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Journal of Photochemistry and Photobiology A: Chemistry 170 (2005) 7–14
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Photocatalytic decolorization of methyl orange in aqueous medium of TiO_2 and Ag–TiO_2 immobilized on γ-Al_2O_3

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Received 26 April 2004; received in revised form 5 July 2004; accepted 5 July 2004
Available online 25 August 2004

Abstract

TiO_2, synthesized through a sol–gel procedure with acetylacetone chelating agent, was immobilized on γ-Al_2O_3 and deposited with photoreduced Ag. The prepared catalysts were characterized and applied for decolorization of methyl orange (MO). The photoactivity of TiO_2/γ-Al_2O_3 is affected by the H_2O/Ti molar ratio applied in the sol–gel process. The optimal calcination temperatures of the TiO_2/γ-Al_2O_3 locate in the ranges from 723 to 773 K and 773 to 873 K as TiO_2 prepared with H_2O/Ti of 10 and 1, respectively. Incorporating photoreduced Ag to TiO_2/γ-Al_2O_3 leads to reduction reaction of methyl orange in addition to oxidation reaction, and yields a significant increment in decolorization efficiency. The optimal Ag load on TiO_2/γ-Al_2O_3 and dosage of Ag/TiO_2/γ-Al_2O_3 in the photodecolorization of methyl orange are about 1.0% and 1.0 g/L, respectively. The photocatalytic rate is proportional to the Ag load and catalyst dosage raised to the powers of 0.45 and 0.71, respectively.

Keywords: Photocatalytic; Methyl orange; Ag; TiO_2; γ-Al_2O_3

1. Introduction

Recently, photocatalytic processes have been receiving much attention, particularly for the complete destruction or mineralization of the toxic and non-biodegradable compounds to carbon dioxide and inorganic constituents in both water and gas phases [1–4]. Among the photocatalysts applied, titanium dioxide is the most popular one due to the peculiarities of chemical inertness, suitable bandgap energy, non-photocorrosion and non-toxic influence on the microorganisms, etc. Owing to the policies of efficient utilization of solar energy, high quantum efficiency and convenience of operation, the present researches of the photocatalytic processes have focused on the designs and constructions of new light energy sources, photochemical reactors, preparations of novel photocatalysts and their supports [1].

Irradiation of TiO_2 semiconductor by light with energy equal to or greater than its bandgap energy leads to excitation of an electron from the valence band to the conduction band. Charge separation is then formed. The electrons in the conduction band behave as a cathode and promote the reduction reactions of oxidized compounds with potentials positive to that of the lowest conduction band. On the other hand, positive holes (h^+) are generated in the valence band. The holes show high affinities for electrons and behave as an anode to oxidize the reduced compounds with potentials negative to that of the highest valence band or to oxidize the adsorbed H_2O or OH^- to hydroxyl radical ($HO^\bullet$). Hydroxyl radicals are very reactive neutral species, which react rapidly and non-selectively with the contaminants preadsorbed on titanium dioxide surface. Accordingly, $HO^\bullet$ is the chief oxidant for photocatalytic degradation in wastewater treatment [2,5].

In the past few years, titanium dioxide-suspended systems were widely applied for the photocatalytic processes. It revealed a fair photoactivity, but the separation of the finely powdered titanium dioxide from the slurry system was very difficult. Hence, the immobilization of TiO_2 on supports to improve the separated efficiency has attracted much attention.

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doi:10.1016/j.jphotochem.2004.07.012

However, the immobilization usually decreases the overall photoactivity of TiO_2 [1,6–8]. Also, the blue shift of the absorption band occurs with immobilization, and then decreases the utilization of solar energy [9,10]. Recently, binary metal oxides systems, such as TiO_2/SiO_2 [11–15], were investigated to enhance photoactivity. An analysis of these systems reveals that large surface area and preferential adsorption of the reacted molecules on SiO_2 will promote the photoactivity [12]. Additionally, Fu et al. [11] indicated that the surface acidity of TiO_2 increased with addition of SiO_2. These surface acidic sites were said to be in the form of stronger surface hydroxyl groups, which accepted holes generated by illumination and sequentially oxidized the adsorbed molecules and prevented recombination of electrons and holes. Therefore, the photoactivity increases, however, it needs to be further improved for commercial application.

Aluminum oxide, with high surface area and acidity, is widely used as catalyst's support. Kato [16] also pointed out that γ-Al_2O_3 was not harmful to the photocatalytic activity of TiO_2. Furthermore, introduction of platinum or silver to the titanium dioxide photocatalytic system can increase the photocatalytic efficiency [2,17–21]. Unfortunately, few reports concerned about the immobilization of TiO_2 on γ-Al_2O_3 with deposited metal [13,21]. Accordingly, TiO_2/γ-Al_2O_3 photocatalysts with and without photodeposited Ag are prepared and characterized by X-ray diffraction (XRD), UV-diffusion reflectance spectroscopy and FTIR. Finally, methyl orange is used as a probe for the photocatalytic decolorization due to the relatively high toxicity and complex structure, which both make it difficult to be treated by microorganisms.

2. Experimental

γ-Al_2O_3 (Merck) with a surface area and a pore volume of 162 m^2/g and 0.45 cm^3/g, respectively, was used as carrier. The particle size of the γ-Al_2O_3 was sieved to be in the range from 200 to 270 mesh. Titanium isopropoxide (TTIP; TCI, EP), acetylacetone (ACAC; Lancaster, EP), ethanol (Scharlace, 99.8%), HCl (Ferak, GR) and silver nitrate (Katayama Chem. Co., special grade) were all used as received. Methyl orange (MO; Merck) was dissolved in ultra pure water (Milli Pore Q^+) to a desired concentration. The pH of the solution was adjusted to the desired value by NaOH or HCl and measured by a pH meter (Suntex, SP-701). The prepared MO solution was stored in the dark and used within a week.

A 0.5 M solution of TTIP in ethanol was prepared; subsequently, ACAC was added to result a clear-yellow solution. A molar ratio of ACAC/TTIP = 1 was used. The solution was stirred at room temperature for 3 h. H_2O of pH 1.5 or 7.0, adjusted by HCl and NaOH, was added drop by drop to the solution under vigorous stirring, and the prepared TiO_2 were designed as A- and N-types corresponding to the acidic and neutral media, respectively. The molar ratio of H_2O/TTIP was a studied factor and changed from 1 to 20. This sol was stirred at room temperature for 3 h, after which γ-Al_2O_3 powder was added slowly with vigorous stirring. The final solution was kept on stirring at 323 K for 24 h. The solid samples were filtered, washed by water and dried in air at 373 K for 24 h, eventually calcinated at the desired temperature for 3 h. Then, the TiO_2/γ-Al_2O_3 proceeded photoreduction [22] with silver nitration to make $Ag/TiO_2/\gamma$-Al_2O_3 photocatalysts by an UV light source (Philip, HPI–T400 W).

The bonding structures of the prepared photocatalysts were analyzed by FTIR (Jasco, FTIR-410 with DR-81). XRD (Rigaku D/Max III.V) technique and UV-diffusion reflection spectroscopy (Hitachi, U3010) were applied to study the crystal type and absorption bandgap energy. The surface area and pore volume were determined by BET method (Micromeritics, ASAP2400).

The photoactivity test was conducted in a Pyrex glass reactor of about 80 mm in diameter and 100 mm in height. The reactor was provided with a water jacket to control the reaction temperature. The cover of the reactor had ports for sampling, a thermal meter, a gas disperser and a condenser. A 400 W medium pressure mercury lamp (Philip, HPI-T400 W) was used as the light source. A magnetic stirrer operated at 600 rpm was used to provide a good mixing.

At the beginning of a run, 300 mL MO solution was fed to the reactor, and then it was kept at 303 K. The desired amount of the photocatalyst was added, and oxygen or nitrogen was bubbled through the gas disperser into the reactor at 250 mL/min. After 2 h premixing, to attain the adsorption equilibrium of MO on the photocatalyst, the run was started by illuminating the light source. Samples were periodically taken from the reactor and analyzed by an UV–vis spectrophotometer (Perkin-Elemer, λ2).

3. Results and discussion

3.1. Characteristics of the prepared TiO_2/γ-Al_2O_3 photocatalysts

Fig. 1 depicts the XRD profiles of the pure γ-Al_2O_3 carrier and $Ag/TiO_2/\gamma$-Al_2O_3 photocatalysts. It appears that the TiO_2 is amorphous after calcination at 473 K, and γ-Al_2O_3 surface is almost covered by TiO_2, since the peaks near 38° and 46° belong to γ-Al_2O_3 and are severely suppressed. Increasing calcination temperature to 673 K transfers TiO_2/γ-Al_2O_3 to the anatase phase. Further increasing the calcination temperature to 973 K yields the rutile phase in addition to the anatase phase. The fraction of rutile phase increases with decreasing H_2O/Ti applied in the sol–gel procedure. Incorporation of Ag to TiO_2/γ-Al_2O_3 cannot alter the XRD patterns and reveals no Ag diffraction peak, which may be ascribed to little content. The crystal size of TiO_2/γ-Al_2O_3 increases from 15.7 to 25.2, 10.5 to 20.1 and 8.5 to 17.7 nm as the calcination temperature increases from 673 to 973 K with H_2O/Ti of 1, 10 and 20, respectively, as shown in Fig. 2. With lower H_2O/Ti ratio, TTIP is not completely hydrolyzed and leads to larger crystal size. Also, increasing calcination