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Enhanced photocatalytic activity of supported TiO_2: dispersing effect of SiO_2

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Abstract

The physical and photocatalytic properties of the TiO_2 loaded on a unique silica using a TiO_2 sols, which was prepared by the hydrolysis of titanium *n*-butoxide in water ($pH = 1.1$) containing different alcohols and alcohol concentration, have been examined. Compared to the bare TiO_2 prepared in parallel, all the supported TiO_2 showed a higher photoactivity for the oxidation of acetophenone in water. The supported catalyst were mainly anatase crystallites of smaller size, and had a slightly higher adsorptivity toward the organic substrate. Upon the change of alcohols and alcohol concentration in the sol–gel mixture, the supported TiO_2 exhibited different response from the bare TiO_2 in the crystal structures and photoactivity. In addition, the supported TiO_2 showed a higher photoactivity on a silica of smaller particle size than on the silica of larger particles. The results suggest that the dispersion effect of silica is operative, which could be the basic role of any porous support for the TiO_2 photocatalysis. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Titanium dioxide; Photocatlysis; Silicon dioxide; Dispersion effect

1. Introduction

TiO_2 photocatalysis has been studied worldwide as a potential technique for the water treatment [1–3]. In this system TiO_2 functions as a photocatalyst, and upon the illumination by the light of wavelength equal or smaller than 350 nm, many organic pollutants (alcohols, phenols, aromatics, surfactants, dyes, and pesticides) can be completely decomposed into carbon dioxide and corresponding inorganic anions. While the TiO_2 suspension has been employed in most of the studies, the supported TiO_2 on a stationary support is more likely to be used in any commercial application of this technique because of its easier recovery of TiO_2 particles from the purified effluents.

The supported TiO_2 on a porous solid of silica, alumina, an activated carbon, clays and zeolites has been studied [4–12], and in most cases these catalysts show a higher phototocatalytic activity than the parent TiO_2 prepared in parallel for the oxidation of organic pollutants in water. The authors have ambiguously attributed this enhanced photoactivity to the increased effective surface area of the supported semiconductor particles, and to the increased adsorption of organic substrates on the catalyst surface (carbon, silica, and ZSM-5) [6–8], and as well as to the effective separation of the photogenerated electrons and holes by the electric field of the zeolite framework [7–10]. From these results, however, one common feature may be true that for a variety of any porous supports the basic role is the dispersion effect to the formation of TiO_2, although the adsorption and the charged framework of zeolite could be another important factors influencing the photocatalytic processes. Answer to this question could be instructive to the further search of an appreciate support for TiO_2 photocatalyst.

The purpose of present work is to rule out the dispersion effect. Silica has been selected as a unique support since it has been used widely in industry and does not possess a charged framework, but a moderate hydrophobicity. The experiment was designed to examine how the TiO_2 colloids, prepared under different conditions by a sol–gel technique, affects the formation of the supported TiO_2 and thereafter the photocatalytic activity for the oxidation of acetophenone in water, and to evaluate the difference performed by the silica of different particle size. All the results have been compared to those of the TiO_2 prepared in parallel, and suggest that the dispersion effect of silica is operative.

2. Experimental section

The supported TiO_2(20% w/w) samples were prepared by mixing a titania sol with the powder of silica (Shanghai

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Fongcheng Chemical Manufacture) for 1 h, and the solid after the removal of solvent was heated at 120°C overnight and finally calcined at 450°C in open air for 6 h. The TiO_2 sol was synthesized by the hydrolysis of titanium *n*-butoxide (Shanghai Chemicals Supplier, 98%) in acidified water. Typically, 29 g of $Ti(but)_4$ dissolved in 10 ml of alcohol was added slowly into 200 ml of water containing 1.2 ml of concentrated nitric acid, and the mixture was then fluxed for 8 h. The final TiO_2 sol appeared milky and was used as the TiO_2 source for the preparation of supported TiO_2 catalysts. A parallel TiO_2 powder was also prepared without addition of support under the same synthetic conditions as the supported sample. This procedure was always followed, except when noted otherwise in the text.

The photocatalytic activity of various catalysts was evaluated by measuring the loss of acetophenone (Shanghai Chemicals Supplier, 99%) from the aqueous phase. A round-shaped glass reactor containing 0.500 g of the supported catalyst or 0.100 g of TiO_2 powder and 100 ml of acetophenone solution (50 ppm) was stirred in the dark for 1 h, and then irradiated through a Pyrex glass filter by a high-pressure mercury lamp (375 W, Beijing P. E.). Temperature of the suspension was kept at 20 ± 1°C in a thermostatic water bath, and total irradiation was 1 h for each sample in the comparison runs. After irradiation, small aliquots of the suspension were withdrawn by syringe, filtered through a Millipore filter membrane and analysed on a JASO HPLC equipped with a UV-detector and a YWG-C18 column. The eluent consisted of methanol and water at a volume ratio of 30 : 70, and the detection wavelength was 240 nm. The percentage of the photocatalytic degradation of AP was then calculated by $(C_1\text{–}C)/C_1$, where C_1 was the concentration of AP in bulk after the dark equilibrium and before the irradiation, while C was the concentration after the irradiation.

The light intensity of the mercury lamp was measured by a ferroxalate actinometry. Since the lamp emits at several wavelengths 365, 405, 435 and 547 nm with a relative area (A_i) of 25.5%, 12.2%, 29.3% and 33.0%, respectively, the total intensity per second in the range of 365–547 nm was calculated by a formula of $I_{\mathrm{total}} = n_{\mathrm{Fe}^{2+}}/\sum A_i\Phi_i$. The intensity at 365 nm, effective to TiO_2 photocatalysis, was then corrected by $A_i I_{\mathrm{total}}$ to be 5.03×10^{-7} einteins $\cdot s^{-1}$. Powder X-ray diffraction patterns were recorded on a X' Pertmpd X-ray diffractometer using a Cu Kα anode as the radiation source. The crystallite size was estimated by using the Scherre equation.

3. Results and discussions

3.1. Effect of alcohols

It has been known that the photocatalytic efficiency of TiO_2 is greatly influenced by its crystal structure, particle size, surface area and crystallinity [1,3,9]. It would be then interesting to examine how the preparation variables effect the properties of the TiO_2 when loaded on a support. For this purpose, we prepared a series of TiO_2 sols by the hydrolysis of titanium *n*-butoxide in an acidified water, using different alcohols as a co-solvent. This TiO_2 sol was then loaded into a unique support of silica, followed by calcination at 450°C.

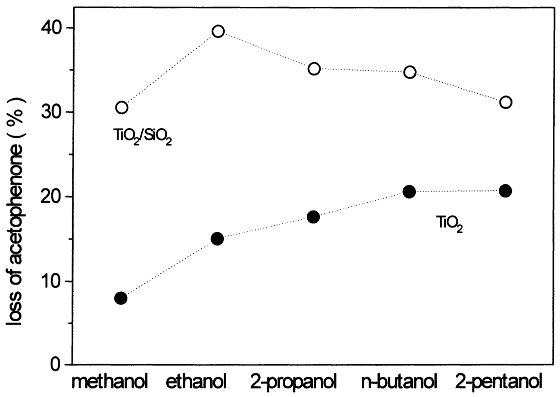

Fig. 1. The photoactivity of the supported TiO_2 on silica and the bare TiO_2 prepared with different alcohols for the photodisappearance of acetophenone in water.

Fig. 1 shows the effect of different alcohols on the activity of supported TiO_2, and TiO_2 prepared in parallel. All the supported TiO_2 have a higher photoactivity than the TiO_2 prepared in parallel, as reported before. However, the changes in photoactivity with the alcohol is different in both the sets of samples. The photoactivity of the bare TiO_2 is gradually increased when the solvent in the preparation of TiO_2 sol change from methanol to 2-pentanol, while the activity of supported TiO_2 photocatalyst shows an initial increase from methanol to ethanol and then decreases gradually to 2-pentanol. Obviously the presence of alcohol has influenced the hydrolysis of the titanium butoxide, even though its amount added in the mixture was quite small (alcohol : water = 1 : 20 v/v). The results for the supported TiO_2 may suggest that there exist some interactions between the particles of TiO_2 colloids and SiO_2 support during the loading processes.

This effect was also found in the XRD analysis of the samples (Fig. 2, the peak at $2\theta = 26.5°$ is due to silica diffraction). The alcohol affects not only the crystal structure of the TiO_2 produced, but also the particle size. The bare TiO_2 contains both anatase and rutile phases (diffraction at $2\theta = 25.3°$ and 27.3°, respectively). Upon the solvent change from methanol to 2-pentanol, the content of anatase increases from 68% to 91%, also with a decrease in the particle size from 11.6 nm to 10.5 nm. When the TiO_2 is loaded on silica, however, only the anatase diffraction can be seen and the crystallite size is further decreased from 7.5 nm to 6.7 nm. During the hydrolysis of titanium *n*-butoxide, alcohol as a co-solvent will participate in the ligand exchange and influence the diffusion of the positive-charged $Ti(OH)_x(OR)_y{}^{n+}$ species as well. Since methanol has a stronger polarity and lower viscosity than 2-pentanol, it will

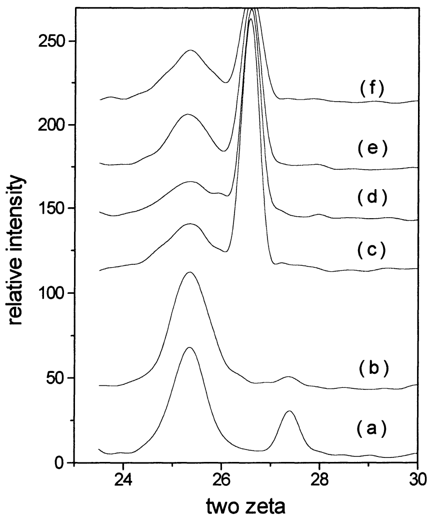

Fig. 2. XRD patterns of the bare TiO_2 (a, b) and the supported TiO_2(c–f). The co-solvent used for the preparation of TiO_2 sol was methanol (a, c) and 2-pentanol (b, d). (e) and (f) is the TiO_2 supported on B-SiO_2 and A-SiO_2, respectively, prepared with ethanol as a co-solvent. The relative intensity at $2\theta = 25.3^\circ$ from (a) to (f) is 73, 80, 31, 26, 37, and 34, respectively. The higher intensity means a higher crystallinity of anatase in the sample.

make the hydrolysis and the diffusion easier so that the TiO_2 particle in the colloids is larger than in 2-pentanol. During the heating treatment at 450°C, the TiO_2 particles must sinter each other to growth, but the size of the final pigments is determined mainly by its original size in the colloids. When silica particles are added in the suspension, the TiO_2 colloidal particles are well dispersed over the support particles because of their surface interaction so that during the calcination step the sintering between the dispersed TiO_2 particles is greatly depressed, resulting in a smaller particle than the bare TiO_2.

The increased photoactivity of bare TiO_2 from methanol to 2-pentanol suggests that the photoactivity is proportional to the decrease in the crystallite size, probably because of a larger driving force for charge transfer existed in a Quantum-sized TiO_2 of semiconductor particles [3,13], and is proportional as well to the increased anatase content in the sample (the rutile is less photoactive than the anatase [14] due to its low capacity to adsorb oxygen). However, an opposite was observed for the supported TiO_2 (Fig. 1). The photoactivity is decreased, instead of increased, from ethanol to 2-pentanol. This reminds us of the effect of amorphous TiO_2 on the photocativity, since the rutile phase was not found in the 20% TiO_2-loaded samples, which is mostly due to the phase depression by silica support [9]. It has been shown recently by Ohtani et al. [15] that amorphous TiO_2 has a negligible photoactivity as compared to the crystalline TiO_2. Because the polarity of alcohol co-solvent decreases in the order of methanol to 2-pentanol, there is higher portion of amorphous TiO_2 present in the TiO_2 sol when the co-solvent is substituted from methanol to 2-pentanol. Upon thermal treatment at 450°C, the amorphous TiO_2 is completely transferred into crystalline TiO_2 [15] so that the bare TiO_2 shows the photoactivity that is mainly determined by its crystallite size and anatase content. In the presence of silica particles, however, the initial TiO_2 particles are so dispersed that the degree of the sintering and crystallization as well of amorphous TiO_2 is suppressed, resulting in the decrease in both the particle size and the crystallinity of the anatase crystallites, as shown in Fig. 2. Both the factors are then responsible for the decline in photoactivity observed. In this respect, the adsorption of acetophenone has no relation with the decreasing in the photoactivity, as will be shown below.

The higher photoactivity of the supported TiO_2 than the bare TiO_2 is related to two factors: smaller particle size (thus a larger surface area) and a higher adsorptivity toward the organic substrate, both of which could be cooperative in making the photocatalytic reaction of organic substrate more accessible to the active sites on the TiO_2 surface. The dark adsorption of acetophenone (50 ppm of initial concentration) was 3% on bare TiO_2 ($1.0\,g\,l^{-1}$) and 8% on the supported catalysts ($5\,g\,l^{-1}$, corresponding to the net TiO_2 of $1.0\,g.\,l^{-1}$), and no regular increasing or decreasing in such an adsorption was observed among the catalysts for either bare TiO_2 set or the supported samples.

3.2. *Effect of alcohol content and SiO_2 particle size*

Since a small amount of alcohol addition influences the TiO_2 property, we then extended the experiment of using higher content of alcohol in the mixture and the result is shown in Table 1. The supported TiO_2 prepared by the alcohol of lower concentration has higher photoactivity, while the parent TiO_2 is almost the same. The increase of alcohol concentration in the mixture can slow down the hydrolysis, and the resulted sol will possess higher content of amorphous TiO_2. Because the amorphous TiO_2 can be completely transferred into crystalline TiO_2 at 450°C, the bare TiO_2 shows almost the same photoactivity. For the supported TiO_2, the amorphous TiO_2 phase will mainly remain even after calcination, since silica particles will suppress the crystallization of the highly dispersed amorphous TiO_2 into anatase crystallites. Therefore, a lower photoactivity for the prepared with the ethanol of higher concentration was observed.

Table 1
Percentage of acetophenone loss after irradiation of 1 h in the presence of TiO_2/SiO_2 and TiO_2 catalysts

Experimental condition	TiO_2	TiO_2/SiO_2
The sol was prepared with ethanol : water = 1 : 1	18	17
The sol was prepared with ethanol : water = 1 : 2	19	22
The sol was prepared with ethanol : water = 1 : 20	15	40

The TiO_2 sol was prepared with different concentration of ethanol at 100°C.

The particle size of silica support was then expected to influence the formation of the supported TiO_2 and hence the photoactivity. We examined two silica that have different particle size (B-SiO_2 is larger than A-SiO_2 as obtained from a sedimentary experiment), and loaded the silica with the same TiO_2 sol. Two loaded catalysts show a similar pattern of anatase diffraction (Fig. 2), but the crystallite size is larger on B-SiO_2 (8.3 nm) than on A-SiO_2 (7.7 nm). For the photocatalytic oxidation of acetophenone, TiO_2/A-SiO_2 catalyst made 40% of acetophenone loss in one hour, while the TiO_2/B-SiO_2 sample had 31% of acetophenone molecules disappeared. It is worth noting here that acetophenone has almost the same adsorption on these two catalysts (8%). The result of this section indicates that smaller particles of silica support makes the TiO_2 particles dispersed more efficiently, and thus the resulting catalyst has a higher photoactivity.

4. Conclusions

The present study has confirmed that for the photocatalytic elimination of organic pollutants in water the supported TiO_2 has a higher activity than the parent TiO_2 prepared in parallel. This enhanced photoactivity is related to the increased adsorption of organic substrate, to the increased surface area of the supported TiO_2, and perhaps to the absence of rutile phase in the supported samples. The latter two are closely related to the fact that the TiO_2 is highly dispersed over the porous silica. It can be predicted here that as a support for TiO_2 photocatalyst any porous support would function basically the same as a dispersing reagent, even though the other properties such as adsorptivity and the charged framework of the support can affect the photocatalytic processes [7–10]. The determining factor for the magnitude of the supported TiO_2 photoactivity will be the property of the original TiO_2 sol that is used for the TiO_2 loading. This report also suggests that the more efficient support for TiO_2 photocatalyst is the support of smaller particle size. However, the small particles of support will then cause another problem in the engineering of the catalyst separations.

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