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TiO_2 photocatalytic films on stainless steel: The role of Degussa P-25 in modified sol–gel methods

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Abstract

The role of Degussa P-25 loading (0–100 g/L) in the alkoxide sol was investigated for the synthesis of immobilized TiO_2 photocatalytic films on 304 stainless steel using the P-25 powder-modified sol–gel method (PPMSGM). The structural properties of the films (PPMSGFs) obtained after gel drying and calcination at 600 °C were examined using different materials characterization techniques including X-day diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The photocatalytic activities of films with good adherence to the stainless steel support were evaluated using 4-chlorobenzoic acid (4-CBA) as a model organic contaminant and UV-A radiation. The P-25 loading did not have a significant effect on the size of the crystallites in the films. However, increasing the P-25 loading in the sol resulted in an increase in (i) the amount of crystalline material retained on the support (i.e., for both anatase (1 0 1) and rutile (1 1 0) crystal phases); (ii) the number of grains (aggregates of P-25 particles and crystallites formed from the alkoxide sol); (iii) the number of pores in the film (in the range of 0–50 g/L); and (iv) the number of microcracks on the surface of PPMSGFs. On the other hand, increasing the P-25 loading in the sol resulted in a decrease in the size of grains on the surface of PPMSGFs. XPS analysis revealed the presence of Cr^{3+}, Mn^{3+} and Fe^{3+} on the surface of PPMSGFs as a result of diffusion of these species from the stainless steel support during film calcination at 600 °C. The concentration of these foreign species on the film surface decreased with an increase in the P-25 loading in the sol. Increasing P-25 loading in the sol yielded films with higher photocatalytic activity but a concentration of 50 g/L P-25 in the sol was found as the maximum for obtaining films with good adherence on the stainless steel support. Increase in the photocatalytic activity of the films with increasing P-25 loading in the sol was mainly attributed to the enhancement of the number of P-25 active sites exposed to the solution due to film morphology and surface characteristics and to the reduction in Cr^{3+} and Fe^{3+} concentrations on the surface of the films.

Keywords: Photocatalytic; Photocatalysis; TiO_2; Degussa P-25; Activity; Active sites; Structural property; Powder; Modified; Sol–gel; Coatings; Films; Immobilized; Water treatment; Water purification

1. Introduction

Titanium dioxide is an excellent photocatalyst and has been extensively tested in environmental applications dealing with water and air purification [1–8] and photochemical solar cells [9,10]. So far, TiO_2 photocatalysis has been proven to be effective for the degradation of numerous toxic organic contaminants in water and air [1–8]. In applications dealing with water purification, reactors utilizing the TiO_2 catalyst as immobilized films on an appropriate support have a unique advantage over reactors utilizing suspended TiO_2 powder. This is because the reactors based on catalyst immobilization eliminate the requirement for a filtration step to separate the catalyst in the treated effluent. This filtration step can be a tedious and costly process. Therefore, more and more studies are devoted to the design and development of highly active immobilized-type TiO_2 photocatalytic films [2–8].

The sol–gel method is considered as an effective approach for the preparation of immobilized TiO_2 films on various substrates [11–14]. In this method, heat treatment at higher calcination temperature is usually required to obtain the desired crystal phase and good adherence to the support (i.e., glass, stainless steel) [14]. However, a higher than optimum calcination temperature often leads to a significant reduction in the photocatalytic activity of TiO_2 films. This is mainly due

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to a reduction in surface area caused by crystal sintering and pore collapse as well as due to crystal phase transformation from anatase to rutile.

Initial research work by Balasubramanian et al. has demonstrated that incorporating 30 g/L Degussa P-25 powder into an isopropoxide sol followed by dip coating of a stainless steel substrate (3 0 4), drying, and calcination at 600 °C (i.e., defined as a TiO_2 powder-modified sol–gel method) can yield relatively thick TiO_2 films with enhanced photocatalytic activity, excellent adherence to the support and much higher hardness compared to those obtained using the unmodified sol–gel procedure [15,16]. More recently, Keshmiri et al. used a similar approach to synthesize TiO_2 powder modified-TiO_2 composite thick films (i.e., defined as CSG coatings) by incorporating 5% pre-calcined Degussa P-25 powder into a different type of titania sol followed by calcination of the film at 700 °C [17]. This kind of composite sol–gel (CSG) TiO_2-TiO_2 photocatalyst also exhibited high photocatalytic activity and excellent mechanical stability. Therefore, incorporating Degussa P-25 powder into a precursor titania sol showed to be a good strategy for developing high performance immobilized TiO_2 films with excellent mechanical stability [15–17].

In a previous study, Balasubramanian et al. reported results on the synthesis, characterization, and evaluation of TiO_2 films prepared by the P-25 powder-modified sol–gel method only for a P-25 loading of 30 g/L [15,16]. These results were very promising with respect to photocatalytic activity, morphology, and hardness of the films and encouraged further optimization of this P-25 powder-modified sol–gel (PPMSG) method for the synthesis of P-25 powder-modified TiO_2 films (PPMSGFs) immobilized on stainless steel.

Consequently, the objectives of this work are: (1) to investigate the effect of Degussa P-25 loading in the precursor sol on film crystallinity, strength of adhesion, hardness, morphology, thickness and pore structure as well as on the properties of TiO_2 particles in the film and (2) to evaluate the photocatalytic activity of these immobilized TiO_2 films. This is the first report on a systematic study of the role of Degussa P-25 loading in the sol using the PPMSG method. Here, we report results on the effect of P-25 loading on (i) the properties of TiO_2 films immobilized on stainless steel 304 and (ii) the photocatalytic activity of these films.

2. Experimental

2.1. Preparation of TiO_2 films with the P-25 powder-modified sol–gel method

Fig. 1 is a schematic of the steps for the preparation of TiO_2 films using the PPMSG method as originally reported by Balasubramanian et al. [15,16]. Commercial ultrapure titanium isopropoxide (TTIP, 97%, Aldrich,), isopropanol (i-PrOH, 99.9%, Fisher Scientific), diethanolamine (DEA, 99%, Fisher Scientific), and nanophase TiO_2 Degussa P-25 powder (50 m^2/g; 85–70% anatase + 15–30% rutile; mean particle diameter of 30 nm) were used for the preparation of the TiO_2 powder-modified sol. A 0.5 M solution of TTIP in i-PrOH was prepared and a certain amount of DEA was added to the solution to yield a DEA/TTIP molar ratio of 4. The solution was stirred at room temperature for approximately 2 h. Subsequently, water was added dropwise under vigorous stirring conditions. A molar ratio of H_2O/TTIP of 2 was used. A clear and stable sol was obtained using this process. The TiO_2 powder-modified sol was prepared by adding different loadings of Degussa P-25 powder into the sol. The powder was added slowly under vigorous stirring to minimize the formation of large agglomerates. A thick, white, viscous modified sol with suspended TiO_2 powder was obtained. Before dip coating a stainless steel support, this modified sol was stirred rapidly for more than 12 h to better disperse the P-25 in the sol. The uncoated stainless steel substrates were cleaned with ethanol and methyl ethyl ketone (99.8%, Fisher Scientific). The clean substrates were dried at 125 °C for 24 h. A dip-coating apparatus, equipped with an adjustable motor to control the pull-out rate, was used to dip in and pull out the substrate at a constant withdrawal velocity of 12.3 ± 0.5 cm/min. After dip coating was completed, the coatings were dried at room temperature for 24 h, and then placed into a multi-segment programmable high temperature furnace (Paragon Model HT-22-D, Thermcraft Inc., Winston-Salem, North Carolina) for calcination. The furnace temperature was incremented at a ramp rate of 3.0 °C/min until 100 °C; this temperature was held for 1 h. The temperature of the oven was subsequently increased at a ramp rate of 3.0 °C/min to a final temperature of 600 °C and was held at this value for one hour. Finally, the films were cooled naturally to room temperature (approximately a 15 h cooling period).

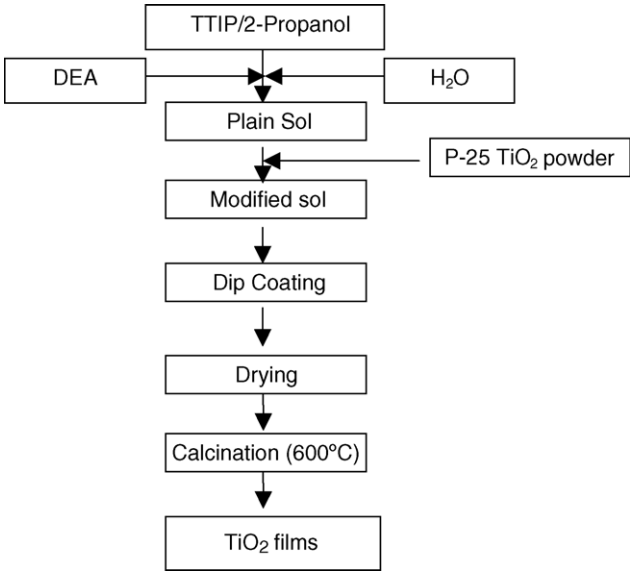

Fig. 1. Schematic of the preparation steps in the TiO_2 powder-modified sol–gel method.

2.2. Characterization of TiO_2 films

The crystal phase composition of the TiO_2 films coated on stainless steel was determined by X-day diffraction (XRD) using a Siemens Kristalloflex D500 diffractometer with Cu Kα