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Preparation of Co- and Cr-doped mixed crystal TiO_2 powders and comparison of the photocatalytic degradation abilities under sunlight irradiation

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ABSTRACT

The Co-doped, Cr-doped, and undoped mixed crystal TiO_2 powders were prepared by sol–gel and treatment methods and were characterized by thermogravimetric-differential thermal analysis, X-ray powder diffraction, and Fourier transform infrared technologies. And then these three kinds of prepared TiO_2 powders were used as catalysts in the degradation of Acid Red B (C.I. Carmosine 14) dye in aqueous solution under sunlight irradiation and their photocatalytic activities were also compared. The results showed that the Co-doped mixed crystal TiO_2 powder treatment at 600°C for 3.0 h showed highest photocatalytic activity among three photocatalysts. Apparently, the doped cobalt ions can not only restrain the growth of TiO_2 crystallites, which finally decreases the particle size and increase the specific surface area of TiO_2 particles, but also trap the photogenerated electrons and restrain the combination of hole-electron pairs. Otherwise, the mixed crystal can enhance the absorption ability for sunlight and cause the separation of holes and electrons. Thus, the prepared Co-doped mixed crystal TiO_2 powder is applicable for the treatment of wastewater under sunlight irradiation.

Keywords: Co- and Cr-doped mixed crystal TiO_2; Degradation; Acid Red B (C.I. Carmosine 14) dye; Sunlight irradiation

1. Introduction

Some semiconductor oxides as potential photocatalytic materials are applicable for the treatment of environmental pollutants [1–5]. Among them, titanium dioxide (TiO_2) is the best choice for photocatalytic degradation because of its chemical stability, nontoxicity, and high photocatalytic activity in the decomposition of organic pollutants in wastewater [6]. However, the TiO_2 can show high photocatalytic activity only under the ultraviolet light irradiation, which accounts for about 4% of the total amount of solar radiation [7,8]. Thus, in order to utilize TiO_2 as photocatalysts effectively for treating various wastewaters, it is essential to improve their photochemical properties under sunlight radiation.

Many researchers have developed the modification methods to enhance the photocatalytic activity of TiO_2 under visible light. Among them, transition metal doping is a focus investigated extensively [9–12]. It is because that the dopants of transition metal in the TiO_2 lattice can efficiently trap the photogenerated

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electrons [13–15]. Additionally, it has been known that the mixed crystal can also enhance the absorption ability of TiO_2 to visible light because of low energy band gap of rutile phase ($E_{bg} < 3.2$ eV) [16]. However, to the best of our knowledge, the past researches with respect to transition metal doped TiO_2 mainly focused on the utilization of visible light or ultraviolet light [17–19], but did not deal with the effect of phase transformation of TiO_2. It could be presumed that the doping of transition metal and phase transformation of TiO_2 should have the cooperative effect on improvement of the photocatalytic activity.

In the present study, the Co-doped and Cr-doped mixed crystal TiO_2 powders were prepared adopting sol–gel and treatment methods. The mixed crystal was realized by heat treatment which caused the phase transformation of Co-doped and Cr-doped TiO_2 powders. And the photocatalytic activities of Co-doped and Cr-doped mixed crystal TiO_2 powder were investigated by degradation of Acid Red B (C.I. Carmosine 14) dye, an azo dye, under sunlight irradiation. It is well known that azo dyes are non-biodegradable, diffluent, and steady compounds existing in a wide concentration range in industrial effluents and their release is an important source of contamination. The production and consumption of azo dyes account for over 50% of the total dyes around the world [20]. Here, Acid Red B (C.I. Carmosine 14) dye is chosen as a model compound and the concentrations are simulated as the aquatic life. The molecular structure of Acid Red B (C.I. Carmosine 14) dye is shown in Fig. 1. In addition, some influence factors, such as treatment temperature, metal ion doping content, sunlight irradiation time, pH value, and initial concentration of Acid Red B (C.I. Carmosine 14) dye solution, on the photocatalytic degradation were studied. It was found that, under sunlight irradiation, the Co-doped mixed crystal TiO_2 powder showed higher photocatalytic activity than that of Cr-doped mixed crystal TiO_2 powders. The cobalt doping and the mixed crystal show an obvious cooperative effect on improving the photocatalytic activity of TiO_2 powder. Thus, this method is an advisable treatment technology for the detoxification of wastewater because it can efficiently utilize sunlight.

2. Experimental section

2.1. Materials

Acid Red B (C.I. Carmosine 14) dye (CG-R) (A.R. purity, CAS No.: 3567-69-9, Tianjin Kaiyuan Reagent Corporation, China) was purchased and chosen as the model organic pollutant. All other chemicals came from high purity Fluka or Aldrich products. Tetrabutyl titanate ($Ti(OBu)_4$, SP, CAS No.: 5593-70-4, Shanghai Chemistry Reagent Corporation, China), ethanol alcohol (CH_3CH_2OH, AR, CAS No.: 64-17-5, Beijing Chemistry Reagent Corporation, China), hydrochloric acid (HCl, AR, CAS No.: 7647-01-0, Beijing Chemistry Reagent Corporation, China), cobalt nitrate ($Co(NO_3)_2{\cdot}6H_2O$, AR, CAS No.: 10141-05-6, Shanghai Chemistry Reagent Corporation, China), and chromium nitrate ($Cr(NO_3)_3{\cdot}9H_2O$, AR, CAS No.: 7789-02-8, Shanghai Chemistry Reagent Corporation, China) were used to prepared a series of Co-doped and Cr-doped mixed crystal TiO_2 powders. The water purified by a Milli-Q water system (Millipore) was used throughout.

2.2. Preparation of Co-doped and Cr-doped mixed crystal TiO_2 powders

A series of Co-doped mixed crystal TiO_2 powders were prepared according to the following procedure. Twenty milliliters of tetrabutyl titanate ($Ti(OBu)_4$, SP, CAS No.: 5593-70-4, Shanghai Chemistry Reagent Corporation, China) was dissolved into 80 mL ethanol alcohol (CH_3CH_2OH, AR, CAS No.: 5593-70-4, Beijing Chemistry Reagent Corporation, China) (solution A). Solution B consisted of distilled water and cobalt

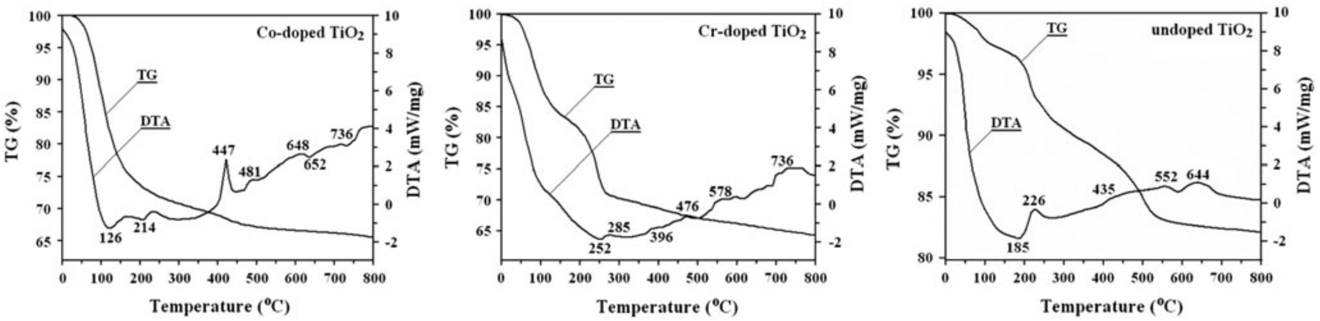

Fig. 1. TG-DTA curves of Co-doped, Cr-doped, and undoped TiO_2 dry gel powders.

nitrate ($Co(NO_3)_2 \cdot 6H_2O$, AR, CAS No.: 10141-05-6, Shanghai Chemistry Reagent Corporation, China) in the required stoichiometry (the atomic proportions of Co to Ti are 0.25, 0.50, 0.75, and 1.00, respectively). Then the solution B was added to solution A by dropwise under vigorous stirring. At the same time, a small quantity of hydrochloric acid (HCl, AR, CAS No.: 7647-01-0, Beijing Chemistry Reagent Corporation, China) solution was added to the mixed solution for adjusting pH value to prevent the rapid formation of TiO_2 precipitates. The resulted mixture was stirred at room temperature for about 24.0 h for slow hydrolysis until the transparent sol was obtained. The sol was then aged for 4.0 d till the formation of gel, and then the gel was dried in oven at 110℃ and became gel powder after ground. After that, the gel powder was treated at different temperatures for 3.0 h in muffle furnace. Otherwise, a series of Cr-doped mixed crystal TiO_2 powders were also prepared by the same method except that the cobalt nitrate is replaced by chromium nitrate ($Cr(NO_3)_3 \cdot 9H_2O$, AR, CAS No.: 7789-02-8, Shanghai Chemistry Reagent Corporation, China). Correspondingly, for comparison the undoped mixed crystal TiO_2 powder was also prepared in this way without the addition of cobalt nitrate and chromium nitrate.

2.3. Characterization of Co-doped and Cr-doped mixed crystal TiO_2 powders

The X-ray powder diffraction (XRD) patterns were determined by XRD measurements (Bruker AXS, D8 Advance, Bruker Company, Germany) using Ni-filtered Cu Kα radiation in the range of 2θ from 20° to 70° for confirming the crystal phase of Co-doped and Cr-doped TiO_2 mixed crystal powders. The Fourier transform infrared (FT-IR) analyses were carried out adopting FT-IR spectrometer (Perkin–Elmer 2000, Perkin-Elmer Company, USA). The crystallization behaviors of the xerogel powder were monitored with a thermogravimetric-differential thermal analysis (TG-DTA) instrument (Mettler Toledo 851^e, Mettler Toledo Company, Switzerland). It was performed in the presence of Ar atmosphere (200 mL/min) from room temperature to 800℃ at a heating rate of 10℃/min.

2.4. Determination of photocatalytic activities of Co-doped and Cr-doped mixed crystal TiO_2 powders

The degradation of Acid Red B (C.I. Carmosine 14) dye in aqueous solution under sunlight irradiation was performed to evaluate the photocatalytic activities of Co-doped and Cr-doped mixed crystal TiO_2 powders. The experimental conditions such as 10.0 mg/L Acid Red B (C.I. Carmosine 14) dye solution, 1,000 mg/L Co-doped or Cr-doped mixed crystal TiO_2 powder, 50 mL total volume and 6.0 h sunlight irradiation were kept throughout the course of the investigation, except for special illumination. The detailed processes are as follows. The Co-doped or Cr-doped mixed crystal TiO_2 powder was first mixed with Acid Red B (C.I. Carmosine 14) dye solution well by vigorous stirring and then placed in the dark for 30 min. After the balance of adsorption and desorption, the suspension was irradiated by sunlight. The experiments were carried out outdoor in Shenyang city (China, longitude and latitude: E 123°24′ N 41°50′; date: 10–30 April 2013; time: 9:30 am–3:30 pm in every day; temperature: 16–20℃; average light flux: 8.2×10^4 Lm). The suspensions at definite intervals were sampled to monitor the changes of Acid Red B (C.I. Carmosine 14) dye concentration. Sampled suspensions were centrifuged at 4,000 rpm for 30 min to remove the TiO_2 powder and then analyzed with UV–vis spectrophotometer (Cary-50, Varian Company, USA). The ion chromatography (ICS-90, Dionex Corporation, California, USA) and high-performance liquid chromatography (Pro-210, Varian Company, USA) were also used to observe the mineralized anions and degradation process.

3. Results and discussion

3.1. Thermal analysis of prepared TiO_2 powders

Fig. 1 shows the TG-DTA curves of (0.25 mol %) Co-doped, (0.25 mol %) Cr-doped, and undoped TiO_2 dry gel powders. It is found that the temperature of phase transformation for undoped TiO_2 powder is about 435℃. However, for Co-doped and Cr-doped TiO_2 powders the temperatures of phase transformation are 447 and 476℃, respectively. It indicates that the Co^{3+} and Cr^{3+} ions as dopants restrain the phase transformation of TiO_2 powder a little.

3.2. XRD patterns of prepared TiO_2 powders

Fig. 2 shows the XRD patterns of (0.25 mol %) Co-doped, (0.25 mol %) Cr-doped, and undoped mixed crystal TiO_2 powders. For the three cases, the characteristic diffraction peak of rutile phase TiO_2 at 27.5° (2θ) and anatase phase TiO_2 at 25.4° (2θ) can be found synchronously, which proves that the prepared TiO_2 powders are all mixed crystal. In addition, it can be seen clearly that the intensities of anatase diffraction peaks of Co-doped and Cr-doped TiO_2 powders are stronger than that of undoped TiO_2 powder. It

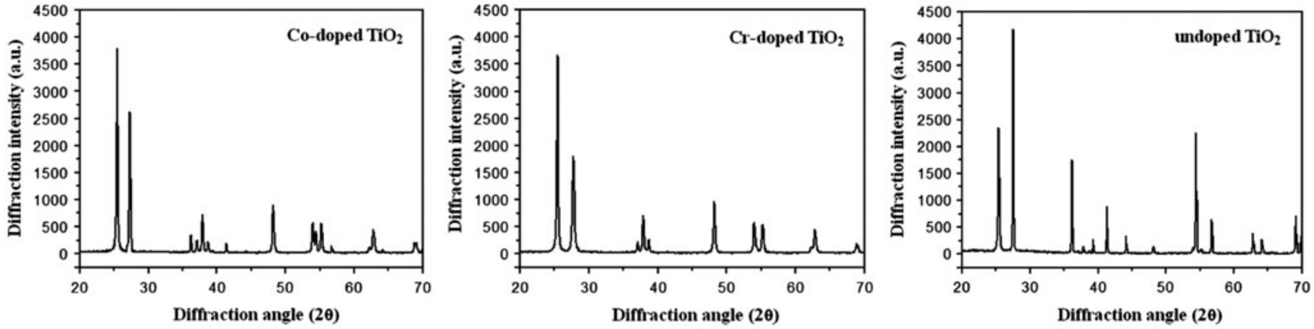

Fig. 2. XRD patterns of Co-doped, Cr-doped, and undoped TiO_2 mixed crystal powders.

also indicates that the phase transformation is prevented more or less due to the doping of metal ions. This is in good agreement with the TG-DTA analyses. The average crystal sizes of the Co-doped, Cr-doped, and undoped TiO_2 particles are about 40, 45, and 67 nm, respectively, as calculated by applying the Scherrer equation to the full width at half maximum of the (101) crystal phase of anatase TiO_2. Otherwise, for Co-doped TiO_2 powder, the phases of cobalt oxides are not observed in the XRD patterns. One possible reason is that the cobalt amount is too low to be detected by XRD. The other is that the radii of Ti^{4+} (0.68 Å) and Co^{3+} (0.72 Å) ions are similar. Thus, all the cobalt ions probably enter the crystal lattice of TiO_2 particles and locate at interstices or occupy some of the titanium lattice sites, forming a cobalt–titanium interstitial solid solution. The formation of solid solution will restrain the growth of TiO_2 crystal which finally decrease the particle size and increase the specific surface area of catalyst. Therefore, the photocatalytic activity of TiO_2 is improved significantly. While for the Cr-doped TiO_2, the Cr^{3+} ion doped in the TiO_2 will act as the new recombination center, which prompts the recombination of photogenerated electron-hole pairs. Thus, the photocatalytic activity decreased [21].

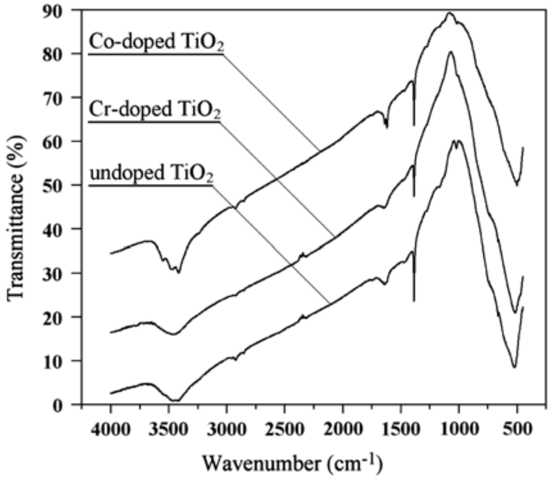

Fig. 3. FT-IR spectra of Co-doped, Cr-doped, and undoped TiO_2 mixed crystal powders.

3.3. FT-IR spectra of prepared TiO_2 powders

In general, the anatase phase TiO_2 gives only one characteristic peak at 500 cm^{-1} between 450 and 750 cm^{-1}, while the rutile phase TiO_2 offers two characteristic peaks at 510 and 640 cm^{-1} in FT-IR spectra, respectively [22,23]. All these characteristic peaks correspond to the TiO_2 crystal lattice vibration. From Fig. 3 it can be seen that for three samples the main peaks appear at 505–500 cm^{-1}. Besides, one shoulder peak also appears at 600–595 cm^{-1} for three samples. All these peaks indicate the formation of mixed crystal TiO_2 powers. It is interesting that the peak at 505 cm^{-1} and shoulder peak at 595 cm^{-1} of undoped mixed crystal TiO_2 slightly cause red-shift and blue-shift, respectively, after addition of Co^{3+} or Cr^{3+} ions. Thus, it can be presumed again that the metal ions enter the crystal lattice of TiO_2 particles and destroy the integrative crystal. However, the peaks of cobalt and chromium oxides are not observed, because the cobalt and chromium amount is too low. Otherwise, as shown in Fig. 3, for three mixed crystal TiO_2 powders, the strong and wide peaks at 3,445 and 1,652 cm^{-1} should be attributed to the surface-adsorbed water and hydroxyl groups [24]. Whereas, the peak at 1,380 cm^{-1} should be attributed to the COO^- symmetrical stretching vibration which indicates the existence of few rudimental organic compounds.

3.4. Effect of treatment temperature on photocatalytic activity of metal-doped mixed crystal TiO_2 powders

The photocatalytic activities of mixed crystal TiO_2 powders at different treatment temperatures were investigated as shown in Fig. 4. It was found that, when the (0.25 mol %) Co-doped mixed crystal TiO_2

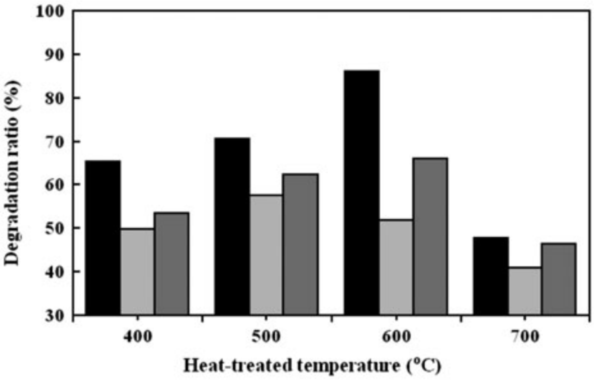

Fig. 4. Effect of treatment temperature on photocatalytic activities of Co-doped, Cr-doped, and undoped mixed crystal TiO_2 powders (experimental condition of photocatalytic degradation: 10.0 mg/L Acid Red B (C.I. Carmosine 14) dye solution, 1,000 mg/L metal-doped or undoped mixed crystal TiO_2 powder, pH 6.0 solution acidity, 50 mL total volume, and 6.0 h sunlight irradiation). ■: Co-doped mixed crystal TiO_2; □: Cr-doped mixed crystal TiO_2; and ▩: undoped mixed crystal TiO_2.

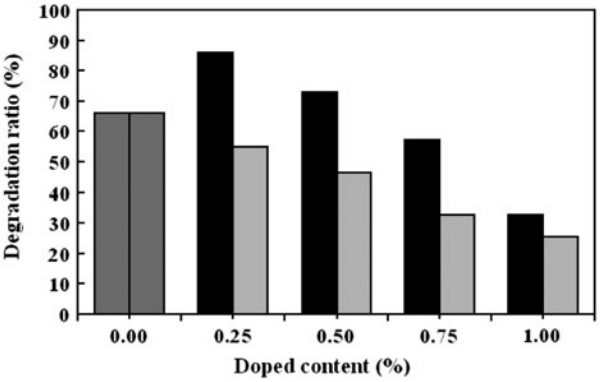

Fig. 5. Effect of metal ion doping content on photocatalytic activity of mixed crystal TiO_2 powder (experimental condition of photocatalytic degradation: 10.0 mg/L Acid Red B (C.I. Carmosine 14) dye solution, 1,000 mg/L metal-doped or undoped mixed crystal TiO_2 powder, pH 6.0 solution acidity, 50 mL total volume, and 6.0 h sunlight irradiation). ■: Co-doped mixed crystal TiO_2; □: Cr-doped mixed crystal TiO_2; and ▩: undoped mixed crystal TiO_2.

powder, which was treatment at 600℃ for 3.0 h, was adopted as photocatalyst, the best degradation ratio of Acid Red B (C.I. Carmosine 14) dye could be obtained under sunlight irradiation. This phenomenon can be explained by the effect of mixed crystal. In general, the anatase phase TiO_2 powder mainly absorbs the ultraviolet light, and then the photocatalytic degradation of organic pollutants could occur. And that the rutile phase TiO_2 powder hardly shows the photocatalytic activities, because the electrons and holes photogenerated by the ultraviolet or visible light irradiation recombine easily. Only when a rutile phase TiO_2 layer is about to form on the surface of anatase phase TiO_2 particles at 600℃ [25], the photogenerated electron-hole pairs can be separated efficiently. So the Co-doped and Cr-doped mixed crystal TiO_2 powders both show the highest photocatalytic activity at 600℃ treatment temperature. However, for undoped mixed crystal TiO_2 powder, the highest photocatalytic activity appears at 500℃ treatment temperature.

3.5. Effect of metal ion doping content on photocatalytic activity of metal-doped mixed crystal TiO_2 powders

The effect of metal ion doping contents on the photocatalytic activity of metal-doped mixed crystal TiO_2 powders was studied in this work. From Fig. 5, it is observed that the highest degradation ratio of Acid Red B (C.I. Carmosine 14) dye is obtained when the Co^{3+} doping content is about 0.25 mol %. Whether above or below this value, the degradation ratios both decrease. The following reasons can be used to explain this phenomenon. The appropriate Co^{3+} doping amount can effectively trap the photogenerated electrons and then reduce the recombination chance of photogenerated electron-hole pairs. Hence, it can obviously enhance the photocatalytic activity of mixed crystal TiO_2 powder. Below this value, the Co^{3+} ions are too few to show this effect. While above this value, many Co^{3+} ions can cover the active sites on the surface of the mixed crystal TiO_2 particles. What's more, the distance between two traps become so near that the electrons and holes can recombine more easily. Thus, only when the Co^{3+} content is appropriate, the Co-doped mixed crystal TiO_2 powder can show the highest photocatalytic activity. However, for Cr^{3+} doped mixed crystal TiO_2 powder, the Cr^{3+} ions in the TiO_2 lattice may act as a new recombination center of photogenerated electron-hole pair. Thus, the photocatalytic activity becomes lower than that of undoped mixed crystal TiO_2 powder once the Cr^{3+} ions are added.

3.6. The ion chromatograms and HPLC of Acid Red B (C.I. Carmosine 14) dye solutions during photocatalytic degradation

The ion chromatograms of Acid Red B (C.I. Carmosine 14) dye solutions during degradation are shown in Fig. 6. They clearly prove that the sulfur and nitrogen heteroatoms in Acid Red B (C.I. Carmosine 14) dye molecule are gradually converted to SO_4^{2-} and NO_3^- inorganic anions during photocatalytic degradation. It can obviously be seen that the peak intensities belonging to SO_4^{2-} and NO_3^- anions increase along with

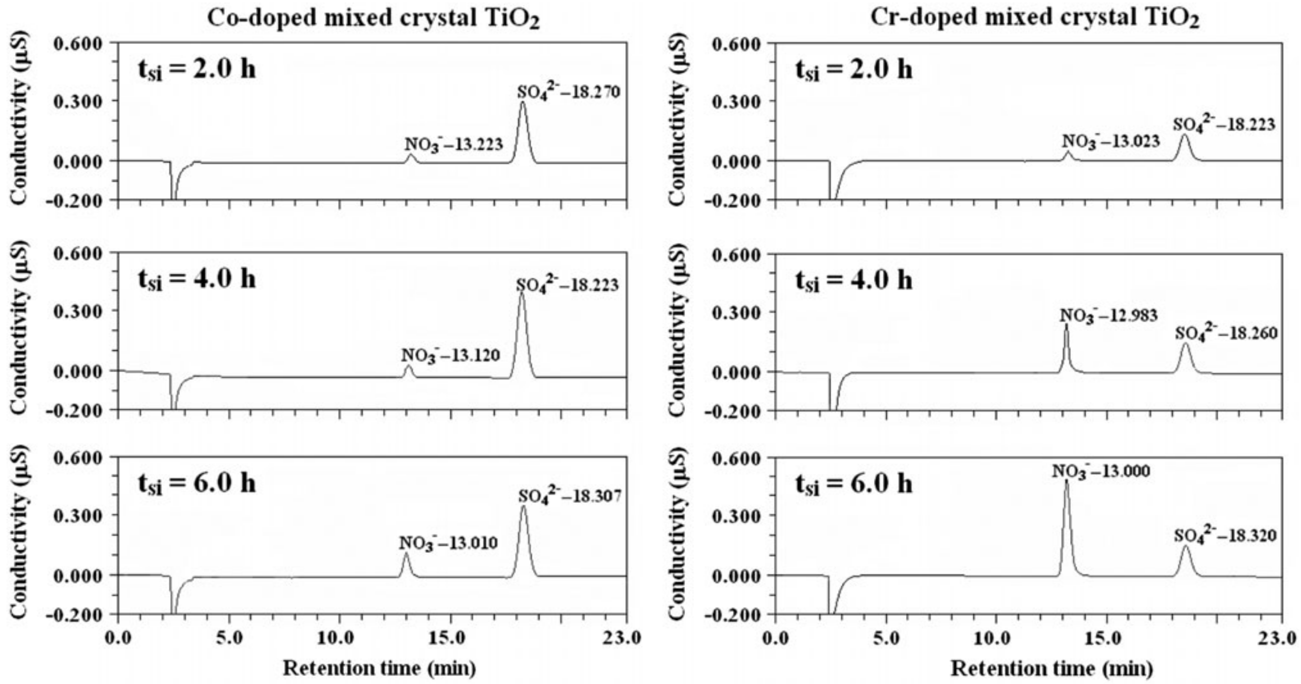

Fig. 6. The ion chromatograms of Acid Red B (C.I. Carmosine 14) dye solutions with sunlight irradiation time (experimental condition of photocatalytic degradation: 10.0 mg/L Acid Red B (C.I. Carmosine 14) dye solution, 1,000 mg/L metal-doped mixed crystal TiO_2 powder, pH 6.0 solution acidity, and 50 mL total volume).
t_{si}: sunlight irradiation time.

elevating irradiation time. However, the peak intensities of SO_4^{2-} and NO_3^- anions for the Co-doped mixed crystal TiO_2 powder seem to be much higher or lower than the corresponding ones for Cr^{3+} doped mixed crystal TiO_2 powder, respectively. This phenomenon is due to the differences between doped Co and Cr ions. Because of the high catalytic activity of the Co-doped mixed crystal TiO_2 powder, under sunlight irradiation the nitrogen atoms in Acid Red B (C.I. Carmosine 14) dyes can be turned into various nitrogen species, in which the NH_4^+ cations and a series of nitrogen oxides (NO_x) as well as nitrogen gas (N_2) can not appear in ion chromatograms [26]. Generally, the amount of stable SO_4^{2-} anions can be used to illuminate the degradation degree of Acid Red B (C.I. Carmosine 14) dye. Therefore, as shown in Fig. 6, through the peak intensities of SO_4^{2-} anions the Co-doped mixed crystal TiO_2 powder shows the higher photolytic activity than Cr-doped mixed crystal TiO_2 powder.

3.7. Effect of sunlight irradiation time on degradation of Acid Red B (C.I. Carmosine 14) dye

Fig. 7 shows the comparison of degradation ratios of Acid Red B (C.I. Carmosine 14) dye in the presence of (0.25 mol %) Co-doped, (0.25 mol %) Cr-doped, and undoped mixed crystal TiO_2 powders under sunlight irradiation at different moments. It is observed in Fig. 7(a) that the degradation ratios all mount up fleetly along with the increase of sunlight irradiation time. Naturally, the photocatalytic activity of (0.25 mol %) Co-doped mixed crystal TiO_2 powder is obviously better than those of (0.25 mol %) Cr-doped and undoped mixed crystal TiO_2 powders. The degradation ratio using (0.25 mol %) Co-doped mixed crystal TiO_2 powder reaches 84% through 6.0 h sunlight irradiation, but they are only 52 and 69%, respectively, for using (0.25 mol %) Cr-doped and undoped mixed crystal TiO_2 powders at the same sunlight irradiation time. And that, all Acid Red B (C.I. Carmosine 14) dyes are almost degraded under sunlight irradiation combined with (0.25 mol %) Co-doped mixed crystal powder after 8.0 h, while the corresponding degradation ratios are 62 and 78%, respectively, for (0.25 mol %) Cr-doped and undoped mixed crystal TiO_2 powders under the same condition.

In addition, in order to infer the degradation rates of Acid Red in these three systems, the reaction kinetics were studied. Here, the data of $-\ln(C_t/C_0)$ for first-order reaction as a function of sunlight irradiation time (t_{si}) was calculated. In fact, as shown in Fig. 7(b), the results indicate that all calculated values of $-\ln(C_t/C_0)$ are approximately linear with the sunlight irradiation time all through. That is, the photocatalytic

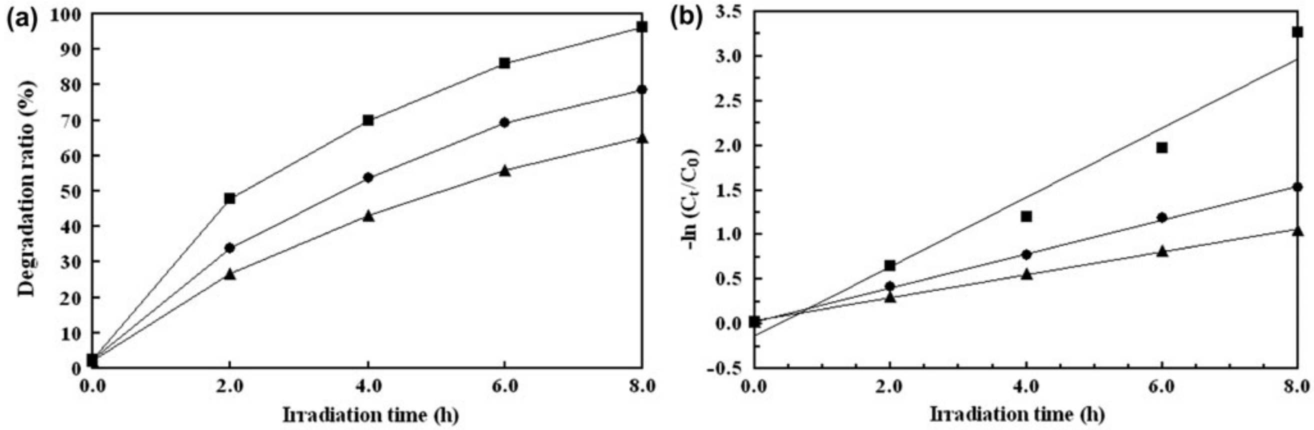

Fig. 7. Effect of irradiation time (a) and reaction kinetics (b) on degradation of Acid Red B (C.I. Carmosine 14) dye (experimental condition of photocatalytic degradation: 10.0 mg/L Acid Red B (C.I. Carmosine 14) dye solution, 1,000 mg/L metal-doped mixed crystal TiO_2 powder, pH 6.0 solution acidity, and 50 mL total volume).
■: Co-doped mixed crystal TiO_2; ▲: Cr-doped mixed crystal TiO_2; and ●: undoped mixed crystal TiO_2.

degradation processes of Acid Red in these three systems conform to pseudo-first-order kinetics reactions. The rate constants are 0.3895, 0.1289, and 0.1894 h^{-1}, respectively. Thus, the order of degradation rates in these three systems can be judged as Co-doped mixed crystal TiO_2 > undoped mixed crystal TiO_2 > Cr-doped mixed crystal TiO_2.

3.8. Effect of solution pH value on degradation of Acid Red B (C.I. Carmosine 14) dye

The pH value of Acid Red B (C.I. Carmosine 14) dye solution was varied from 3.0 to 9.0 at 2.0 intervals and the influence on the photocatalytic degradation was reviewed. From Fig. 8 it is noticed that the best degradation ratios are all obtained when the pH value is about 3.0 for three kinds of prepared TiO_2 powders. As the pH value increases, the degradation ratios all decrease. Particularly, between pH 5.0 and pH 7.0, the degradation ratios decrease quickly. Of course, it is clearly observed that at any pH value the degradation ratio for (0.25 mol %) Co-doped mixed crystal TiO_2 powder is better than those for (0.25 mol %) Cr-doped and undoped mixed crystal TiO_2 powders. As well known, in general, the point of zero charge (P_{ZC}) of various TiO_2 powders is about pH 6 [27]. Above this pH value, the surfaces of TiO_2 particles are negatively charged which adsorb cationic species readily, while below this pH value they are positively charged which adsorb anionic species easily [28]. Some ionic dyes having negative charges after ionization can be adsorbed on the surface of TiO_2 particles below P_{ZC}. For the presence of sulfonate anion, the Acid Red B (C.I. Carmosine 14) dye ion in aqueous solution is negatively charged in a wide pH range, so it can be close to or adsorbed on the surfaces of TiO_2 particles easily when the solution pH value is below P_{ZC}. Out of question, that is helpful for the photocatalytic degradation of Acid Red B (C.I. Carmosine 14) dye. Therefore, the degradation ratios of organic pollutants like Acid Red B (C.I. Carmosine 14) dye in aqueous solution decrease with the increase of pH value above the P_{ZC}.

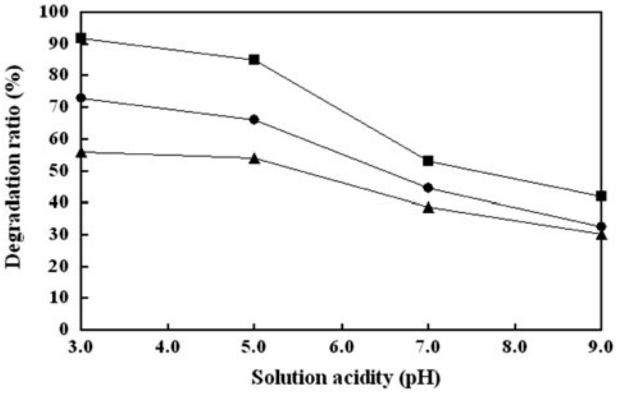

Fig. 8. Effect of solution pH value on degradation of Acid Red B (C.I. Carmosine 14) dye (experimental condition of photocatalytic degradation: 10.0 mg/L Acid Red B (C.I. Carmosine 14) dye solution, 1,000 mg/L metal-doped mixed crystal TiO_2 powder, 50 mL total volume, and 6.0 h sunlight irradiation).
■: Co-doped mixed crystal TiO_2; ▲: Cr-doped mixed crystal TiO_2; and ●: undoped mixed crystal TiO_2.

3.9. *Effect of initial concentration on degradation of Acid Red B (C.I. Carmosine 14) dye*

For photocatalytic reaction, the initial concentration is an important factor. As shown in Fig. 9, in order to study the influence of initial concentration on photocatalytic degradation, a series of Acid Red B (C.I. Carmosine 14) dye solutions with different concentrations were used ranging from 5.0 to 25.0 mg/L. It is found that the degradation ratios utilizing (0.25 mol %) Co-doped, (0.25 mol %) Cr-doped, and undoped mixed crystal TiO_2 powders all increase slightly from 5.0 to 10.0 mg/L. And then they all decrease with the further increase of concentration. In fact, that is just the accepted law in photocatalytic degradation reaction using TiO_2 powder as photocatalyst. The increase of Acid Red B (C.I. Carmosine 14) dye concentration is not propitious to the transmission of sunlight into the inner solution, and subsequently decreases the light intensity that arrives at the surface of TiO_2 particles. Thus, for very high concentration of Acid Red B (C.I. Carmosine 14) dye solution the degradation ratio decreases obviously.

3.10. *Possible process of photocatalytic degradation of Acid Red B (C.I. Carmosine 14) dye*

Possible process of photocatalytic degradation of Acid Red in the presence of metal-doped mixed crystal TiO_2 powder under visible light irradiation is proposed. When the treatment temperature reached 600℃, a rutile phase TiO_2 layer formed on the surface of metal-doped anatase TiO_2 particles. Additionally, a very thin crystal interphase or anticipated transition state should be yielded between anatase and rutile phase TiO_2 at the same time. When TiO_2 absorbs a photon of energy that is equal to or greater than its energy band gap, an electron may be promoted from the valence band to the conduction band, thus, generating the electron-hole pair [29]. Because of comparatively narrow energy band gap ($E_{bg} < 3.2$ eV), the rutile phase TiO_2 layer could be excited firstly by visible light. And then the photogenerated electrons transfer from valence-band to conduction-band of the rutile phase TiO_2 layer. Thus the electron-hole pairs are yielded synchronously. For the continuous irradiation of visible light or quantum tunnel effect of nanometer folium, these photogenerated electrons can penetrate the thin crystal interphase and enter the conduction-band of anatase phase TiO_2 part. Moreover, due to the presence of Cr^{3+} ions, the photogenerated electrons will be captured at once and then the Cr^{3+} ions can be reduced to Cr^{2+} ions. Therefore, the photogenerated electrons and holes were separated completely. The holes directly oxidize the organic pollutants or indirectly degrade them through HO• radicals. Finally, the poisonous organic molecules could be converted to the CO_2 and H_2O molecules as well as other nontoxic inorganic ions. However, because of the strong reductive ability, the Cr^{2+} ions can easily be oxidized by holes. It will increase the photocatalytic activity of mixed crystal TiO_2 powder.

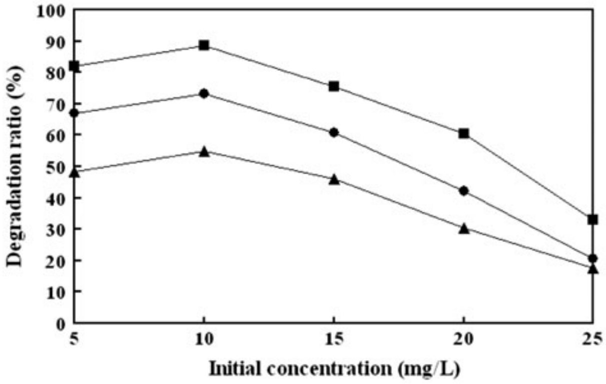

Fig. 9. Effect of initial concentration on degradation ratio of Acid Red B (C.I. Carmosine 14) dye (experimental condition of photocatalytic degradation: 1,000 mg/L metal-doped mixed crystal TiO_2 powder, pH 6.0 solution acidity, 50 mL total volume, and 6.0 h sunlight irradiation). ■: Co-doped mixed crystal TiO_2; ▲: Cr-doped mixed crystal TiO_2; and ●: undoped mixed crystal TiO_2.

4. Conclusions

The Co-doped, Cr-doped, and undoped mixed crystal TiO_2 powders were prepared by sol–gel and treatment methods. And the comparisons of their photocatalytic activities were conducted through the degradation of Acid Red B (C.I. Carmosine 14) dye in aqueous solution under sunlight irradiation. The results showed that the photocatalytic activity of Co-doped mixed crystal TiO_2 powder is better than those of Cr-doped and undoped mixed crystal TiO_2 powders. The Acid Red B (C.I. Carmosine 14) dye in aqueous solution with 10.0 mg/L concentration can be completely decomposed within 8.0 h under sunlight irradiation in the presence of (0.25 mol %) Co-doped mixed crystal TiO_2 powder. Thus, this improved method can be used to treat the dyestuff wastewater under sunlight irradiation effectively.

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