adsorption test was performed using Cr(VI) and TiO_2 dispersion for the same reaction time. From the XPS results, we can find the O (1s), Ti (2p), Cr (2p) and C (1s) signals at the peaks of 530.1 eV, 458.7 eV, 577.3 eV and 285.0 eV, respectively. Fig. 5(a) illustrates the XPS spectra of Cr (2p) peak of the used TiO_2 photocatalysts. As indicated by the vertical tic marks which give the Cr ($2p_{3/2}$) binding energies for various oxidation valence states [18], Cr(III) is predominantly present on the surface of TiO_2 after the photocatalytic reduction of Cr(VI) (curves 1 and 2). In contrast, when the photocatalyst was only immersed in the Cr(VI) solution, the adsorbed Cr(VI) not Cr(III) species on the surface of the photocatalyst was much less (curve 3), because the reduction of adsorbed Cr(VI) to Cr(III) was inhibited in TiO_2 suspensions without UV irradiation.

The slight adsorption of Cr(VI) anions ($Cr_2O_7^{2-}$) on the TiO_2 surface is also reflected by the UV–vis DRS spectrum in Fig. 5b (curve 3), where the charge transfers from O^{2-} to Cr^{6+} yields the absorption band near 460 nm [18]. Compared with naked TiO_2, the two bands in the visible region observed evidently near 450 nm and 620 nm (curves 1 and 2) are typically assigned to d–d transitions of Cr(III) either in an octahedral or in a distorted octahedral environment [19,20]. This further confirms that Cr(III) species may deposit on the surface of the TiO_2 catalysts during the photocatalytic reduc-
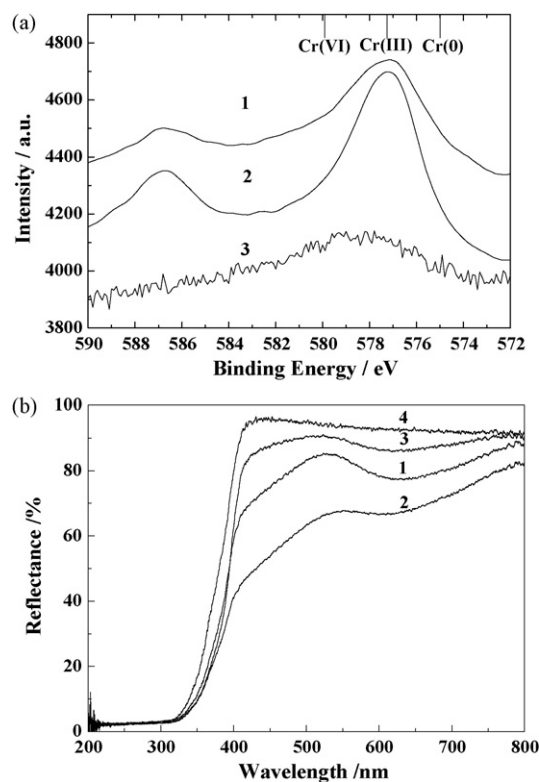

Fig. 5. (a) XPS spectra of Cr (2p) levels of the used TiO_2 in the (1) single, (2) binary and (3) adsorption systems. (b) UV–vis DRS of the used TiO_2 in the (1) single, (2) binary, (3) adsorption systems and (4) naked TiO_2.

tion of Cr(VI). Compared with the TiO_2 used in the single system of Cr(VI) photo-reduction, both the absorption in Fig. 5b and the XPS signals in Fig. 5a for the TiO_2 used in the binary system are stronger, which suggests that the accompanied photo-oxidation of salicylic acid favors the deposition of Cr(III). This is very rational because the photo-reduction of Cr(VI) can be accelerated by the accompanied photo-oxidation of salicylic acid.

Our observation of the deposition of Cr(III) species is similar to the observation of Colón et al. [15,16], who assigned this species to a complex between Cr(III) and salicylic acid. If it is so, we should detect carbon content in the atomic composition of the surface of B-TiO_2 than that of S-TiO_2, because the formation of the Cr(III)–salicylic acid complex (a carbon-containing species) is impossible on S-TiO_2. By comparing the XPS spectra of C (1s) levels of the used TiO_2 in the single, binary and adsorption systems shown in Fig. 6, however, the carbon content on the surface of B-TiO_2 is qualitatively the lowest. Therefore, we may conclude that the deposited Cr(III) in the binary system is not a complex between Cr(III) and salicylic acid.

Increased deposition of Cr(III) species is in general unfavorable to the photocatalytic activity of the photocatalyst. Thus, the photo-reduction of Cr(VI) and/or the photo-oxidation of salicylic acid over the used TiO_2 photocatalysts was further investigated in the single and binary systems. When the used TiO_2 with Cr(III) deposition was reused for the photocatalytic treatment of Cr(VI) alone, salicylic acid alone and their mixture solution, a deactivation phenomena was observed, especially for the photo-oxidation of salicylic acid alone as shown in Fig. 7, implying Cr(III) deposition decreases the TiO_2 photocatalyst activity. It is interesting to note that both the photo-reduction of Cr(VI) alone and the photo-oxidation of salicylic acid alone over the used S-TiO_2 (curve 3 in Fig. 7) are faster than that over the used B-TiO_2 (curve 4 in Fig. 7). The poorer photocatalytic
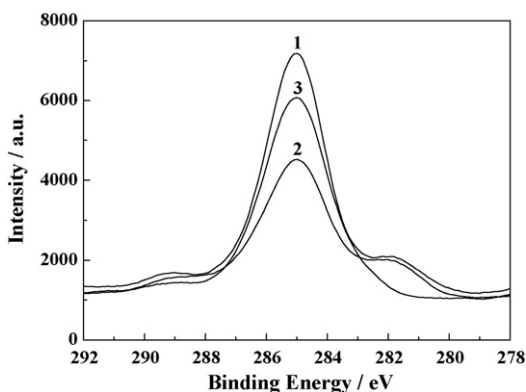
Fig. 6. XPS spectra of C (1s) levels of the used TiO_2 in the (1) single, (2) binary and (3) adsorption systems.

activity of B-TiO_2 in the single system than that of the used S-TiO_2 is attributed to the greater amount of Cr(III) deposition on the surface of the former than on the latter (Fig. 5), and the deposited Cr(III) is unfavorable to the photocatalytic activity of the photocatalyst.

When the photocatalytic reduction of Cr(VI) and oxidation of salicylic acid over the used TiO_2 photocatalysts were performed simultaneously in the binary system, much greater conversions for both Cr(VI) and salicylic acid were observed as shown in Fig. 7 (curves 1 and 2). After an illumination of 300 min, the conversion of Cr(VI) and salicylic acid achieved as high as 77% and 93%, respectively, over both the used S-TiO_2 and B-TiO_2. This demonstrates that the presence of salicylic acid will much depress the deactivation effect of the Cr(III) species deposited on the surface of TiO_2. The synergistic effect in the photo-reduction of Cr(VI) and the photo-oxidation of salicylic acid can increase charge separation.
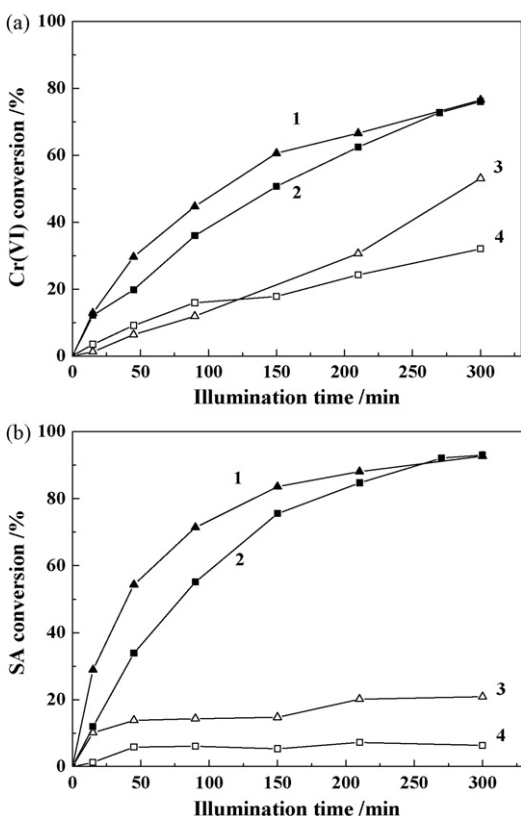

Fig. 7. Photocatalytic conversions of (a) Cr(VI) and (b) salicylic acid in the binary (1, 2) and single (3, 4) systems over the used S-TiO_2 (1, 3) and B-TiO_2 (2, 4).

4. Conclusion

To evaluate correctly the kinetics of a photocatalytic process and the chemical stability of the photocatalyst during service, it is necessary to select properly the methods for analysis of the revolved chemical species. Because Cr(VI) is an important pollutant, its photocatalytic reduction has been extensively studied. Cr(VI) has a characteristic absorption at 348 nm, which is often used to determine the Cr(VI) concentrations during the photocatalytic treatment. However, when the photo-reduction of Cr(VI) is carried out in the presence of organic pollutants, the determination of Cr(VI) by measuring the absorption at this wavelength (348 nm) may be seriously interfered by the intermediates generated from the photo-oxidation of the organic pollutants. Indeed, we have found that by using this analytic method, the photocatalytic conversion of Cr(VI) is much under-estimated in the presence of salicylic acid, which is attribute to the interference of the photogenerated intermediates from the degradation of salicylic acid. This incorrect selection of the analysis method may lead to an incorrect conclusion that the TiO_2 photocatalyst may suffer a serious deactivation in the simultaneous photocatalytic reduction of Cr(VI) and oxidation of salicylic acid. By using the diphenylcarbazide colorimetric method, which measures the absorbance at 540 nm and diminishes the interferences from the degradation intermediates of salicylic acid, it has been found that the conversion of about 100% has been achieved for both the reduction of Cr(VI) and the oxidation of salicylic acid. By using this appropriate analytical method (and HPLC), the deactivation of photocatalyst is further re-investigated in the related photocatalytic system. It has been demonstrated that there is only a slight deactivation of the photocatalyst in the photoreduction of Cr(VI) alone and the photocatalytic treatment of the mixture of Cr(VI) and salicylic acid. XPS and UV–vis DRS analysis declare that the slight deactivation originates from Cr(III) species deposited on the TiO_2 surface after the photocatalytic reduction of Cr(VI). Although the deposited Cr(III) species can lead to mild deactivation of the TiO_2 photocatalyst, its deactivation effect is greatly inhibited by the presence of salicylic acid. It is well-known that the simultaneous photo-reduction of Cr(VI) and photo-oxidation of organic pollutants has a best merit which is that the rate and extent of removing both types of pollutants are much increased. The present work will add another important advantage of this treatment, i.e., the deactivation of the photocatalyst in the photocatalytic reduction of Cr(VI) will be inhibited in the simultaneous photoreduction of Cr(VI) and photo-oxidation of organic pollutants.

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