

TiO₂-ZrO₂ Preparation and Its Elimination Efficiency on Triclosan

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Abstract

Titania zirconia (TiO₂-ZrO₂) photocatalyst were successfully synthesized using the sol-gel impregnation method containing commercial titania and zirconium (IV) oxide chloride as precursor. X-ray powder diffraction was used to characterize the phases of the photocatalyst, the rutile type was not detected even at 700°C. Photocatalytic degradation of triclosan was employed to test photoactivity of the catalyst on different molar ratios of Ti/Zr and calcination temperatures, respectively. TiO₂-ZrO₂ catalysts were more photoactivity than commercial TiO₂. Photodegradation efficiency of removing triclosan was close on molar ratio of Ti/Zr 1/20 and 1/1 and the highest removal was observed at 500°C.

Keywords: TiO₂-ZrO₂, triclosan, photocatalysis.

1. Introduction

Triclosan(5-chloro-2-(2,4-dichlorophenoxy) phenol, TCS), known as one of pharmaceutical and personal care products (PPCPs), has been widely used in a variety of consumer products, including tooth paste, detergent, soap, shampoos, skin care creams and cosmetics[1, 2]. Triclosan, which is hard to be decomposed against hydrolysis, has been detected in the aquatic environment (waste water, surface water and lake sediments) [3-5] and even be found in human milk and fatty tissues [6, 7]. In addition, carcinogenic dioxins might arise in the manufacture of triclosan reported by the Environmental Protection Agency of United States, and it has been reported that dioxins can be formed when the triclosan-contaminated natural waters are exposed to the sunlight [8]. Due to its widely existing and carcinogenic effects, the presence of triclosan in the aquatic environment and its potential adverse impacts on ecological and public health has been concerned increasingly. The removal of triclosan from natural waters has drawn extensive interests [2, 9-11].

Adsorbents (activated carbon, zeolites, soil, etc.), thermal destruction and biodegradation as traditional methods, which are used to remove recalcitrant organic chemicals, suffer the drawbacks such as requiring long period of treatment, large energy input or only transferring the contaminants from one phase to another. Photocatalysis, one of advanced oxygen technologies and promising technologies, can provide a cost-saving alternative method removing organic substrates from water [12-14]. Titanium dioxide (TiO₂) is applied in heterogenous photocatalysis because of excellent physical and chemical properties. Under UV irradiation, TiO₂ can be photoactivated, and generate hydroxyl radicals (\cdot OH) which can mineralize most organic compounds for its strong oxidation. Titanium and zirconium have similar physicochemical properties as they are in the same group (IVB) and both oxides TiO₂ and ZrO₂ are n-type semiconductors with similar physicochemical properties. The combination of TiO₂ and ZrO₂ has been investigated for its advantages such as strong acid-base, extended specific surface area and mechanical strength [15-17].

The paper reports the physicochemical properties of TiO_2 - ZrO_2 prepared by sol-gel impregnation and the influence of the molar ratio and calcination temperature of $\text{TiO}_2/\text{ZrO}_2$.

2. Experiment

2.1 Reagents

Triclosan(5-chloro-2-(2,4-dichlorophenoxy)phenol, TCS 97%), titania (TiO_2 99.8% 40nm anatase) and zirconium (IV) oxide chloride (ZrO_2 36%) were purchased from Aladdin (Shanghai China). Ammonia and sodium hydroxide were purchased from Sinopharm Chemical Reagent Co., Ltd (China) and used in the experiments were of analytical grade.

2.2 Preparation of ZrO_2 - TiO_2 particles

ZrO_2 - TiO_2 catalysts on different Ti/Zr molar ratios (1/20, 1/4, 1/2 and 1/1) were prepared by means of sol-gel impregnation method using $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and TiO_2 (99.8% 40nm anatase) as precursors[18]. The ZrO_2 - TiO_2 binary semiconductor was obtained by precipitation of TiO_2 on $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ solution in deionized water, using ammonia as precipitating agent which was dropped slowly into the suspension until at pH 10. The gel was filtered and washed with plenty of deionized water for eliminating Cl^- , and finally dried in oven at 110°C overnight and calcined at 500, 600 and 700°C for 2h respectively. Samples were named TZ500-a, TZ500-b, TZ500-c and TZ500-d (500 means calcined at 500°C , a, b, c and d are Ti/Zr molar ratios 1/20, 1/4, 1/2 and 1/1, respectively).

2.3 XRD characterization

X-ray powder diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffraction spectrometer (Germany) using Cu K_α radiation. Data were collected from $2\theta=10^\circ \sim 90^\circ$ in a step-scan mode (step 0.02° , time per step 0.1s). Qualitative phase analysis was performed with software MID Jade 5.0[19].

2.4 Photocatalytic experiments

Experiments were carried out in a home-made laboratory reactor (500ml) using a high pressure 250 W Hg lamp (250W \times 365nm, TianMai Light Source Co., China) as light source. Aqueous solution 400ml volume of TCS, pH value of 10.8~11.2 was selected to increase the solubility of TCS with 1mol/L sodium hydroxide, was filled in the reactor. The initial concentration of 50 mg/L TCS was used in the experiments. Before each experiment, 40mg catalyst was dispersed in the solution and stirred with magnetic stirrer for 20min to reach adsorption equilibrium in the dark prior to illumination. All the experiments were performed at ambient temperature (18°C). At pre-selected time intervals, 2ml aliquots were taken from the suspension and put into glass vials.

The concentration of TCS was analyzed by high performance liquid chromatography (Agilen1200-HPLC, Agilent Co., America) consisting of Diode Array Detector. The mobile phase methanol/ water (90:10, v/v) with a shim-pack reverse phase column (250mm \times 4.6mm) were used. Injection volume was 20 μl , a flow rate was 1ml/min, and 35°C column temperature and detection wavelength of 280 nm was applied. All the samples collected were filtered through micro syringe filters (0.45 μm).

3. Results and Discussions

3.1 X-ray powder diffraction (XRD)

XRD patterns of samples calcined at 500-700°C on 1/2 molar ratio of Ti/Zr were shown in Fig.1. Both of anatase and zirconia phase were observed; the diffraction peak area of zirconia was larger for its higher amount. No trace diffraction of rutile structure was detected for ZrO₂ doped TiO₂ after heat treatment at 700°C. Zirconium as a stabilization agent could suppress the transformation from anatase to rutile when the calcination temperature increased to 600 and 700°C, while the temperature of anatase to rutile was 550°C-600°C [20, 21]. Zr⁴⁺ is considered to retard the transformation by forming interstitial Ti³⁺ cations that suppress atomic transport in the anatase structure [22].

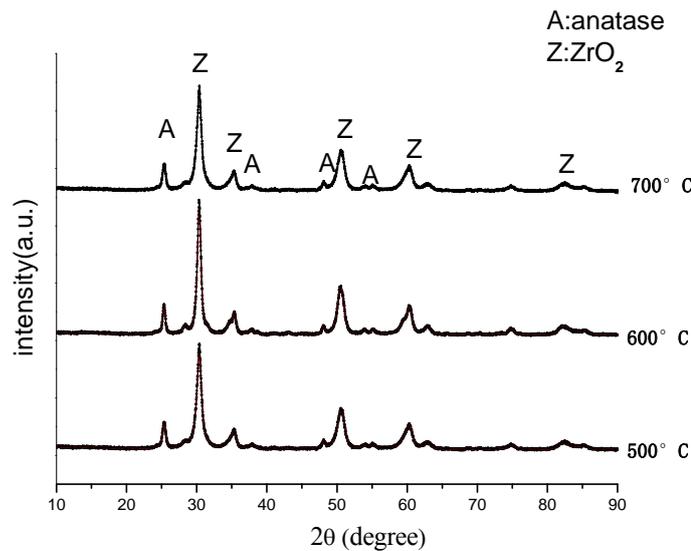


Fig.1. XRD of TZ-c photocatalyst calcined at 500, 600 and 700°C.

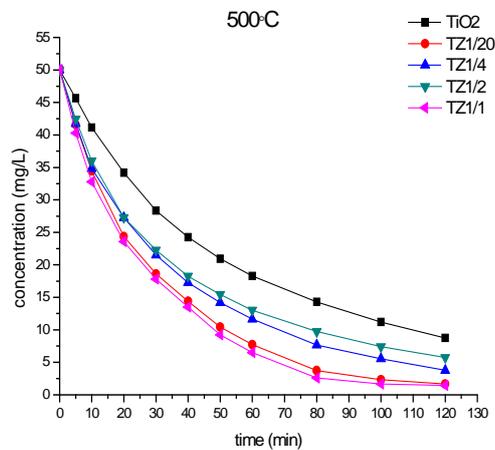
3.2 Photocatalytic experiments

The experiment of photocatalytic degradation of TCS in aqueous suspensions of the TiO₂-ZrO₂ photocatalysts at various calcined temperatures and Ti/Zr molar ratios were shown in the Fig.2. The photocatalytic behavior of commercial TiO₂ was measured as a reference. It could be clearly seen from Fig.2a, Fig.2b and Fig.2c that all the degradations of TCS by composite semiconductors were better than that of commercial TiO₂ via modified by ZrO₂. In the TiO₂ photocatalytic degradation, the concentration of TCS dropped by 63.4% after UV irradiation for 60min. As for ZrO₂-TiO₂ photocatalytic process, TZ500-d sample exhibited a much higher efficiency in photocatalytic degradation. The concentration decreased rapidly during 120 min from 50.09 mg/L to 1.43 mg/L, and 87.02% TCS was removed after 60 min and nearly completely degraded in 120 min of irradiation.

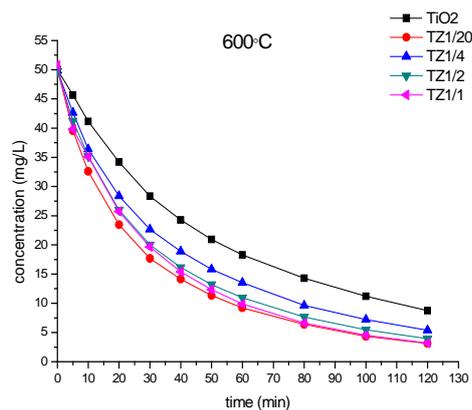
The removal of TCS decreased with the decreasing of Ti/Zr molar ratio was shown in the Fig.2. ZrO₂ could raise the surface area of the samples that had been reported [23]. The surface area was becoming smaller that could provide surface sites which could adsorb reactants molecules such as TCS and hydroxyl group which was favor for forming hydroxyl radicals ($\cdot\text{OH}$) to enhance photocatalytic activity was becoming smaller. Simultaneously, ZrO₂ could be a charge separation centre to enhance the charge trapping and inhibit the e^-/h^+ pair recombination [23]. However, the degradation efficiency on Ti/Zr 1/20 was higher than Ti/Zr 1/4 and 1/2. It might be two possible reasons for this phenomenon: one was that surface sites was provided by doping with much more amount of ZrO₂ that was mentioned above; the

other was that the recombination of electron and hole was decreased doping excess amount of ZrO_2 . It is known that separation of electron and hole might take place in the binary oxide of TiO_2 and ZrO_2 [24]. In this process, electrons and holes produced both by TiO_2 and ZrO_2 would be recombined with each other to reduce the photocatalytic activity. However, comparing with Ti/Zr 1/4 and 1/2, there was much more electrons and holes left to enhance the photocatalytic efficiency after recombined with that produced by TiO_2 in the condition of excess amount of ZrO_2 .

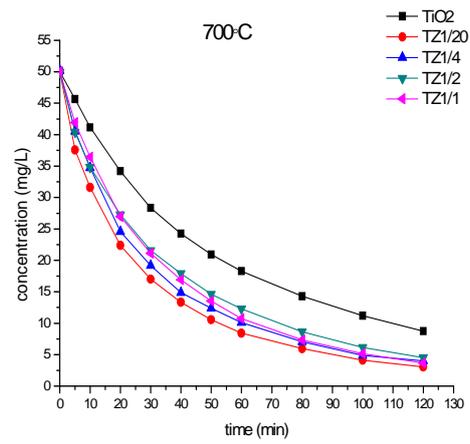
The plots of $\ln(C_0/C)$ versus irradiation time are shown in Fig.2b, and they give straight lines. TCS photodegradation followed the pseudo-first-order kinetics with respect to different samples of Ti/Zr molar ratios that demonstrated by experimental data and the rate constant and coefficient were shown in table 1. The calcination temperature also influences the photocatalytic efficiency. The degradation of TCS was a little decreasing with the elevation of calcination temperatures at the same Ti/Zr molar ratio, which maybe was because of the growth of particle size that had been proved by XRD.



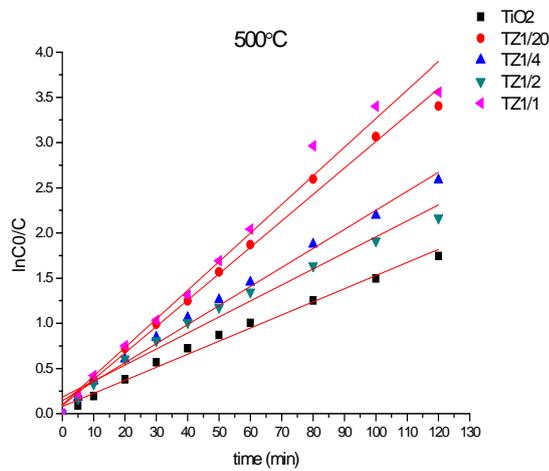
(a)



(b)



(c)



(d)

Fig.2. photocatalytic degradation of TCS and kinetic of photodegradation of TCS at photocatalyst calcined at 500°C (a) 600°C (b) 700°C (d) kinetics at 500°C

Table 1. Kinetic constant for sample at different calcination temperatures

Sample	Calcination temperature (°C)	Rate constant (k)	R ²
TiO ₂	18°C	0.0145	0.9893
TZ-1/20	500°C	0.0292	0.9932
	600°C	0.0225	0.9776
	700°C	0.0225	0.9776
TZ-1/4	500°C	0.0210	0.9912
	600°C	0.0182	0.9842
	700°C	0.0182	0.9842
TZ-1/2	500°C	0.0177	0.9741
	600°C	0.0208	0.9823

	700°C	0.0208	0.9823
TZ-1/1	500°C	0.0316	0.9819
	600°C	0.0227	0.9872
	700°C	0.0227	0.9872

4. Conclusions

Triclosan, as one of PPCPs have been detected in aquatic environment and have been harmful for human health. Photocatalysis, as one of promise advanced oxygen technologies, has good degradability for triclosan.

Photocatalyst of TiO₂-ZrO₂ was successfully prepared by wet impregnation method. A series of Ti/Zr molar ratios at different calcination temperatures was applied to photocatalytic degradation of target contaminant. The synthesized photocatalysts were more efficient than commercial TiO₂. The most photoactive catalyst was calcined at 500°C at 1:20 and 1:1 molar ratio of Ti/Zr, respectively

ZrO₂ doping TiO₂ can improve the ability of photodegradation probably due to mutually working effects that the surface area are enhanced by doping with Zr⁴⁺ which is also as a charge separation centre for electrons trapping to improve the degradation of tricolsan.

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