

Advances in
Chemical Engineering

Volume 36



Advances in **CHEMICAL ENGINEERING**

PHOTOCATALYTIC TECHNOLOGIES

VOLUME 36

Edited by

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Paris • San Diego • San Francisco • Singapore • Sydney • Tokyo
Academic Press is an imprint of Elsevier



Academic Press is an imprint of Elsevier
Radarweg 29, PO Box 211, 1000 AE Amsterdam, The Netherlands
32 Jamestown Road, London NW1 7BY, UK
30 Corporate Drive, Suite 400, Burlington, MA 01803, USA
525 B Street, Suite 1900, San Diego, CA 92101-4495, USA

First edition 2009

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Library of Congress Cataloging-in-Publication Data

A catalog record for this book is available from the Library of Congress

British Library Cataloguing in Publication Data

A catalogue record for this book is available from the British Library

ISBN: 978-0-12-374763-1

ISSN: 0065-2377

For information on all Academic Press publications
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Printed and bound in USA

09 10 11 12 10 9 8 7 6 5 4 3 2 1

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CHEMICAL ENGINEERING

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VOLUME **36**

ADVANCES IN
CHEMICAL ENGINEERING

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PREFACE

In recent years, the international community has been increasingly concerned about the stresses imposed on the natural environment by many chemical and energy-generating processes. As a result, the world is witnessing an accelerated development and implementation of new green technologies. These green technologies are called to provide ecologically responsible solutions for the much needed supply of drinking water, clean air, and various forms of energy.

Photocatalysis holds great promise for delivering these ground-breaking technologies. Photocatalysis is a truly environmentally friendly process where irradiation, either near UV or solar light, promotes photoexcitation of semiconductor solid surfaces. As a result, mobile electrons and positive surface charges are generated. These excited sites and electrons accelerate oxidation and reduction reactions, which are essential steps for pollutant degradation and other photoinduced chemical transformations such as water splitting.

Photocatalysis and its related technological issues have been strongly influenced by recent publications. The present Volume 36-*Photocatalytic Technologies* of the Elsevier's *Advances in Chemical Engineering Series* aims at offering a comprehensive overview of the state-of-the-art photocatalytic technology. In order to accomplish this, several prominent researchers were invited to contribute a chapter for the Volume 36.

Chapter 1 examines the phenomenological principles involved in the modeling of photocatalytic reactions including the photo-adsorption of chemical species. This chapter proposes a method to quantify photo-adsorbed species onto irradiated TiO_2 . The technique is applied to the oxidation of phenol and benzyl alcohol.

Chapter 2 considers the removal of inorganic water contaminants using photocatalysis. Metal cations react via one-electron steps first leading to unstable chemical intermediates, and later to stable species. Three possible mechanisms are identified: (a) direct reduction via photo-generated conduction band electrons, (b) indirect reduction by intermediates generated from electron donors, and (c) oxidative removal by electron holes or hydroxyl radicals. The provided examples show the significance of these mechanisms for the removal of water contaminants such as chromium, mercury, lead, uranium, and arsenic.

Chapter 3 addresses the photocatalytic mineralization of organic species in water and its enhancement by using ferric ions. This methodology uses Photo-CREC reactors with Fe-promoted TiO_2 . It is shown that 5 ppm of Fe in water provides an optimum iron concentration able to maximize the rates of

oxidation and mineralization for both phenol and its aromatic intermediates. This chapter also describes a parallel-series kinetic reaction network. This reaction network and the derived kinetic parameters are most suitable for describing the improved phenol photocatalytic oxidation with ferric ions.

Chapter 4 reports research progress on hydrogen production via water splitting using photocatalysis. It is stated that while water splitting with UV light shows good prospects, water splitting under visible light requires a significant efficiency improvement provided by an enhanced utilization of irradiated photons per molecule of hydrogen produced. In order to accomplish this, new nanomaterials manufactured under close control of crystallinity, electronic structure, and morphology are proposed.

Chapter 5 addresses the scaling-up in photocatalytic reactors with catalyst irradiation being identified as a most important engineering design parameter. It is stated that the photocatalytic reactor design involves a skilful combination of a highly and uniformly irradiated photocatalyst, and an intensive mixing of the TiO_2 suspension. In order to attain these design objectives, several reactor designs are reviewed such as a multiple tube reactor, a tube light reactor, a rotating tube reactor, and a Taylor vortex reactor.

Chapter 6 describes solar-powered photocatalytic reactors for the conversion of organic water pollutants. Nonconcentrating reactors are identified as some of the most energetically efficient units. It is reported that the absorption of radiation is a critical parameter in the efficiency reactor evaluation. The radiative transfer equation (RTE) solution under the simplified conditions given by the P1 approximation is proposed for these assessments.

Chapter 7 reports a scaling-up procedure for photocatalytic reactors. The described methodology uses a model which involves absorption of radiation and photocatalyst reflection coefficients. The needed kinetics is obtained in a small flat plate unit and extrapolated to a larger reactor made of three concentric photocatalyst-coated cylindrical tubes. This procedure is applied to the photocatalytic conversion of perchloroethylene in air and to the degradation of formic acid and 4-chlorophenol in water.

Chapter 8 addresses the treatment of contaminated air streams using photocatalysis. Special attention is given to the distinction between reaction kinetics and mass transport processes. The reviewed studies show the evolution from the early days of TiO_2 photocatalysis, where the aim was to understand the basic process parameters, to today's development of phenomenological models assisting in the scaling-up of units.

In summary, the present issue of *Advances in Chemical Engineering* Volume 36 offers an up-to-date overview and discussion of principles and applications of photocatalytic reaction engineering. Altogether, Volume 36 is an invitation to reflect on the possibilities of photocatalysis as a promising technology for green reaction engineering.

Hugo I. de Lasa and Benito Serrano Rosales,
December 2008.

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Determination of Photoadsorption Capacity of Polychrystalline TiO₂ Catalyst in Irradiated Slurry

Vincenzo Augugliaro^{1,*}, Sedat Yurdakal^{1,2}, Vittorio Loddo¹, Giovanni Palmisano¹, and Leonardo Palmisano¹

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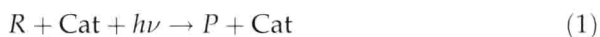
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1. INTRODUCTION

In the field of heterogeneous catalysis the need of kinetic investigation is strictly connected to the main task of a chemical engineer, that is, designing properly a chemical reactor. A successful reactor design should thus start from reliable kinetic models that describe the rate of catalytic reactions and, therefore, from the reaction mechanisms, which means understanding reactions at a molecular level. In catalysis, due to the complex nature of this phenomenon, adsorption and desorption of reactants as well as several steps for surface reactions must be taken into account. For heterogeneous photocatalysis, which may be considered a special case of heterogeneous catalysis, the previous considerations hold true with the added difficulty that the light absorbed by the photocatalyst affects both adsorption (photoadsorption) and surface reactions.

The use of irradiation to initiate chemical reactions is the principle on which heterogeneous photocatalysis is based. When a wide band gap semiconductor like titanium dioxide (Carp et al., 2004) is irradiated with suitable light, excited electron-hole pairs result that can be applied in chemical processes to modify specific compounds. If recombination or lattice reaction does not involve all the photogenerated pairs, the conduction band electrons participate in reduction reactions on the catalyst surface while positive holes are involved in oxidation reactions. Suitable substrates must be adsorbed on the catalyst surface for the occurrence of a photoreaction process which always starts with the substrate(s) adsorption and eventually ends with the product(s) desorption. On these grounds heterogeneous photocatalysis is defined as follows (Braslavsky, 2007): *“Change in the rate of a chemical reaction or its initiation under the action of ultraviolet, visible, or infrared radiation in the presence of a substance, the photocatalyst, that absorbs light and is involved in the chemical transformation of the reaction partners.”* Symbolically overall photocatalytic reaction is expressed by the equation:



where R and P are reactants and reaction products, respectively, present in the gas or liquid phase, Cat is the solid photoadsorbent (photocatalyst), and $h\nu$ is the symbol of photons able to be absorbed by the photocatalyst.

The knowledge of heterogeneous photocatalytic systems has grown very much since the pioneering work on water photolysis carried out with a semiconductor electrode (Fujishima and Honda, 1972). The basic principles of heterogeneous photocatalysis are now well established (Fujishima et al., 1999; Kaneko and Okura, 2002; Schiavello, 1997) and also the applicative aspects of this technology are being investigated in the fields not only of environment remediation (Augugliaro et al., 2006; Fujishima et al., 2000; Mills and Le Hunte, 1997) but also of green chemistry (Gonzalez et al., 1999; Mohamed et al., 2002; Yurdakal et al., 2008a). There are, however, many

important aspects waiting to be investigated. One of these is the correct approach for the determination of the photoadsorption capacity under photoprocess occurrence, that is, of the amount of substrate adsorbed on the surface of a photocatalyst which is being irradiated.

Photon absorption by photocatalyst is regarded as the first stage of photoexcitation of heterogeneous system; the photoexcitation pathways of wide band gap solids may involve photogeneration of excitons and/or free charge carriers, depending on photocatalyst features such as fundamental absorption band, extrinsic/intrinsic defect absorption bands, or UV-induced color center bands. Independently of photoexcitation type, photon absorption has two main effects: (i) it changes the characteristics of photocatalyst surface and (ii) it generates active photoadsorption centers. A typical case of the first effect is that band gap irradiation induces superhydrophilicity (photoinduced superhydrophilicity, PSH) on the TiO_2 surface, which shows hydrophobic features under dark conditions (Fujishima and Zhang, 2006; Fujishima et al., 2000; Wang et al., 1997). This PSH is accompanied by photocatalytic activity, as both phenomena have a common ground, so that the surface-adsorbed compounds may be either photooxidized or washed away by water.

The second important effect is that irradiation absorption generates active states of the photoadsorption centers with trapped electrons and holes. By definition (Serpone and Emeline, 2002) *“the photoadsorption center is a surface site which reaches an active state after photoexcitation and then it is able to form photoadsorbed species by chemical interaction with substrate (molecules, or atoms, or ions) at solid/fluid interface.”* In turn, the active state of a surface photoadsorption center is *“an electronically excited surface center, i.e. surface defect with trapped photogenerated charge carrier that interacts with atoms, molecules or ions at the solid/gas or solid/liquid interfaces with formation of chemisorbed species.”*

Adsorption initiated by light absorbed by the solid surface (photoadsorption) can be expressed by the following simple mechanism (Ryabchuk, 2004):



where S is the photoadsorption center, S^* the active state of photoadsorption center, M the substrate in the fluid phase, and $M_{\text{p-ads}}$ the photoadsorbed substrate. Equation (2) describes the photoexcitation of adsorbent with formation of active S^* centers and Equation (4) the adsorption of molecule M or “chemical decay” of the active states S^* , while Equation (3) depicts the “physical decay” of S^* state.

For a liquid–solid catalytic reaction the common technique for determining the adsorbed amount of a species dissolved in the solution is that of performing experiments in a batch not-reacting system and of measuring: (i) the volume of liquid solution; (ii) the concentration of the adsorbing species in the starting solution; and (iii), after that a known mass of catalyst is added to the liquid and steady-state conditions are reached, the concentration decrease determined in the starting solution due to the added catalyst. This procedure is based on the adequate assumptions that the catalyst's superficial features are not affected by the composition of the surrounding fluid phase and that the measured decrease of the species amount in the solution is equal to the amount of species adsorbed on the catalyst. The same procedure cannot be applied for the photoadsorption determination; in fact, photoadsorption occurs under the simultaneous presence of irradiation and of reducing and oxidizing species needed for charge carriers to be trapped on the semiconductor surface. Under these conditions the photo-reaction also starts so that the measured decrease of species in the batch-irradiated slurry is determined both by photoadsorption and by reaction, these contributions being indistinguishable from the solution side.

This complexity determines that investigations on heterogeneous photocatalytic processes sometimes report information only on dark adsorption and use this information for discussing the results obtained under irradiation. This extrapolation is not adequate as the characteristics of photocatalyst surface change under irradiation and, moreover, active photoadsorption centers are generated. Nowadays very effective methods allow a sound characterization of bulk properties of catalysts, and powerful spectroscopies give valuable information on surface properties. Unfortunately information on the photoadsorption extent under real reaction conditions, that is, at the same operative conditions at which the photoreactivity tests are performed, are not available. For the cases in which photoreaction events only occur on the catalyst surface, a critical step to affect the effectiveness of the transformation of a given compound is to understand the adsorption process of that compound on the catalyst surface. The study of the adsorbability of the substrate allows one to predict the mechanism and kinetics that promote its photoreaction and also to correctly compare the performance of different photocatalytic systems.

This chapter presents a quantitative method to determine the photoadsorption capacity of a polycrystalline semiconductor oxide irradiated in liquid–solid system. The determination is performed under reaction conditions so that it is really indicative of the photoadsorption capacity. The method uses the experimental results obtained in typical batch photoreactivity runs; on this ground it has been applied to the following photocatalytic processes carried out in aqueous suspensions: (i) oxidation of phenol in the presence of a commercial TiO_2 catalyst (Degussa P25) and (ii) oxidation of benzyl alcohol in the presence of a home-prepared TiO_2

catalyst. The influence on photoactivity of substrate concentration, catalyst amount, and irradiation power is investigated. The kinetic modeling of the photooxidation processes is carried out by taking into account the photoadsorption phenomenon by means of three types of isotherm equations, that is, Langmuir, Freundlich, and Redlich–Peterson. Nonlinear regression analysis applied to all the photoreactivity results allows establishing the most appropriate correlation for the photoadsorption isotherm and also to determine the values of the model parameters. The best fitting model is evaluated by choosing the Marquardt's percent standard deviation (MPSD) as error estimation tool.

2. EXPERIMENTAL

Photoreactivity runs of phenol degradation were carried out in aqueous suspensions of a commercial TiO_2 (Degussa P25) while for benzyl alcohol degradation a home-prepared nanostructured TiO_2 specimen was used. The preparation method of home-prepared catalyst is summarized here; the details are elsewhere reported (Addamo et al., 2004). The precursor solution was obtained by slowly adding 5 mL of TiCl_4 drop by drop into a 200-mL beaker containing 50 mL of water; during the addition, which lasted 5 min, the solution was magnetically stirred by a cylindrical bar (length, 3 cm; diameter, 0.5 cm) at 600 rpm. After that the beaker was closed and mixing was prolonged for 12 h at room temperature, eventually obtaining a clear solution. This solution was transferred to a round-bottom flask having on its top a Graham condenser (Palmisano et al., 2007a). The flask was put in boiling water, thus determining the boiling of the solution; the duration of the boiling was of 0.5 h, obtaining a white suspension at the end of the treatment. The suspension was then dried at 323 K by means of a rotovapor machine (model Buchi Rotovapor M) working at 150 rpm, in order to obtain the final powdered, poorly crystalline anatase-phase catalyst.

The flow-sheet of the experimental setup is shown in Figure 1. The details are reported elsewhere (Palmisano et al., 2007b). A cylindrical batch photoreactor of Pyrex glass with immersed lamp was used for the photocatalytic runs of benzyl alcohol and phenol oxidation. On the top of the reactor three ports allowed the inflow and outflow of gases, the pH and temperature measurements, and the withdrawal of samples for analysis.

The catalyst was used in aqueous suspension well mixed by means of a magnetic stirrer. The reacting mixture was illuminated by a mercury medium-pressure lamp (type B, Helios Italquartz, Milan, Italy) coaxial with the photoreactor. A Pyrex thimble surrounding the lamp allowed the circulation of distilled water in order to cool the lamp and cutoff infrared radiation; in these conditions the reactor temperature was of 295 ± 2 K. Lamps of 125, 500, or 1,000 W electric power were used; average irradiances