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Dynamics and characterization of an innovative Raschig rings–TiO_2 composite photocatalyst

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Abstract

This study presents a novel supported photocatalyst on Raschig glass rings using polyethylene-graft-maleic anhydride (PEGMA) as a functionalized copolymer to fix TiO_2 Degussa P25 on the glass rings. The immobilized photocatalyst presented long-term stability and could be reused during the photodegradation of 4-chlorophenol (4-CP) without a loss in activity. Aqueous solution of 4-CP (0.49 mM or 35 mg C/L) at their natural pH of 5.6 and TiO_2 loaded Raschig rings showed complete decomposition of 4-CP within 5 min under irradiation with a medium pressure mercury lamp. The dependence of the 4-CP photodegradation was investigated as a function of: (a) gas atmosphere of the reaction, (b) concentration of the electron acceptor (H_2O_2), (c) initial concentration of 4-CP (d) intensity of the applied light and (e) pH of the solution. By X-ray photoelectron spectroscopy (XPS), the percentage of the elements and the binding energies (BE) was determined for the main elements on the catalyst surface. Scanning electron microscopy (SEM) determined a coating with variable a thickness of ∼100–300 nm on the glass rings. This is equivalent to a TiO_2 Degussa P25 coating of ∼10 layers thick. By atomic force microscopy (AFM) the increase in the roughness radius of TiO_2 pores was observed from 37.6 nm before use to 46.4 nm after use. This indicates that the catalyst pore diameter has increased as observed by AFM. The BET area of the sample was observed to increase from 29.4 m^2/g for the catalyst before use to 40.7 m^2/g for the TiO_2 Raschig glass rings samples after use.

Keywords: TiO_2/glass rings; Catalyst synthesis; 4-CP degradation; XPS; AFM; EM

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1. Introduction

During the past decade, heterogeneous photocatalysis has been increasingly used in the preparation of fine chemicals and in water and air purification [1–3]. More than 1600 references have appeared during the last 10 years in reviewed journals where TiO_2 is used as a photocatalyst [4–7]. Two obstacles hinder the application of this semi-conductor TiO_2 in suspensions for the oxidative abatement of toxic and/or recalcitrant non-biodegradable compounds (a) the separation of the semiconductor after the process a step that is expensive in terms of manpower, time and energy (centrifugation or other form of separation) and (b) the low quantum yield of the process hindering the overall efficiency.

This study focuses on the stable fixation of TiO_2 on glass Raschig rings. Supported TiO_2 coated on glass has led in many cases to TiO_2 leaching into the solution during the photo-activated degradation of the pollutant [8,9]. This study presents an innovative route to anchor the TiO_2 powder suspension on glass rings using a negatively charged polyethylene-graft-maleic anhydride copolymer (PEGMA)

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interface to anchor the positive TiO_2 on the surface of glass rings. The choice of Raschig rings was arrived at during the preliminary runs, when scanning different supports because it presented favorable kinetics and long-term stability as a support for particulate TiO_2 [10]. The photocatalyst fulfilled the following three requirements: (a) it did not degrade by the radicals produced in the solution necessary to degrade 4-CP, (b) it did not allow leaching of the TiO_2 during reactor operation and (c) it presented acceptable kinetics able to decompose 4-CP in the minutes range. This last property important due to the expensive UV-photons used during the degradation process.

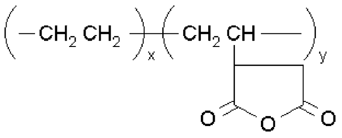
TiO_2 anchoring on polyethylene block-copolymer films containing negatively charged anhydride groups has been reported by our laboratory [11]. TiO_2 nano-sized particles graft on the anhydride groups of the copolymer block polyethylene film. The anchoring of the TiO_2 goes through the carboxylic group interacting electrostatically with the Ti-cation and leading to the formation of the –COO–Ti^{4+} bond. This study reports the coating with a negatively low cost commercial copolymer powder dissolved in an organic solvent in a solution that was used to coat the Raschig glass rings. Subsequently the thin polymer film on the rings with the anchoring groups was exchanged with TiO_2.

In recent years there has been a growing concern related to the health impact of chlorinated organic compounds. Chlorophenols constitute a group of organic substances that are introduced into the environment as result of man-made activities, such as wood preservatives, waste incineration, pesticide, herbicides and fungicides residues in water bodies. As of late, chlorocarbons found in water bodies are largely due to the bleaching of pulp with chlorine and the chlorination of water for disinfection purposes [12]. Chlorocarbons have been recognized as a threat to human health since their half-lives reach up to several years and have been listed in the 55 priority pollutants by the US EPA [13]. Therefore, the development of effective methods for their removal from water bodies is warranted. A recent comprehensive review article of Esplugas et al., [14] lists in Table 15 several studies using TiO_2 suspensions for 4-CP treatment and in some cases TiO_2 deposited on flat glass surfaces. Our laboratory has recently reported the degradation of chlorocarbons with TiO_2 suspensions under mercury light irradiation [15].

2. Experimental

2.1. Materials and reagents

The 4-chlorophenol (4-CP), acids, bases and H_2O_2 were Fluka p.a. and used as received. The TiO_2 Degussa P-25 photocatalyst was a gift from Degussa Switzerland, 6340 Baar. The Raschig rings used were 4 mm × 4 mm in size and were made out of soda lime glass 1 mm thick. The soda lime glass used was made up by: 70% SiO_2, 10% (Na_2O, CaO, MgO K_2O) and 5% (Fe_2O_3, Al_2O_3). The polyethylene-graft-maleic anhydride powder (PEGMA) was a Sigma-Aldrich product No. 456624, CAS Number 106343-08-2, melting point 107 °C, M_w 2300 (average molecular wt.). The structure of PEGMA is



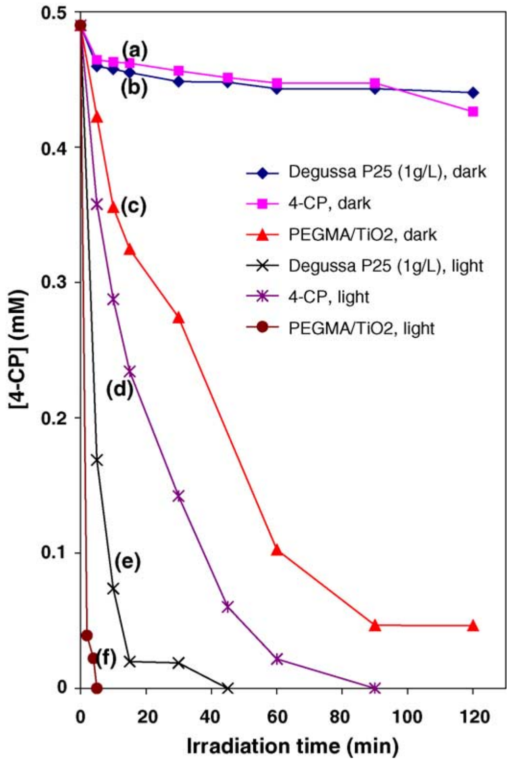


Fig. 1. Disappearance of 4-CP in aqueous solution as determined by HPLC in the dark and under mercury light irradiation (400 W) in the presence of H_2O_2 (10 mM) in air atmosphere. Initial solution at pH 5.6. The traces describing the catalysts are labeled from (a) through (f) in the captions. For other details see text.

Other polyethylene-graft copolymers films were assayed as interfacial films to charge negatively the Raschig glass rings, but after preliminary scanning the one used beginning in Fig. 1 was selected. It showed the most suitable kinetics during the model organic compound used in this study.

2.2. Catalyst preparation

The Raschig rings were washed with detergent and then etched with HF 5%, for 10 min at 50 °C. After rinsing with bi-distilled water, the Raschig rings were immersed in the PEGMA 5% copolymers dissolved in toluene, drained and dried overnight in a vacuum oven. The dried rings were dipped in a well-dispersed TiO_2 Degussa P25 suspension (5 g/L) and dried at 110 °C for 1 h. The immersion in TiO_2 suspensions was repeated again to increase the TiO_2