

Photonic efficiency for methanol photooxidation and hydroxyl radical generation on silica-supported TiO₂ photocatalysts

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Abstract

Hydroxyl radical species are considered to be responsible for many oxidation pathways of chemical compounds initiated by advanced oxidation technologies and particularly in heterogeneous photocatalytic processes. However, not many attempts have been made to quantify the generation rate of these species for newly developed photocatalysts, especially for the large number of supported photocatalysts synthesized during the last years. This work focuses on the evaluation of the photonic efficiency for the hydroxyl radical generation on several silica-supported TiO₂ photocatalysts recently developed. The study has been carried out by using methanol as hydroxyl radical scavenger. The influence of the mesoporous structure of the support and of its titania loading on the photonic efficiency of the materials has been analyzed. The importance of diffusional restrictions within the porous structure of the support has also been investigated by using a larger hydroxyl radical scavenger molecule, namely *n*-butanol.

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1. Introduction

Advanced oxidation technologies have been widely proposed during recent years for the detoxification of a large number of chemical pollutants present in industrial wastewater [1,2]. Many of these processes are based on the use of hydroxyl radicals as strong oxidants resulting in the non-selective degradation of almost all toxic and non-biodegradable pollutants. Among them, the photocatalytic oxidation has been demonstrated to be applicable for a wide number of potential applications [3–10]. These processes are based on the use of a semiconductor material that generates electron/hole pairs when being illuminated with radiation above the energy of its band-gap. The most widely used

semiconductor materials are based on TiO₂. Many attempts to improve their catalytic properties have been made in order to facilitate its commercial application in the liquid phase.

In order to compare the activity of different photocatalytic materials, reaction rates must be referred to either the incident or the absorbed photon flux. These parameters, called photonic efficiency or quantum yield, respectively, have traditionally been used by different authors but not always with the same meaning. Definition and standardized methods for their calculation can be found in the literature [11,12], together with others parameters such as relative photonic efficiencies for different materials determined employing the same experimental conditions.

One of the usual ways to modify a photocatalyst is to deposit the semiconductor onto an inert support in order to improve the recovery of the solids after the reactions [13,14]. The results found in the literature show that the presence of

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the support usually reduces the activity of the catalysts. Usually, this can be explained by higher restrictions of the mass transport of the chemicals to the photocatalyst surface [15] and by a lower photon flux absorbed by the semiconductor due to an increased light scattering by the support. However, despite the large number of supported photocatalysts prepared in the last years, not many attempts have been made to quantify the activity of these materials in terms of standardized parameters such as photonic efficiencies.

Hydroxyl radical species have been proposed to be the responsible for many oxidation pathways of chemical compounds initiated through heterogeneous photocatalytic processes [7]. The $\bullet\text{OH}$ radical generation takes place through the oxidation of bound OH^- ions or water molecules adsorbed on the material, being the primary step that leads to the total mineralization of the pollutants. For that reason, the measurement of the rate of the hydroxyl radical generation is one of the most important parameters to be studied during the evaluation of newly developed photocatalysts. This measurement leads to very useful results for the comparison of the photoactivity of different materials, independent of the specific degradation mechanism of the selected pollutants.

In order to quantify the rate of $\bullet\text{OH}$ generation, it has been proposed to use a well-known hydroxyl radical scavenger, i.e., methanol. Previous studies [16–19] have demonstrated the possibility of using high concentrations of methanol to quantify the complete hydroxyl radical production from the photogenerated holes at the semiconductor surface.

We have studied the photonic efficiencies of the hydroxyl radical generation for some silica-supported TiO_2 photocatalysts developed recently [20]. In particular, the photocatalytic oxidation of methanol yielding formaldehyde has been investigated. These results have been compared with the photocatalytic activity obtained when Degussa P25 TiO_2 was used as photocatalyst. As the silica support plays an important role for the activity of these materials, the diffusion of chemicals inside the porous structure of the support has also been investigated. Among the different variables involved in the synthesis of the catalysts studied here, the influence of the titania loading and of the type of silica support has been analyzed.

2. Experimental procedure

2.1. Catalysts synthesis and characterization

The silica-supported TiO_2 photocatalysts have been prepared employing a previously reported method [20]. The incorporation of TiO_2 clusters into the support was accomplished via a sol–gel route, starting with the required amount of titanium tetraisopropoxide and resulting in the condensation of TiO_2 inside the porous structure of the

support. Two different types of mesoporous silica materials have been used as supports: an amorphous commercial SiO_2 (Grace Sylopol 2104, GrSiO_2) with a wide pore size distribution of mesopores and a mesostructured silica material called SBA-15 with a very well-defined pore size.

The characterization of the samples shows the presence of nanocrystalline clusters of anatase with different sizes in the range of 6–12 nm depending on both the type of support and the wt.% of titania loading. The activity of these materials is also affected by the titania loading and the chosen silica support. Details about the synthesis, characterization and photoactivity of these materials have been reported previously [20,21].

2.2. Photocatalytic activity tests

The photoreactor consisted of a Pyrex reactor with an effective volume of 1 l. UV irradiation was performed by a 150 W medium pressure mercury lamp (Heraeus TQ-150) placed inside a quartz jacket and equipped with a cooling tube. Cooling of the system was achieved by the circulation of an aqueous 0.01 M CuSO_4 solution resulting in the absorption of radiation wavelengths below 325 nm, thus avoiding photolytic processes. The UV-A incident photon flow, determined by ferrioxalate actinometry, was 1.10×10^{-5} einstein $\text{l}^{-1} \text{s}^{-1}$. The lamp was switched on 30 min before the beginning of the reaction to stabilize the power of its emission spectrum line at 365 nm. The temperature of the cooling agent was also stabilized to perform the reactions at 25 ± 0.1 °C.

Reactions were carried out suspending the amount of catalyst required to obtain a titania concentration of $0.5 \text{ g TiO}_2 \text{ l}^{-1}$. It has been experimentally verified that this catalyst concentration leads to a negligible UV-A radiation flux through the outer wall of the reactor with all tested photocatalysts. The suspensions were sonicated and saturated with molecular oxygen by bubbling for 30 min. Afterwards, methanol was added in the desired concentration and thereafter suspensions were stirred in the dark for 30 min to reach the adsorption equilibrium prior to the irradiation.

Samples were withdrawn at regular intervals from the upper part of the reactor with the catalyst being removed from the liquid phase by filtration through $0.22 \mu\text{m}$ nylon syringe filters. The extent of the photodegradation was determined by measuring the formaldehyde production employing the Nash method [22]. This method is based on the reaction of formaldehyde with acetylacetone and ammonium to form a coloured product with a maximum of absorbance at 412 nm, measured after an incubation time of 60 min. For the *n*-butanol photodegradation experiments, butanol concentrations were measured following the same colorimetric method as that used for formaldehyde analysis, but measuring the absorbance at 385 nm after an incubation time of 24 h at 25 °C.

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