Journal of Catalysis 330 (2015) 154-166

Contents lists available at ScienceDirect

Journal of Catalysis

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

Heterogeneous photocatalysis: Light-matter interaction and chemical effects in quantum efficiency calculations



JOURNAL OF CATALYSIS

Mario J. Muñoz-Batista^a, Anna Kubacka^{a,*}, Ana B. Hungría^b, Marcos Fernández-García^{a,*}

^a Instituto de Catálisis y Petroleoquímica, CSIC, C/ Marie Curie, 2, 28049 Madrid, Spain ^b Departamento de Ciencia de Materiales, Ingeniería Metalúrgica y Química Inorgánica, Facultad de Ciencias, Universidad de Cádiz, 11510 Puerto Real, Cádiz, Spain

ARTICLE INFO

Article history: Received 10 April 2015 Revised 13 June 2015 Accepted 27 June 2015

Keywords: Anatase Ceria Degradation Quantum efficiency and yield UV Sunlight Reactor

ABSTRACT

In this contribution we analyze the calculation of the quantum efficiency observable in the gas-phase heterogeneous photocatalytic oxidation of toluene. To this end, we carried out porosimetry, UV-visible optical, and TEM tomography measurements together with the mathematical modeling of the most significant physico-chemical factors influencing the quantum efficiency observable. Critical factors concern physical properties related to the light-matter interaction as well as the chemical properties defining the outcome of the reaction. Among the firsts, we analyze the effective catalyst surface area illuminated and provide a detailed formulation of the radiation model, including main absorbance, transmittance and reflectance events. For chemical properties not only the activity but also the selectivity was considered. The work was carried out with a dual aim. First, by scanning a basis set containing most common reactor geometries and light sources, we illustrate quantitatively (numerically) and qualitatively (relative among factors) the importance of each one of the above mentioned factors in quantum efficiency calculations. Second, using a series of samples with "continuous" variation of chemical, textural, morphological and optical properties we calibrate the goodness of common simplifications utilized to represent the above mentioned physical/chemical factors and measure their numerical effects in the quantum efficiency observable. Combination of these two approaches provides a general scheme to bundle and interpret all physico-chemical factor effects in quantum efficiency outputs and can serve as a guide to calibrate current quantum efficiency formulations accuracy.

© 2015 Elsevier Inc. All rights reserved.

1. Introduction

Photocatalysis is an active field of research exploiting light to chemical energy conversion within a wide number of applications concerning the degradation of pollutants or the synthesis of valuable compounds. Photocatalytic reactions differ from conventional ones by the requirement of a radiation field to activate the catalyst [1–5]. This singular characteristic demands to establish a specific concept to measure catalytic performance in the case of heterogeneous photocatalysis. Although the literature reveals the utilization of multiple expressions to report photocatalytic activity, the quantum efficiency concept is well established as a descriptor with universal validity [6–10]. In the absence of mass transfer limitations, the intrinsic photocatalytic efficiency of a reaction is measured by the ratio between the rate of the photoreaction and the rate of photon absorption by the photocatalyst at a set of well

defined conditions. The difficulty in measuring this observable has led, as above mentioned, to alternative formulations and/or simplifications, particularly in use is the apparent photonic efficiency which considers all available photons instead of the fraction absorbed by the catalyst [5–9,11–15].

Probably of more importance is the fact that the quantum efficiency or yield definition requires the measurement and/or modeling of several properties of the system with have not been explored in a common basis to date. As heterogeneous photocatalysis is a complex process involving light, the radiation field, and a nanostructured solid material, usually a semiconductor and particularly titania, a significant number of physico-chemical properties of the system as a whole affect the photo-chemical process.

In first place, light-matter interaction in photocatalytic processes is governed by the optoelectronic properties of the semiconductor catalyst. The definition of the quantum efficiency requires to know the rate of photon absorption, which in turn demands to solve the radiative transfer equation for the light-matter (reactor-catalyst) system through modeling and numerical calculation. For a gas phase reaction, this leads to the local superficial rate



^{*} Corresponding authors.

E-mail addresses: ak@icp.csic.es (A. Kubacka), mfg@icp.csic.es (M. Fernández-García).

of photon absorption concept [8,14]. To provide a rigorous analysis, such task must take into account the fraction of light transmitted, reflected and adsorbed at each point of the catalyst surface and the subsequent solving of the system of nonlinear equations representing the whole reaction (reactor + catalyst) system.

A second effect of the light-matter interaction usually dismissed is the fact that in a powdered, nanostructured material, even in the form of a thin film, shadowing effects take place [5–14]. Such effects are controlled or driven by the morphological properties of the catalyst and, as we will show, are dominated by the secondary particle size and porosity. Even within a simplified scheme, the modeling of the shadowing effects requires the adequate knowledge of catalyst morphology, very frequently with intensive use of microscopy tools.

In second place and as occurring in any catalytic reaction, irrespective of whether triggered by photons or thermally, the final, chemical outcome is primarily defined by using the activity and selectivity concepts. As different product molecules require, in the case of heterogeneous photocatalysis, a different number of charge carries to be produced, chemical effects are of significance in the calculation of the quantum efficiency parameter. In short, not only the reaction rate is needed to calculate such observable, also the frequently dismissed selectivity parameter must be taken into account.

In this contribution we would provide a general scheme to bundle all these concepts in a single formulation of the quantum yield efficiency parameter with a dual aim. Using such a formulation we first would like to provide a guide to show the absolute (numerical) and relative (among the set of influential parameters) importance of the above mentioned light-matter interaction and chemical effects in the calculation of the quantum efficiency. To provide a study with general application, we will illustrate the situation using the most broadly used reactor configurations and light sources. Additionally, we will consider increasing levels of mathematical complexity in the modeling of the light-matter interaction. Such basis set of light-matter interaction and chemical "variables" or "effects" intends to provide results with application in almost all situations studied in gas phase heterogeneous photocatalytic reactions and thus to serve as a guide for researchers as to the importance of including or dismissing any of the above mentioned effects in the quantum efficiency calculation and, in turn, a way to estimate the error within a specific set of variable(s) values.

Second, using titania and a composite of ceria and titania we will study thoroughly the calculation of the quantum efficiency in a set of samples with high activity both under UV and visible light illumination conditions. While nanostructured ceria is an active photocatalyst upon UV and visible light excitation [16–18], the contact between ceria and titania is known to provide rather active materials irrespective of the illumination wavelength [19]. Such contact has been applied for the elimination of organic pollutants through reduction and/or oxidation reactions [20-34] and, very recently, for the inactivation of microorganisms [29,31]. Due thus to the broad application (within the heterogeneous photocatalysis field) of the ceria-titania system, as well as the relatively different optical properties (in terms of the UV or visible region importance) of the two semiconductors, a set of samples with increasing quantities of ceria deposited onto a titania substrate seems an ideal choice for calibrating the importance of dismissing physical pieces of the mentioned light-matter and morphological effects as a function of the light source nature. Toluene photo-mineralization was chosen to test activity of all samples utilized in this study as it is thought to be an important constituent of anthropogenic emissions in urban atmospheres. Additionally, its photooxidation is a very demanding reaction and thus constitutes a tough chemical test to assess the potential of the TiO₂-based systems in the photo-elimination of organic pollutants [35–37].

2. Experimental

2.1. Catalyst preparation

Materials were obtained by means of a microemulsion preparation method utilizing *n*-heptane (Scharlau) as organic media, Triton X-100 (Aldrich) as surfactant and hexanol (Aldrich) as cosurfactant. A TiO₂ reference sample was obtained as a first step using a water in oil microemulsion and titanium tetraisopropoxide as precursor. In all composite samples and the CeO₂ reference, cerium(III) nitrate (Alfa Aesar) was introduced in the aqueous phase of a microemulsion. After stirring for 30 min, the stoichiometric (to obtain the corresponding Ce(III) hydroxide) quantity of tetramethylammonium-hydroxide (TMAH) was introduced from the aqueous phase of a similar microemulsion under stirring for ca. 5 min. For nanocomposite samples, a titanium tetraisopropoxide solution in isopropanol (2:3) was subsequently added dropwise on the Ce-containing microemulsion. Water/M (M = Ti, Ce, or Ce + Ti) and water/surfactant molar ratios were, respectively, 110 and 18 for all samples [38,39]. The resulting mixture was stirred for 24 h, centrifuged, and the separated solid precursors rinsed with methanol and dried at 110 °C for 12 h. After drying, the solid precursors were subjected to a heating ramp $(2 \circ C \min^{-1})$ up to 500 $\circ C$, maintaining this temperature for 2 h. Sample names are Ti or TiO₂ and Ce or CeO₂ for, respectively, the titania and ceria references. and *x*CeTi for the composite ones, where *x* is the molar Ce/Ti ratio.

2.2. Characterization details

The BET surface areas and average pore volume and size were measured by nitrogen and mercury physisorption (Micromeritics ASAP 2010 and AUTOPOR IV 9500 apparatus, respectively). Ce/Ti composition was analyzed by using inductively coupled plasma and atomic absorption (ICP-AAS; Perkin–Elmer, Optima 3300 DV). UV–visible transmission or diffuse reflectance spectroscopy experiments were performed with a Shimadzu UV2100 apparatus using, for diffuse experiments, BaSO₄ as reference.

Secondary particle size was examined by high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) on a JEOL 2010 field emission gun transmission electron microscope operated at 200 kV. Secondary particle size distributions were obtained by analyzing at least 100 aggregates from the HAADF-STEM micrographs. The dimensional analysis of the aggregates was performed by fixing the longest longitude as primary axis and defining the orthogonal directions as secondary axes. Tomography studies were also performed to characterize the three dimensional morphology of the agglomerate of primary particles. For the tomography studies, a single tilt series of HAADF-STEM images was recorded over a wide angular range (typically from -70° to $+70^{\circ}$) every 2° using a Fischione ultra-narrow gap tomography holder. Images were aligned sequentially using Inspect 3D. Reconstructions were performed with Inspect 3D using an iterative routine (SIRT) which constrains the reconstructed volume to best match the original images when re-projected back along the original tilt directions. Surface rendering after a segmentation process was undertaken using Amira software.

2.3. Reaction system

Gas phase photooxidation tests were carried out with toluene and using a setup presented at Section 2 of the Supporting information file (Fig. S1). The gas-phase photooxidation was tested in a continuous flow annular photoreactor containing $0.3-1.1 \text{ mg cm}^{-2}$ of photocatalyst as a thin layer coating on a Pyrex tube. The corresponding amount of catalyst was suspended in 1 ml of ethanol, Download English Version:

https://daneshyari.com/en/article/6527038

Download Persian Version:

https://daneshyari.com/article/6527038

Daneshyari.com