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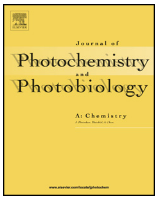

Influence of lattice distortion and oxygen vacancies on the UV-driven/microwave-assisted TiO_2 photocatalysis

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ABSTRACT

The influence of lattice distortions on TiO_2 photocatalysis produced by subjecting commercially available P25 titania samples to a heat treatment in the temperature range 645–800 °C was examined; it caused the initial anatase-to-rutile ratio of 81/19 to decrease to 1/99 at the highest temperature. The photoactivities of these heat-treated samples were established through the photodegradation of 4-chlorophenol (4-CP) exposed to UV irradiation alone, UV/microwave irradiation (2.45 GHz), and to UV irradiation accompanied with conventional heating at a temperature otherwise identical to that under UV/MW irradiation. Raman band intensities of pure anatase (143 cm^{-1}), pure rutile (446 cm^{-1}) and of the heat-treated P25 specimens were examined *in situ* after being exposed to microwave irradiation for about 4 min. Changes are attributed to a microwave non-thermal effect involving oxygen vacancies that affect the specimens' photoactivities as determined by subjecting samples of Evonik P25 titania (AEROXIDE® TiO_2 P25) and Ishihara ST-01 TiO_2 to a heat treatment in the presence of molecular hydrogen. Such treatment caused lattice distortions of both systems that affected the kinetics of degradation of the chlorophenol under various irradiation conditions. UV/visible absorption spectra of the heat/H_2-treated specimens displayed a broad unresolved absorption envelope at wavelengths above 400 nm that has been attributed to oxygen vacancies and thus to *F*-type color centers in accord with an earlier study by Kuznetsov and Serpone. The presence of such defects, particularly in the heat/H_2-treated samples, and the influence of the microwaves caused the photodegradation kinetics for the 4-CP to be enhanced significantly.

1. Introduction

Although the ecofriendly process involving TiO_2 as a potential photocatalyst in one of the well-known advanced oxidation processes (AOP) is widely employed [1], the method used in the purification of wastewaters is not without issues: for example, the speed with which such systems are treated. This problem was resolved by improving the photocatalyst's activity through the simultaneous use of both UV and microwave (2.45 GHz) radiations [2]; however, the photoactivity of TiO_2 was hardly affected when the microwave radiation was substituted by conventional heating (CH; e.g. from an oil bath). The phenomenon involved a specific effect (e.g., a non-thermal effect) of the microwaves that was examined from various approaches: (i) the influence of the microwave specific effect on improving the affinity of the TiO_2 surface toward organic pollutants [3]; (ii) the increase in the amount of $^{\bullet}OH$ radicals generated by the photooxidation of water [4]; (iii) the influence of the microwave's radiation fields (magnetic field versus electric field) on the photocatalyst's activity in that the photoactivity of TiO_2 (P25) is enhanced by the synergistic effect between the magnetic and electric fields of the microwave radiation [5]; (iv) the enhanced TiO_2 photoactivity by microwave irradiation under cooling conditions to ambient heating attributed not only to a microwave thermal effect, but also to a significant non-thermal effect that implicated hot-spots on the TiO_2 particle surface [6]; and (v) the influence of a microwave specific effect on the intra-gap nitrogen dopant energy level in the N-doped TiO_2 crystal structure [7]. These notwithstanding, the microwave specific effect has not been seen in most commercially available TiO_2 photocatalysts, except perhaps in Evonik P25 TiO_2 wherein the microwaves had an accelerating effect in the degradation of a chlorophenol [8].

An examination of possible microwave specific effect(s) that appear in P25 TiO_2 can lead to a further elucidation of microwave specific effects in metal oxides. In this regard, a microwave specific

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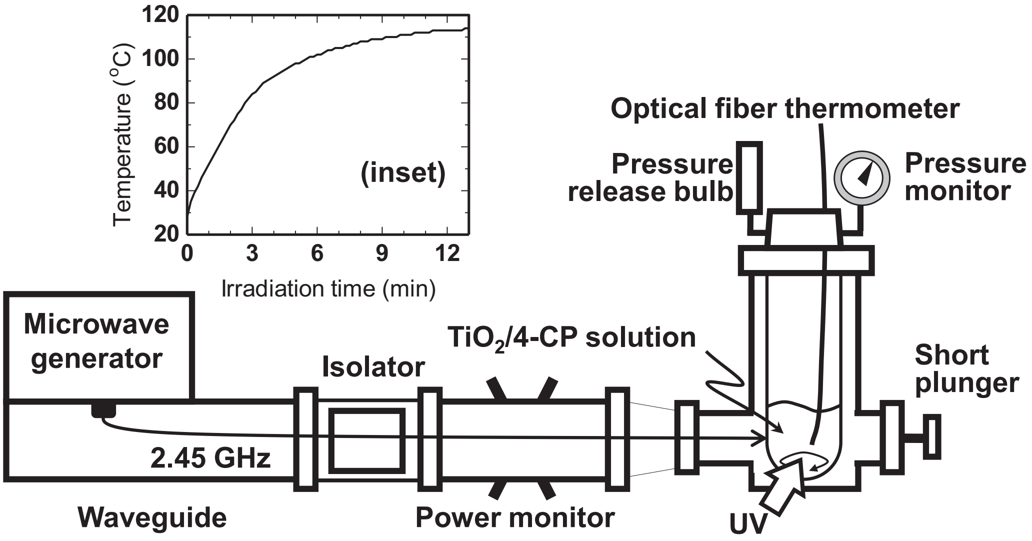

Fig. 1. Experimental setup used in the UV-driven and microwave-assisted photodegradation of 4-CP in aqueous media with TiO_2 dispersions using an integrated UV/MW irradiation method.

effect was reported for N-doped TiO_2 under UV–visible light irradiation [7] wherein the microwaves influenced the N-dopant sites; the microwave-assisted photodegradation dynamics of 4-CP were subdued by the presence of the N states as they inhibited the reaction by acting as electron traps and as recombination centers, thereby inhibiting formation of $O_2^{-\bullet}$ and $^\bullet OH$ radicals. However, the influence of oxygen vacancies in the photodegradation process were not precluded as the microwaves could also impact these lattice and surface defects, not least of which is the role that oxygen vacancies play as electron traps. A comparison of the photodegradation dynamics of 4-CP under vis/MW irradiation, as opposed to vis/CH irradiation (1.70×10^{-2} min^{-1} vs. 0.73×10^{-2} min^{-1}), indicated a possible microwave specific effect through non-equilibrium heating that promoted the photoactivity of the doped specimen [7]. Similar effect(s) could thus influence metal oxides in general, and TiO_2 in particular as it might be affected by the nature of its crystalline structure (e.g. rutile, anatase, and brookite). Accordingly, the focus of this study was to investigate the influence of the microwave radiation on the crystalline anatase-to-rutile content of P25 TiO_2. For comparison, both Evonik P25 and Ishihara ST-01 titanium dioxide specimens were examined with regard to lattice distortion induced by a heat treatment in the two crystalline phases (rutile and anatase), as well as the microwaves' specific effect(s) on the UV-driven and microwave-assisted degradation of 4-chlorophenol.

2. Experimental

2.1. Preparation of TiO_2 particulate specimens

2.1.1. Influence of anatase-to-rutile crystalline ratio

Evonik P25 TiO_2 powdered specimens (62 mg) were placed into an alumina crucible and subsequently heat-treated under air conditions in an electric furnace for 2 h at temperatures between 645 °C and 800 °C.

2.1.2. Influence of oxygen vacancies in TiO_2

Evonik P25 and Ishihara ST-01 (Ishihara Sangyo Kaisha, Ltd.) titanium dioxide specimens were placed in a quartz tube (internal diameter, 8 mm) followed by covering the upper and lower ends with glass wool. Hydrogen gas was then allowed to flow through the packed TiO_2 particles at a temperature of 350 °C for 3 h for the P25 specimen or for 6 h for the ST-01 TiO_2; heat was provided by a heating mantle.

2.2. UV-driven and microwave-assisted photodegradation of 4-chlorophenol

An aqueous 30-mL dispersion consisting of 4-chlorophenol (4-CP; 0.050 mM, pH ~5.5) and TiO_2 particles (loading, 30 mg) was placed in a 150-mL Pyrex glass batch-type cylindrical reactor {Taiatsu Techno Co.; size, 160 mm (height) × 37 mm (internal diameter)} located in the waveguide of the microwave apparatus (see Fig. 1). The reactor was sealed with two Byton O-rings and a stainless steel cap. A pressure gauge and a release bulb were connected to the cover of the reactor. Unless noted otherwise, continuous microwave irradiation was obtained from a Hitachi Kyowa Engineering Co. Ltd. 2.45-GHz microwave generator (maximal power, 800 W) equipped with a power controller, a power monitor, and an isolator (air cooling device). The 39-W continuous microwaves emitted from the magnetron were monitored using a power monitor.

Temperatures of the aqueous TiO_2/4-CP dispersion were measured using an Anritsu Meter Co., Ltd. FL-2000 optical fiber thermometer; the dispersion temperature reached a maximum of 112 °C after 13 min under microwave irradiation (inset Fig. 1), and remained constant thereafter to within a 110–112 °C range. The UV source was a Toshiba 75-W super high pressure Hg lamp located so as to irradiate the sample reactor through the hole on the side of the waveguide. The dispersion was continually stirred during the irradiation.

The photodegradation of 4-chlorophenol was examined using three different irradiation methods: (a) UV-driven degradation (UV); (b) UV-driven/microwave-assisted degradation (UV/MW); and (c) UV-driven degradation with conventional heating (UV/CH) at temperatures otherwise identical to those under UV/MW irradiation. In the UV/CH case, a segment of the cylindrical Pyrex reactor was coated with a metallic film, prepared by the metal-organic chemical vapor deposition technique (MOCVD), on one side at the bottom of the reactor to provide the external heat source (applied voltage to metallic film was typically less than 100 V). The uncoated side of the reactor allowed the UV light through. The rate of increase of temperature by the UV/MW route was continually monitored