



Preparation and photocatalytic properties of TiO₂-P25 film prepared by spray pyrolysis method



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ABSTRACT

TiO₂ films were synthesized by immobilization of Degussa P25 powders on stainless steel support by spray pyrolysis technique. After preparation, the films were annealed at different temperatures in order to obtain materials with different morphological, structural, and textural properties. The photocatalytic activity of obtained films was investigated by monitoring the degradation of arylazo pyridone dye. The results showed that with increasing annealing temperature the photoactivity of films decreased. A comparative photocatalytic activity of the synthesized films and corresponding commercial powders was evaluated under the same experimental conditions. Films generally showed lower photoactivity than powders, due to mass transfer limitations inside film layer, smaller surface exposure to light, and possible presence of metal ions in film layer.

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1. Introduction

Dye pollutants from textile industry can have harmful effects on environment and human health [1,2]. Therefore, cleaning aqueous solutions from dye contaminants is of great importance. Generally, traditional wastewater treatment methods can be broadly classified into chemical, biological, and physical-mechanical processes [3]. Major disadvantage of physical-mechanical processes is that they are not destructive, but only transfer the contamination from one phase to another thus causing secondary pollution. Biological treatment methods are ineffective for decolorization and degradation since most of modern dyes are rarely biodegradable under aerobic conditions [4,5]. Chemical destruction of dyes may be accomplished using chlorine or ozone, but these treatments have limited effect on carbon content and are not economically feasible [6,7].

In recent years considerable attention has been directed toward the photocatalytic processes due to their cost effective and energy efficient operation. In photocatalytic processes metal oxide semiconductors such as TiO₂, ZnO, CdS, ZrO₂, etc. [8–11] are used as photocatalysts. When these semiconductors are illuminated with

light consisting of wavelengths shorter than their band gap, the charge carriers (conduction band electrons and valence band holes) are formed, which are capable of initiating a wide range variety of chemical reactions.

The most widely used photocatalyst is TiO₂, due to its optical and electrical properties, low cost, chemical stability and non-toxicity. In photocatalytic tests TiO₂ is often used in its commercial Degussa P-25 powdered form (70% anatase and 30% rutile phase). The suspended systems (slurry type systems) usually show high photoactivity due to absence of mass transfer limitations. However, the drawback of these systems is the need for the separation of highly dispersed TiO₂ particles from water at the end of the process, which makes the process difficult, time consuming, and expensive. On the other hand, with immobilized systems, these limitations can be overcome. However, the use of immobilized systems also has its disadvantages. In these systems, the accessibility of the catalytic surface (reactive surface area) to the photons and the reactants is reduced [12,13]. Also, due to the increased diffusion length of reactant from bulk solution to the catalyst surface, external mass transfer is reduced, particularly at low fluid flow rate [14].

Different supports have been used for TiO₂ immobilization: glass [15,16], quartz [17,18], stainless steel [19], zeolites [20], etc. Among different methods used for thin films processing, such as anodic oxidation [21], plasma electrolytic oxidation [22], magnetron sputtering [23], electrodeposition [24], dip coating [25], etc.,

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spray pyrolysis method enjoys advantages of reduced production cost and process simplicity. In addition, this method offers great versatility due to the large number of adjustable process parameters such as: the substrate temperature, the type and concentration of precursor, the atomization technique, liquid and gas flow rates, spray geometry, etc. [26].

In our previous work [27], we have described in detail the immobilization of TiO₂ from colloidal solution on stainless steel by spray pyrolysis method and the evaluation of photoactivity of prepared films. In the current paper, we have tried to immobilize the commercial TiO₂ Degussa P25 on stainless steel by the same technique. After preparation, the films were annealed at different temperatures and characterized by X-ray diffraction (XRD), atomic force microscopy (AFM), UV–vis diffuse reflectance spectroscopy (UV–vis DRS), photoluminescence (PL), Brunauer, Emmett and Teller (BET) surface area measurements, and mercury intrusion porosimetry. The photoactivity of prepared films was evaluated and compared with photoactivity of corresponding powders. This comparison allowed realistic evaluation of the advantages and the limits of the investigated immobilized systems against slurry systems.

2. Experimental

2.1. TiO₂ film preparation

The spray pyrolysis apparatus and procedure for the film preparation is presented in detail in our previously published study [28]. Briefly, the sprayer consisted of a two-fluid glass nozzle (capillary end of the inner tube), having an inner diameter of 0.2 mm and outer glass tube. Commercial P25 TiO₂ (Degussa, Germany) was used for coating deposition. TiO₂ suspension (0.022 mol/L) was fed into the inner tube at a flow rate of 44 mL/h using a peristaltic pump. Atomization of TiO₂ suspension is achieved by air flow, introduced to the outer glass tube, with flow rate of 300 L/h. The whole sprayer was a part of home-made computer driven device that enabled nozzle movement at a chosen speed and direction. The distance between the nozzle and substrate was 4 cm, creating a spraying spot on the substrate of diameter of 2 cm. A stainless steel foil, Sandvik OC 404, with thickness of 35 μm and external surface area of 10 cm² (1 cm × 10 cm), was used as the substrate. The substrate temperature during the spraying was maintained by resistive heating. Without spraying, resistive heating creates a relatively uniform temperature over the whole surface of the substrate. The periodic motion of the nozzle during spraying decreased the substrate temperature due to high air flow. The initial temperature of the substrate was 460 °C, while at the center of the spraying spot the temperature dropped to about 100 °C. When the spraying spot moved from the targeted area, the temperature of the substrate was quickly reestablished to its initial value. This situation was continuously repeated over the substrate during the spraying. The nozzle movement was directed parallel to the longer rectangular side of the foil and after each pass, the nozzle pathway was shifted by 0.3 mm in the direction of the shorter rectangular side. The speed of the nozzle movement was 1 cm/s. The nozzle speed provided sufficient time for the deposited precursor drop to undergo several consecutive processes: solvent evaporation, precursor precipitation, drying, and film growth due to crystallization.

After preparation, the films were annealed at different temperatures (500 °C, 600 °C, and 700 °C) in a temperature programmable furnace. The resulted films were marked as F500, F600, and F700, where number designates the temperature of calcination. As prepared samples were used without calcination and marked with symbol F460.

2.2. TiO₂ film characterization

The total mass of catalyst deposited per unit area was determined by weighing the stainless steel foil before and after the catalyst coating [29]. Catalyst layer thickness (film thickness) was calculated based on the mass of deposited catalyst, percentage of anatase and rutile phase, and layer porosity.

The phase composition of films was obtained by XRD analysis using a Philips PW 1051 Powder Diffractometer with Ni filtered CuKα radiation. The patterns were measured in the 2θ range 20–90° with a scanning step of 0.05° and exposure time of 10 s/step. The surface topography and roughness of the samples were analyzed using an AFM (Veeco Instruments, model Dimension V). Micrographs were obtained in tapping mode under ambient conditions, using Tap300 tips (resonance frequency 300 kHz, force constant 40 N/m). Roughness data were obtained using diNanoScope software (version 7.0) and reported values are calculated mean values for a number of different measurements on samples obtained under the same preparation conditions. UV–vis DRS were obtained on an UV–vis spectrophotometer, Specord M40 Carl Zeiss. PL spectra were measured using a Horiba Jobin Yvon Fluorolog FL3-22 spectrofluorometer, combined with a Xe lamp as the excitation light source at room temperature. All the obtained spectra were corrected for the spectral response of the system. The porosity of the samples was examined by mercury intrusion porosimetry (Carlo Erba 2000 Porosimeter with a Macropores Unit 120). The BET specific surface area was determined by nitrogen adsorption at –196 °C on apparatus Sorptomatic 1990 Thermo Finnigen.

2.3. Methods for adherence stability assessment

The good adherence of the coatings to the support is essential for successful application of TiO₂ films. If the adherence of TiO₂ layers is not stable, the immobilized TiO₂ can easily detach from support and act as suspended TiO₂ particles, making the immobilization procedure meaningless. To test adherence stability, the TiO₂ films were flushed with water for 2 h, under the same experimental conditions as were used in photocatalytic tests (*T* = 30 °C, *V* = 100 mL). The adherence stability was quantifiably evaluated by the term “particle loss percentage”, which is equal to the ratio of peeled TiO₂ from support to the amount of immobilized TiO₂ (Eq. (1))

$$\text{particle loss percentage (\%)} = \frac{\text{SPC} \times V}{m_{\text{cat}}} \times 100, \quad (1)$$

where SPC is the suspended particle concentration in treated water, *V* is the total volume of aqueous solution, and *m*_{cat} is a mass of coated TiO₂ on support [30].

2.4. Photocatalytic activity

The photoactivity of prepared TiO₂ films was determined by monitoring the degradation of arylazo pyridone dye, 5-(4-sulphophenylazo)-6-hydroxy-4-methyl-3-cyano-2-pyridone. Dye was synthesized by the diazotization-coupling reaction. A detailed description of the dye synthesis and its structure confirmation were presented elsewhere [31].

The photocatalytic tests were performed in an open cylindrical thermostated Pyrex cell, diameter of 6.8 cm that corresponds to surface area accessible to light of 36.3 cm². An aqueous solution of arylazo dye (100 mL, 3 mg/L) was placed in a cell containing the immobilized TiO₂ samples, which were located 15 mm from the bottom of the cell by a self-made wire support. The thickness of the solution above the substrate was 10 mm. Photocatalytic experiments were done at temperature of 30 °C. The irradiation was performed using Osram Ultra-Vitalux lamp, with a power

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