Applied Catalysis A, General 565 (2018) 20–25

Contents lists available at ScienceDirect

Applied Catalysis A, General

journal homepage: www.elsevier.com/locate/apcata

Hydroxyl radical and free and shallowly trapped electron generation and electron/hole recombination rates in TiO_2 photocatalysis using different combinations of anatase and rutile

Eva Jimenez-Relinque*, Marta Castellote*

Eduardo Torroja Institute for Construction Science (IETcc), Serrano Galvache, 4, Madrid, Spain

ARTICLE INFO

Keywords:
TiO_2
Properties
Hydroxyl radical
Electron
Recombination
Photocatalytic activity

ABSTRACT

Hydroxyl radical (OH·) and electron (e^-) generation in aqueous suspensions during TiO_2 photocatalysis was studied, varying the properties of the photocatalyst and using the molecular probes terephthalic acid (TA) for OH · and resazurin dye (Rz) for electrons. Overall photocatalytic activity was calculated from rhodamine B dye degradation. The percentage of e^- recombination was found as the difference between the results for aqueous Rz in the presence and absence of a hole scavenger (glycerol). The findings show that the properties of the TiO_2 particles affect e^- and OH· generation rates differently. The generation rates of these active species and their overall photocatalytic activity were observed to be heavily dependent upon the physical properties of the TiO_2 used and the recombination percentage.

1. Introduction

The mechanism governing TiO_2-mediated photocatalysis has been widely studied [1,2]. The free carriers (e^- and h^+) generated have been shown to participate in the photocatalytic degradation of adsorbed pollutants, directly or via the formation of reactive oxygen species (ROS) [3,4]. The identification of such species (charge carriers and ROS) and their generation and recombination rates are consequently of scientific and technological significance, for they may contribute to the design of new materials with practical applications.

This study analyzes the oxidative reaction induced by photogenerated OH· and the reductive potential of photogenerated e^-. The rates of e^- and OH· photocatalytic generation from TiO_2 powder obtained by calcining commercial anatase were respectively quantified with terephthalic acid (TA) [3–5] and resazurin dye (Rz) [6–9]. Despite the many reports on the use of Rz dye as an indicator of photocatalytic activity, its utility in that respect has been confined to research on the rate of change in properties such as the absorbance/color associated with photocatalytic reactions Inasmuch as Rz can be specifically reduced by electrons, it may be deemed to be a suitable method for quantifying the rate of e^- formation in photocatalysis. To the authors' knowledge, this is the first study to quantify the e^- generation rate by measuring the decline in Rz concentration with UV–vis spectrophotometry. The use of data gathered with this dye to calculate the electronic recombination rate also provides insight into the effect of e^-/h^+ recombination on reactions photocatalyzed by TiO_2 with different properties. Overall photocatalytic activity is measured as the rhodamine B (RhB) photodecomposition rate constant, for although part of the dye may be sensitized under visible light, RhB is often used to trace photocatalytic activity in construction materials (UNI 11259:2008). The relationships between the generation rates of the active species and their effect on overall photocatalytic performance are discussed.

2. Materials and methods

2.1. TiO_2 powder

Commercial titanium dioxide powder was used as supplied (Hombikat UV100 TiO_2; TiO_2-C). In addition, a number of blends of anatase/rutile TiO_2 were obtained by heating a crucible containing 1 g of powder in a muffle furnace for 4 h at temperatures ranging from 400 °C to 1000 °C.

2.2. TiO_2 characterization

TiO_2 crystallography was determined by X-ray diffraction (XRD) conducted on a Bruker Advance-D8 diffractometer. The specific surface of the powder was found with the Brunauer-Emmett-Teller (S_{BET}) method using a Micromeritics NOVA2000 nitrogen absorption

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* Corresponding authors.
E-mail addresses: eva.jimenez@csic.es (E. Jimenez-Relinque), martaca@ietcc.csic.es (M. Castellote).

https://doi.org/10.1016/j.apcata.2018.07.045
Received 4 April 2018; Received in revised form 30 July 2018; Accepted 31 July 2018
Available online 01 August 2018
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analyzer. The optical properties of the compound were found with diffuse reflectance spectroscopy (DRS) conducted on a Shimadzu UV-2600 UV–vis spectrophotometer.

2.3. Photocatalytic experiments

2.3.1. Hydroxyl radical (OH·) quantification: terephthalic acid (TA) fluorescence (FL)

The amount of OH· forming at the illuminated photocatalyst/water interface was quantified with terephthalic acid fluorescence (TA-FL) [3,5]. Fluorescence was applied to detect the OH· forming on the irradiated sample with highly reactive TA as the chemical probe to speedily generate fluorescent 2-hydroxyterephthalic acid (TAOH) [5]. Earlier studies showed that this method reliably quantifies free OH· generation based on the h^+ photogenerated in photocatalytic materials [3,4]. OH· formation was determined in a suspension of 0.0055 g of TiO_2 powder in 100 mL of a 2 mM TA aqueous solution containing 2 mM NaOH in an aerated Pyrex glass cell, experimental conditions under which TA hydroxylation has been shown to be attributable exclusively to OH· [3].

The suspension was stirred in a dark box until photocatalyst-TA adsorption–desorption equilibrium was reached, after which stirring continued and the powder sample was irradiated uninterruptedly for 20 min. The solution was subsequently centrifuged to remove the photocatalyst and FL intensity in the supernatant solution was measured at 425 nm after excitation at 315 nm. The amount of TAOH generated, determined from a calibration curve, was used to estimate the amount of free OH· formed, assuming a trapping factor of 35% [3,10].

2.3.2. Electron (e^-) reduction: resazurin (Rz) absorbance

The e^- formation rate at the illuminated photocatalyst/water interface was detected by UV–vis absorbance using Rz as the probe molecule. Resazurin (Rz, blue) readily reacts with e^- to yield resorufin (Rf, pink) (Eq. (1)).

$$Resazurin\,(Rz) + 2e^- \rightarrow Resorufin\,(Rf) \tag{1}$$

Rz absorbance at 600 nm was measured for several standard concentrations and the absorbance – concentration values plotted to obtain a calibration curve. The concentration of the e^- generated in the photocatalytic reaction studied was found by extrapolating absorbance at 600 nm of the irradiated TiO_2 powder solution on the x-axis (Rz concentration). In addition to the aforementioned reaction mechanism ($Rz + 2e^- \rightarrow Rf$), electron calculations envisaged a trapping factor of 40% to account for the direct or indirect competition between O_2 and Rz for the photogenerated e^- [11,12].

Two ink formulations were used: (i) 3 g of glycerol and 0.04 g of resazurin dye in 1 L of aqueous solution as described by Mills et al. [13]; and (ii) the same formulation in the absence of glycerol. The glycerol-containing system is known as “intelligent ink” [7] for electron-hole (e^--h^+) recombination is controlled by the hole scavenger (glycerol), affording the photogenerated electrons more time reduce the dye. The degree of electron recombination was calculated by comparing the values for the two formulations.

The experimental procedure involved magnetically stirring 0.0055 g of TiO_2 powder in 50 mL of Rz solution (with or without glycerol) in a Pyrex vial stored in the dark until photocatalyst-Rz adsorption–desorption equilibrium was reached. Stirring then continued as the suspensions were uninterruptedly irradiated. The TiO_2 powder was removed by centrifugation at different irradiation times and the degree of reduction measured in the supernatant solution. UV–vis absorption spectra were collected on a Shimadzu UV-2600 spectrophotometer.

2.3.3. Photocatalytic degradation of rhodamine B

RhB discoloration was conducted under the same conditions as TA fluorescence and Rz absorbance, dissolving 0.05 g of TiO_2 powder in an aqueous solution containing 8 ppm of RhB. The solution was stored in the dark and stirred to saturate RhB adsorption prior to UV irradiation. The change in absorbance recorded by a spectrophotometer during irradiation at a wavelength of 550 nm was used to determine RhB concentration in the solution. As the relationship between the logarithm of the relative RhB concentration in the solution ($\ln(C/C_0)$) and irradiation time was approximately linear, the slope of the expression, i.e., the rate constant (k_{RhB}), was determined for each sample and used as the representative parameter for photocatalytic behavior.

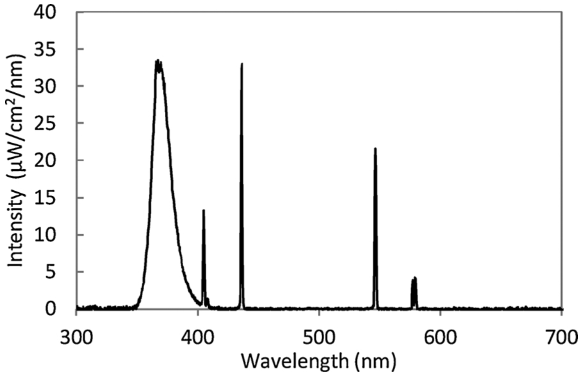

Fig. 1. Light spectrum for Actinic BL 15 W/10 SLV lamps.

2.3.4. Irradiation set up

The light source consisted of two Philips Actinic BL 15 W/10 SLV fluorescent lamps emitting at 350 nm–400 nm (optimally at 360 nm), with four additional narrow peaks at 406 nm, 435 nm, 545 nm and 576 nm. The light spectrum for the lamps is reproduced in Fig. 1. The mean light intensity at the surface of the reaction solution was about 10 W/m².

3. Results and discussion

3.1. Characterization of TiO_2 samples

The XRD- and BET-determined physical properties of the TiO_2 powder used are summarized in Table 1. Anatase was stable up to a temperature of 800 °C, with small amounts (1%) of rutile first appearing in the 900 °C samples and rising to 51% in the 950 °C and to 71% in the 960 °C samples. Anatase disappeared altogether at 1000 °C. Entering the anatase (101) and rutile (110) reflection broadening values into the Scherrer equation [14] showed that the anatase crystallites grew with

Table 1
Physical-chemical and optical properties of TiO_2 samples (A: anatase; R: rutile).

Sample	Phase percentage (%)[a]		Crystallite size (nm)[a]		FWHM (°)[a]		BET surface area (m²/g)	Band gap (eV)
	A	R	A	R	A	R		
TiO_2-C	100	–	8	–	0.99	–	310	3.32
TiO_2-400	100	–	11	–	0.65	–	109	3.30
TiO_2-500	100	–	16	–	0.51	–	79	3.29
TiO_2-600	100	–	32	–	0.37	–	49	3.26
TiO_2-700	100	–	49	–	0.26	–	27	3.25
TiO_2-800	100	–	69	–	0.18	–	13	3.22
TiO_2-900	99.1	1	75	163	0.17	0.074	9.5	3.22
TiO_2-950	44.9	51.1	90	138	0.18	0.075	3.4	2.94
TiO_2-960	28.5	71.5	91	136	0.21	0.076	3.2	2.91
TiO_2-1000	–	100	–	137	–	0.075	2.8	2.99

[a] Estimated from the broadening of anatase (101) and rutile (110) XRD reflections.

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