

Modification of carbon-coated TiO₂ by iron to increase adsorptivity and photoactivity for phenol

B. Tryba^{a,b}, M. Toyoda^{a,*}, A.W. Morawski^b, M. Inagaki^c

^a Department of Applied Chemistry, Faculty of Engineering, 700 Dannoharu, Oita University, Oita 870-1192, Japan

^b Institute of Chemical and Environment Engineering, Technical University of Szczecin, ul. Pulaskiego 10, 70-322 Szczecin, Poland

^c Aichi Institute of Technology, Yakusa, Toyota 470-0392, Japan

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Abstract

Carbon-coated TiO₂ modified by iron, were prepared from TiO₂ of anatase structure and PET modified by FeC₂O₄. Catalysts were prepared by mixing powders of TiO₂ and modified PET and heating at different temperatures, from 400 to 800 °C under flow of Ar gas. High adsorption of phenol was observed on the catalyst heated at 400 °C, confirmed by FT-IR analysis. On this catalyst, fast rate of phenol decomposition was achieved by addition of small amount of H₂O₂ to the reaction mixture. Phenol decomposition proceeded mainly through the direct oxidation of phenol species adsorbed on the catalyst surface due to the photo-Fenton reaction. Iron-modified carbon-coated TiO₂ catalysts heated at 500–800 °C showed almost no phenol adsorption or oxidation.

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1. Introduction

High activity of carbon-coated TiO₂ photocatalysts for adsorption and decomposition of methylene blue in water has been reported. Some advantages of carbon coating of anatase particles were pointed out, the suppression of phase transformation from anatase to rutile at high temperatures, improvement of anatase crystalline structure resulting in high photoactivity, high adsorption of methylene blue on the catalyst surface and no interaction between anatase and organic binders (Tsumura et al., 2002a,b; Toyoda et al., 2003; Tryba et al., 2004a,b). It was proved from diffuse

reflectance spectroscopy measurements that, even after TiO₂ particles were coated by carbon, the carbon-coated anatase particles could work as the photocatalysts, although UV rays coming through the carbon layer were weakened (Tryba et al., 2004a,b). Photoactivity of these carbon-coated catalysts was found to depend on the pollutants that had to be decomposed (Tryba et al., 2004a,b; Toyoda et al., in press). Phenol decomposition on these carbon-coated TiO₂ catalysts was slower than that on the pristine TiO₂ without carbon coating (Tryba et al., 2004a). In the carbon-coated anatase, the pollutants have to be at first adsorbed into coated carbon layers and then to diffuse to the anatase surface. Slow diffusion of adsorbed phenol molecules to TiO₂ surface and also low adsorption were considered to be responsible for a low rate of phenol decomposition.

* Corresponding author. Tel./fax: +8197 554 7904.

E-mail addresses: tryba@cc.oita-u.ac.jp (B. Tryba), toyoda-22@cc.oita-u.ac.jp (M. Toyoda).

Adsorption is very important in the photocatalytic direct oxidation process, because low adsorption of the pollutants may result in their low decomposition (Tori-moto et al., 1997).

Oxygen-containing basic functional groups on the surface of activated carbon were reported to give a high phenol adsorption (Vidic et al., 1997). Especially at low concentrations of phenol solution the chemical structure of the carbon surface was pointed out to play a more important role in the adsorption process than microporous surface of carbon (Nevskaia et al., 2004).

In the present work, the modification of carbon-coated TiO₂ was performed by adding iron oxides onto carbon layer in order to increase the adsorption of phenol and through this, phenol decomposition. The phenol decomposition proceeded through the photo-Fenton process in the system with UV, H₂O₂ and Fe-heterogeneous catalyst as the Fenton reagent.

The Fenton reaction is a widely used and studied catalytic process based on an electron transfer between H₂O₂ and a metal acting as a homogeneous catalyst (Spacek and Bauer, 1995; Bauer et al., 1999; Fallmann et al., 1999; Canton et al., 2003; Neamtu et al., 2003; Shah et al., 2003; Franch et al., 2004; Pera-Titus et al., 2004; Rivas et al., 2004).

Mostly iron added as an iron salt has been used as the homogenous catalyst in photo-Fenton process, but disadvantage of using the homogeneous catalyst is that it cannot be retained in the degradation process. Therefore heterogeneous catalysis, replacing homogenous catalysts by heterogeneous metal supported ones, seems to be more interesting (Pera-Titus et al., 2004). Some Fe-supported catalysts were extensively used in photo-Fenton process, as reported in the literature (Arana et al., 2001; Crowther and Larachi, 2003; Guélou et al., 2003; Yuranova et al., 2004). In presented studies phenol decomposition proceeded through the photo-Fenton process on Fe-modified carbon-coated TiO₂ catalyst and also through the photocatalytic activity of TiO₂. Replacement of TiO₂ catalyst with Fe-modified carbon-coated TiO₂ can give some benefits, like better filtration of catalyst after photocatalytic process, high adsorption of adsorbate on the carbon surface and high decomposition rate due to the photo-Fenton reaction.

2. Experimental

Anatase-type TiO₂ of ST-01 (Ishihara Sangyo Co. Ltd, Japan) and poly(ethylene terephthalate) (PET) were used for preparation of catalysts. Powdered PET was suspended into the aqueous solution of FeC₂O₄ (PET/FeC₂O₄ = 10:1 g g⁻¹). Suspended PET in FeC₂O₄ solution was mixed with magnetic stirrer firstly in ambient temperature for around 20 h, and then at 100 °C until the water completely evaporated. After drying in oven

overnight, thus modified PET was mixed with TiO₂ in mass ratio of TiO₂/PET = 7/3. The powder mixtures (TiO₂-PET, TiO₂-PET modified by FeC₂O₄), were heated at temperatures from 400 to 800 °C in Ar for 1 h.

All samples were characterized by BET surface area, XRD, TG, FT-IR content of iron and OH[•] radicals formation under UV and UV/H₂O₂. BET surface area was determined from the adsorption isotherm of nitrogen at 77 K. XRD analysis was performed with using CuK α radiation. FT-IR spectra were recorded with a resolution of 4 cm⁻¹. Process of PET carbonization was analyzed by TG. Powdered PET and PET modified by FeC₂O₄ were heated in Ar atmosphere up to 400 °C with a rate of 10°/min and then were kept at this temperature for 1 h.

Adsorption capacity of phenol on the prepared samples was determined by suspending the catalysts in the phenol solution and stirring with a magnetic stirrer for 3 h in the dark. After adsorption, photodecomposition of phenol was performed under UV irradiation in the “batch mode” reactor equipped with 3 black light blue fluorescent lamps of 20 W power. Those lamps emit the light at wavelength range of 300–415 nm with maximum at 352 nm. Measured irradiation power flux of UV rays inside the reactor was 1.8 mW cm⁻². For each experiment, catalyst of 0.1 g was suspended in 500 ml of phenol solution with the initial concentration of 2.1 × 10⁻⁴ mol l⁻¹. pH of the reaction mixture was around 6.1. To accelerate the process of phenol decomposition, small amount of H₂O₂ (30 mol%) was added to the reaction mixture (1 ml per 1 l of phenol solution). The change in the phenol concentration was monitored by UV-VIS spectrophotometric method and also by high performance liquid chromatography (HPLC).

Cycling decomposition of phenol under UV and H₂O₂ was performed on the Fe-modified carbon-coated TiO₂ catalyst heat-treated at 400 °C. For those measurements, catalyst was mounted on the adhesive tape and fixed to the metal grid, which was placed inside the reactor. The amount of mounted catalyst was much lower than in the case when suspended solution of catalyst was used, 0.028 g per 500 ml of phenol solution with concentration of ca. 2.1 × 10⁻⁴ mol l⁻¹ and H₂O₂ (1 ml per l).

Content of iron in the catalysts (Fe²⁺ and Fe³⁺) was determined by digestion of catalyst in 5 ml of 6 M HCl for 3 h (Majcen, 1998) and final analysis on the UV-VIS spectrophotometer by using colorimetric method. For iron detection, very sensitive to Fe²⁺, 2,4,6-Tris(2-pyridyl)-1,3,5-triazine reagent was used. Each sample was analyzed at least three times and then the average value was calculated.

Analyses of OH[•] radicals formation on the surface of catalysts under UV irradiation and UV/H₂O₂ were performed by fluorescence technique with using terephthalic acid which readily reacts with OH[•] radicals to

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