Synthesis of TiO_2 Nanoparticles via a Ti(IV) Complex with Stearic Acid and the Photocatalytic Activity for Organic Oxidation

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The nano-sized particles of TiO_2 were prepared by thermal decomposition of titanium(IV) tetrabutanoxide complex with stearic acid at 450 ℃ in the air. It was observed that the amount of stearic acid, used initially for the complex synthesis in 2-propanol at 25 ℃, had great influence on the physical properties of the prepared TiO_2 including crystal structure, the particle size, surface area and the adsorption capacity for organic substrate of a textile dye X3B in water, and thereafter the photocatalytic activity for the dye oxidation. Some samples displayed lower adsorption capacity for the organic substrate in water than a TiO_2 of Degussa p25, but higher photocatalytic activity for the organic oxidation. Possible reason for the observed difference was discussed in the text.

Keywords titanium dioxide, stearic acid, synthesis, photocatalysis

Introduction

Heterogeneous photocatalysis of titanium dioxide has been studied extensively as an alternative technology for the destruction of various organic pollutants in water.[1-4] For large-scale application, the development of a highly efficient photocatalyst becomes nowadays the central issue. According to the postulated mechanism, the oxidation reaction occurs quasi-bimolecularly between organic substrate adsorbed and charge carriers on the illuminated catalyst surface. Increasing the photocatalyst surface area per gram will be one of the most apparent means to improve the photocatalytic efficiency.[2,3]

In recent years special attention has been paid to the synthesis of a mesoporous TiO_2 as for higher surface area.[5,6] However, it is not easy to remove the template of C_{16}-surfactant without damage of the mesoporous structure. In the present study, the TiO_2 samples were prepared by thermal decomposition of a precursor complex of titanium(IV) tetrabutanoxide with stearic acid ($C_{17}H_{35}CO_2H$, STA).[7] The use of STA in the synthesis was to complex the Ti via carboxyl group, and to form a micellar structure of the complex via alkyl group, so that the TiO_2 with a porous structure might be resulted from STA removal. The mesoporous TiO_2 was not obtained in this study, but it was observed that not only the physical properties of the prepared TiO_2 could be regulated by the amount of STA used in the synthesis, but also the photocatalytic activity for the oxidation of a textile dye X3B in water changed correspondingly.

Experimental

Synthesis and characterization

The TiO_2 samples were prepared using a similar method reported by Sato *et al.*[7] In a typical synthesis, 26.4 g of stearic acid was dissolved into 50 mL of 2-propanol, and then 21 g of titanium(IV) tetrabutanoxide (Shanghai Chemicals, 99%) dissolved in 50 mL of 2-propanol was slowly added at room temperature. After

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about two weeks in an open container, the mixture was separated by decantation. The white precipitate was then calcined at 450 ℃ in an open air for 8 h. Following this procedure, a set of TiO_2 powder with the different molar ratio of STA to Ti from 0.2 to 1.6 in the precursor mixture was prepared, and is labeled here as prepared TiO_2 from **T1** to **T6** (Table 1).

Table 1 Physical parameters of prepared TiO_2 **T1—T2** and a commercial TiO_2 of Degussa p25 (**PT**)

Samples	STA/Ti molar ratio	BET (m^2/g)	Anatase (%)	Particle size (nm)	n^s (mol/g)[a]	K (dm^3/mol)[a]
T1	0.2	10	9	32	–	–
T2	0.5	3	75	32	–	–
T3	0.8	37	88	24	1.9×10^{-5}	9.2×10^{3}
T4	1.0	51	96	21	2.5×10^{-5}	7.9×10^{3}
T5	1.2	64	100	17	3.3×10^{-5}	7.3×10^{3}
T6	1.6	86	100	14	3.6×10^{-5}	9.8×10^{3}
PT[b]	–	50	84	24	4.5×10^{-5}	2.4×10^{4}

[a] n^s and K are the amount of X3B adsorbed and the Langmuir adsorption constant, respectively. Both the parameters were estimated from the adsorption isotherms of X3B on TiO_2 in water (Fig. 2). [b] **PT** is the TiO_2 of Degussa p25.

The crystal structures of the samples were determined by powder X-ray diffraction (XRD). The pattern was recorded on a Philips X' Pertmpd X-ray diffractometer using Cu $K\alpha$ radiation at 45 kV and 40 mA. The relative content of anatase phase present in the sample and the crystallite size were estimated from the diffraction intensity and the peak width, respectively. Porous structures of the samples were analyzed by N_2 adsorption at 77 K on an automatic analyzer of ASDI RXM-400, and the BET surface area was calculated using four point method. The results are all collected in Table 1, together with the adsorption parameters for organic substrate of X3B in water.

Dark adsorption and photocatalysis

The adsorption of reactive Brilliant Red X3B (98%, Jining dye manufacture of Shandong Province, China) on TiO_2 from aqueous solution was determined in the dark by mixing 50.0 cm^3 of X3B solution at various initial concentration (C_0) with a fixed weight (0.050 g) of the TiO_2 catalyst. The suspension was shaken in the dark at a constant rate overnight and then filtered through a membrane filter (pore size 0.45 μm, Shanghai Xingya). The absorbance of the filtrate at 540 nm was measured to determine the equilibrium concentration (C_2^b), and the decreased concentration ($\triangle C_2^b = C_0 - C_2^b$) used to calculate the amount of equilibrium adsorption, n_s^2, in the number of dye moles adsorbed per gram of TiO_2.

For the photocatalysis study, the same suspension as above was also set up at the same time. After being equilibrated in a Pyrex reactor overnight, the suspension was irradiated for 15 min by the UV light of wavelength at $\lambda \geqslant 320$ nm from a 75-W Xenon lamp (USHIO, Japan) operated at 5.00 amps by a LPS-200 lamp controller (PTI, US). Then the suspension was filtered and analyzed at 540 nm on a 722 spectrophotometer (Shanghai Analytical Instruments). In the filtrate after irradiation the substrate concentration ($^*C_2^b$) of X3B was obtained. The $^*C_2^b$, C_2^b and C_0 were used in the text for the reaction rate calculation (note that the $^*C_2^b$ decreased linearly with the irradiation time up to 50 min).

Results and discussion

Characterization

It has been generally accepted that the photocatalytic activity of TiO_2 is determined by the recombination rate of e^-/h^+ pair, on which the structural properties of the catalyst would have great influence.[1-5] For this concern, the prepared TiO_2 sample were characterized first by X-ray powder diffraction. Fig. 1 shows the XRD patterns for all the samples calcined at 450 ℃. It can be seen that the diffraction changes regularly from sample **T1** to **T6**. By quantitative analysis (Table 1), this trend is correlated with an increased amount of stearic acid

(STA) initially employed in the precursor complex synthesis. Below the STA/Ti molar ratio of 1.0, the prepared TiO_2 is a mixture of anatase and rutile, and the content of anatase increases continuously from 9% in the sample **T1** to 96% in **T4** (Table 1). Above the STA/Ti molar ratio of 1.0, the TiO_2 becomes totally a pure anatase (**T5** and **T6**).

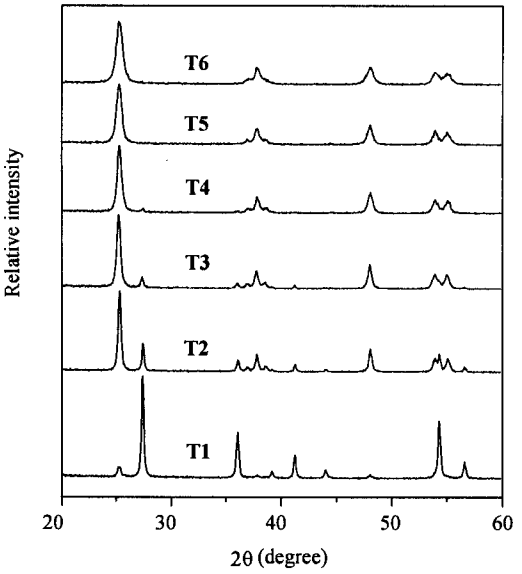

Fig. 1 XRD patterns of the prepared TiO_2 samples from **T1** to **T6**.

Two different pathways may be involved in the formation of the TiO_2 particles. In an organic solvent of 2-propanol, titanium butanoxide itself would hydrolyze into rutile,[8] whereas the Ti(IV) complex formed with STA is decomposed into anatase at 450 ℃ (the conversion of anatase phase into rutile at 450 ℃ is generally impossible). Following this mechanism, the structure transition occurring at STA/Ti ratio of 1.0 (Table 1) is a reflection that the complex is the type of 1:1. Any excess of STA in the mixture would exist as a separate phase, suppressing the sintering of the TiO_2 particles formed during Ti-STA decomposition and STA burning. This is evidenced by the particle size decreasing from **T4** to **T6** (Table 1). In the case of STA/Ti ratio less than 1.0, the content of rutile phase is decreased with the increased STA from **T1** to **T4**, expectedly. It is also seen that the particle size of anatase crystallites decreases regularly from **T1** to **T4** (Table 1), for that, we have no reasonable interpretation at present.

The specific surface area of the samples was less than 100 m^2/g (Table 1). This is unexpected in the view of initial purpose employing the STA as a template for mesoporous material synthesis. The micellar structure formed by Ti-STA complex in 2-propanol may be collapsed after the STA removal at 450 ℃. As evidenced by the linear response of surface area with the particle size, the prepared TiO_2 has also no substantial porous structure. Subsequently, the increased surface area with the amount of STA can be attributed to the decreased particle size. There are three samples (**T4** — **T6**), whose surface area is larger than that of the standard TiO_2 photocatalyst, Degussa p25 (**PT**).

Dark adsorption

The adsorption properties of the catalyst are important to the surface photoreaction and the reaction rate determination as well. The adsorption capacity of the catalyst for the organic substrate of X3B in water was thus measured at room temperature and pH 6. Fig. 2 demonstrates the adsorption isotherms for all the prepared TiO_2, where the amount of equilibrium adsorption, n_2^s, is plotted as a function of equilibrium concentration in the bulk solution, C_2^b. It can be seen that the adsorption increases from **T1** to **T6** regularly. This adsorption order is in agreement with the increased order of N_2 adsorption in gas phase, and with the decreased order in the particle size. The smaller particles of TiO_2 are expected to have a larger surface area and more sites for X3B to be adsorbed on. As we have shown previously,[9] the adsorp tion of X3B on TiO_2 can be described by the Langmuir

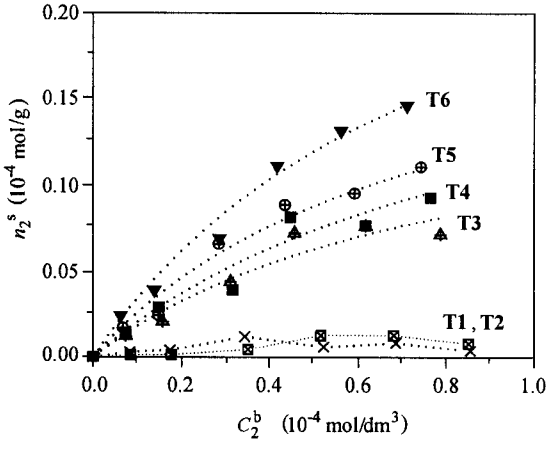

Fig. 2 Adsorption isotherms of X3B on prepared TiO_2 from aqueous solution at 25 ℃ and pH 6.

model with an equation of $n_2^s = n^s KC_2^b/(1 + KC_2^b)$, where n^s is the total amount of adsorption sites and K is the Langmuir adsorption constant. Since the adsorption parameters of n^s and K are important to the rate determination in photocatalysis, these parameters for the samples from **T3** to **T6** have been calculated, and are summarized in Table 1.

Photocatalysis

All the photocatalysis experiments using the light of $\lambda \geqslant 320$ nm were performed only after the dark adsorption equilibrium was achieved. Since no photodegradation of X3B was observed in the absence of TiO_2, any observed decrease of X3B concentration in the aqueous phase ($\triangle^* C_2^b = C_2^b - {}^*C_2^b$) was attributed to the TiO_2 photocatalysis. As we have demonstrated recently,[9] however, the real initial rate, R, of X3B photodegradation includes not only the initial rate, R_{app}, of X3B disappeared in the aqueous phase, but also the initial rate of X3B concentration decreased on the catalyst surface. (The method[9] involves the use of the adsorption parameters shown in Table 1 and the concentration term of C_0, ${}^*C_2^b$ and C_2^b, respectively). Fig. 3 shows the real initial rate, R, as a function of initial equilibrium concentration of X3B, C_2^b, where for samples **T1** and **T2** the apparent initial rate R_{app} is used instead of R because it is difficult to calculate R due to the poor adsorption (Fig. 2).

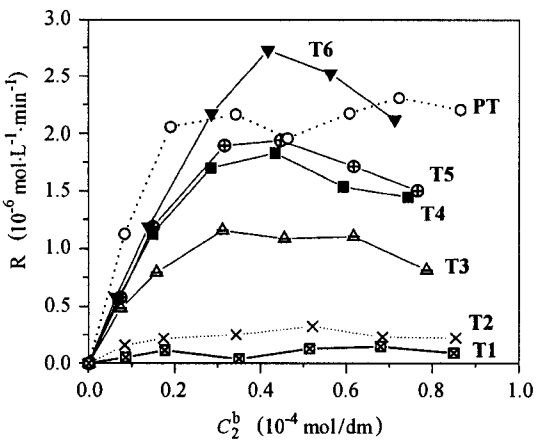

Fig. 3 Real initial rate of the photocatalytic degradation of X3B as a function of the initial equilibrium concentration over prepared TiO_2 (**T1**—**T6**) and a TiO_2 of Degussa p25 (**PT**, open circle), where the rate for **T1** and **T2** are the apparent initial rate (see the text for the details).

It can be seen that for each catalyst the initial rate increases with the initial equilibrium concentration in the early stage, and then it decreases somewhat for most of the samples. The latter has been attributed to the screening effect of the adsorbed dye on the surface,[9] which cuts off part of the UV light and slows down the photocatalytic reactions (note that for X3B in aqueous solution there is a strong absorption band centered at 540 nm with ε 1.38×10^4). Among the prepared catalysts the relative rate of X3B disappearance increases regularly from the sample **T1** to **T6**. For sample **T6**, the activity is even higher than that (open circle) of **PT** (an internationally standard photocatalyst).

The explanation for the photoactivity increasing regularly from sample **T1** to **T6** must take the structural properties into account. Apparently, the change in activity is consistent with all the sequences in surface area, the particle size, and the adsorption capacity toward organic substrate in water. However, the factors determining the photoactivity are complicated, and often interfere with each other.[10-13] For example, the photocatalytic activity of pure TiO_2 has been shown to increase with surface area,[2] the anatase content in the solid,[11] the crystallinity,[12] the surface hydroxyl groups and the adsorbed oxygen,[15] and an optimal particle size of 11 nm for the maximum photocatalytic activity has been evaluated recently by Zhang *et al.*[14] In all the cases, the separation of the electron/hole pairs and their transfer to chemical substrates at the semiconductor surface are very important.[2] For the present case, we conclude that the increased activity from **T1** to **T1** is mainly attributed to the increased content of anatase phase in the sample, even though the surface area and the X3B adsorption on the catalyst increase and the particle size decreases accordingly (Table 1). For other two samples of **T5** and **T6**, which are all pure anatase (Table 1) and possess a similar crystallinity (Fig. 1), the higher activity of **T6** than that of **T5** is due to its larger surface area, and the adsorption ability (K in Table 1) as well.

The question appears for understanding the special performance of Degussa p25 (**PT**). As shown in Fig. 3, the profile of the initial rate R *vs.* C_b^2 on **PT** is obviously different from those for all other prepared TiO_2. There have been several reports with aims to specify the outstanding performance of Degussa p25. Some researchers suggested that the mixed phase of anatase and rutile (Table 1) was responsible for the predominant

photoactivity of Degussa P25,[13] while others did not agree.[14] Here it can also be seen that **T3** has a similar ratio of anatase and rutile to **PT** (Table 1), but its photocatalytic activity is much lower than that of **PT** (Fig. 3). It means the phase composition is not the main factor contributed to **PT**'s special performance. The possible interpretation seems related to the Langmuir adsorption constant (K) of **PT**, that is the largest among all the catalysts listed in Table 1. Definitely the confinement of the target organic substrate to the catalyst surface would be beneficial to efficient charge transfer and suppress the recombination of electron/hole pairs, and then the organic substrate adsorbed more strongly on the catalyst would be more easily photodegraded. In this regard, the primary substrate of X3B and its photodegraded intermediates would be more efficiently disappeared on **PT** than on all prepared catalysts except **T6**. This may be also the reason why the screening effect of the adsorbed dye on **PT** is not much predominant (similar observation[9] for three commercial photocatalysts can be now understood by this new point of view).

The higher photoactivity of **T6** than that of **PT** can be attributed to its pure anatase phase and a reasonable particle size of 14 nm (Table 1). The disagreement of its higher surface area (BET) with lower adsorption capacity (n^s) than that of **PT** is related to the difference between surface area and total adsorbing sites, since the former is measured by N_2 adsorption and the latter is determined by X3B adsorption in water at monolayer coverage. The same interpretation is applicable to the difference between **PT** and **T5**, even though **T5** has a larger surface area. From here it can be seen that the surface area is not the only factor determining the relative photoactivities among different catalysts.

As a conclusion, it has been shown that the structural properties of the prepared TiO_2 can be easily controlled by the amount of STA added into the starting complex. The role of STA in the synthesis is to form a STA-Ti complex of type 1:1, producing TiO_2 particles of anatase, while without STA the titanium butanoxide is hydrolyzed to rutile in 2-propanol. Additional STA would exist as a separate phase in the mixture, and suppress the sintering of the TiO_2 particles formed during Ti-STA decomposition and STA burning. Because of the regular changes in the structure properties, the prepared TiO_2 displays a regular response in the adsorption toward organic substrate in water, and thereafter the activity for the organic photodegradation. Special photoactivity of Degussa p25 has been attributed newly in this report to its strong affinity toward the organic substrate being photocatalytically oxidized. Since the factors influencing the photocatalytic reaction are complicated, this report shows mainly a new method to prepare the TiO_2 photocatalyst with a controllable structure property, especially the pure anatase and larger surface area with probably less surface defects.

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