



Green photo-oxidation of styrene over W–Ti composite catalysts



Mario J. Muñoz-Batista^a, Anna Kubacka^{a,*}, Rafal Rachwalik^b, Belén Bachiller-Baeza^a,
Marcos Fernández-García^{a,*}

^a Instituto de Catálisis y Petroleoquímica, CSIC, C/Marie Curie 2, 28049-Madrid, Spain

^b Institute of Organic Chemistry and Technology, Cracow University of Technology, Warszawska 24, 31-155 Kraków, Poland

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ABSTRACT

A series of WO₃–TiO₂ composite catalysts with variable quantities of tungsten was prepared by a single-pot microemulsion procedure and evaluated in the gas-phase selective photo-oxidation of the aromatic hydrocarbon styrene. Samples improve the performance of TiO₂ by a factor ca. 3 and increase significantly the selectivity to valuable products (as styrene oxide) upon UV and, more importantly, sunlight-type excitation. Optimum performance in terms of both activity and selectivity was achieved under a sunlight-type renewable energy source. A complete structural (bulk and surface) and electronic characterization using Transmission Microscopy, X-ray diffraction (XRD), X-ray Photoelectron (XPS), Raman, and UV–visible spectroscopies and calorimetry with the help of the ammonia probe molecule was carried out. The study was able to detect and quantify the presence of different W entities as a function of the tungsten content of the catalysts. Three species were found to be present throughout the series; oligomeric W species and WO₃ nanoparticles in close contact with anatase-TiO₂ and non-contacting WO₃ platelets. From a spectro-kinetic analysis carried out with the help of electron paramagnetic resonance (EPR), we provide evidence that these W-containing species play different roles in reaction. Activity and selectivity improvements with respect to the bare titania are intimately related with presence of oligomeric W species at anatase surfaces.

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1. Introduction

Heterogeneous photocatalysis by nanocrystalline semiconductors corresponds to a relatively novel technology applied to environmental abatement in both liquid- and gas-phase phases. This is essentially based on the excellent performance and stability of titania, the most prominent photocatalytic material, for the mineralization of typical pollutants, including refractory or non-biodegradable molecules, under mild conditions, e.g., room temperature and atmospheric pressure and using oxygen (air) as oxidant agent [1–4]. Among titania single nanophases, anatase is clearly the most active phase largely because it shows a correct balance between its surface chemistry-related properties and the adequate physical properties for efficient handling of light-triggered charge carriers, allowing them to be involved in chemical steps at the surface [4].

In contrast to studies devoted to photo-degradation of pollutants, relatively fewer studies were conducted on the application of photocatalysis for product synthesis using selective oxidation

routes [5–7]). Within the field of selective photo-oxidations, a particular interesting and active topic concerns the partial oxidation of organic molecules, mostly hydrocarbons and alcohols, to give either aldehyde derivatives with wide use in the chemical industry (flavor, confectionary, beverage, other activities) or to epoxides with application in both chemical and plastic industries [6–14]. Such selective photo-catalytic processes capture a great deal of attention in recent years in the quest to switch to more benign, sustainable process that makes use of environmentally friendly reagents, free of harmful organic solvents and dangerous/costly oxidants, and using mild temperature/pressure operation conditions. Titania fulfils all such conditions for a green process; however, a main drawback is that titanium dioxide is an UV absorber and has to be modified in order to allow the use of renewable energy sources as the sun [1–7]. This modification seeks for the enhancement of the light to chemical energy conversion efficiency by increasing the number of useful photon from the 3–5% corresponding to the UV range to ca. 45–50%, corresponding to the UV–visible range of solar light.

Profiting from both UV and visible lights in selective-photooxidation reactions would thus require the careful engineering of a significant number of physico-chemical variables of a TiO₂-based

* Corresponding authors. Fax: +34 915854760.

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

nanomaterial. First and as mentioned, the managing of light absorption of the anatase phase appears as a key goal. Several strategies have been pursued to address this point, being most popular ones related to the electronic modification of titania through cationic [1,2,4,15,16], anionic [1,2,4,17–20], doping or both [4,21–23], or the use of additional, visible-light-sensitize phases in intimate contact with TiO₂ [4,24,25]. In all cases, the goal is to allow the absorption of visible light photons while making a non-negative or, less frequently, positive impact on charge recombination [16,17,24,21,22,26]. To reach this objective, here we approach a rational design; by starting from the synthesis of a highly selective (e.g., no total oxidation products, CO₂) TiO₂ nanomaterial, we address the two-fold objective of increasing activity, e.g., improving light to chemical conversion, with the simultaneous (more specific) improvement of sunlight-based performance by surface-sensitization of the TiO₂ phase with tungsten [16,27,28]. This is done here within a single-pot synthesis procedure, in order to ensure the minimum modification of the bare TiO₂-anatase phase.

Secondly, the light handling-related requirements as mentioned above have to be woven with our aim to adequately control selectivity to transform styrene into valuable chemicals. This unified goal corresponds to an essentially open yet very active field of research. In this context, the use of W at surface of titania nanomaterials has been shown not only to improve catalytic activity in photo-oxidation of organics, like butyl-acetate [29], 2-propanol [30,31], toluene [32,33], chlorophenols [34,35], and oxalic acid [36], but also to increase selectivity for partial vs. total oxidation for hydrocarbon transformation [21,22,37], or hydrogen production on photo-reforming of alcohols/acids ([38,39]). Thus, W can potentially fulfil all light- and chemical-related objectives upon adequate engineering of physico-chemical properties of the base TiO₂-anatase material. Note that the situation is relatively different from the easy one of increasing activity either upon UV and/or visible light, with has been previously described in a number of cases [16,27–36].

To this end, we studied the transformation of styrene into valuable products upon both ultraviolet and sunlight excitation and analyze both the enhancement of activity and modification of selectivity as a function of the number and nature of the W species present at the surface of anatase. A gas-phase photo-catalytic process is presented as it has an inherent advantages vs. liquid-phase reactions; among them, some were mentioned before, like the absence of harmful organic solvents (not always but frequently used in selective photo-oxidation) [5–7], while others, like the easy recovering (and potentially facile regeneration if needed) of the catalyst, can be now added to the list [1–7]. In this study, we will provide evidence that starting from an anatase nanomaterial showing 100% selectivity for photo-oxidation of this aromatic hydrocarbon into aldehydes, we can adequately modify the selectivity to obtain valuable chemical products as a function of the existent surface W species nuclearity, this done without loss but instead a significant enhancement of photo-activity. A multitechnique approach (morphological analysis, XRD, XPS, Raman, Calorimetry of probe molecules, UV–visible and analysis of optical properties) was used to structurally/electronically characterize the specific W surface modifiers which can be used to maximize photo-oxidation activity/selectivity. The fate of carriers after illumination was investigated using EPR. Opposite trends of activity as selectivity as a function of W content; while photo-activity is maximized for low W content, selectivity to valuable chemicals is increasing with the W content. The rationale being that this result is interpreted on the basis the characterization study which provides strong evidence of the key role played by oligomeric W species present at the surface of or in close contact with TiO₂-anatase.

2. Experimental section

2.1. Catalyst preparation

Materials were prepared using a single-pot microemulsion preparation method using *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 microemulsion with acetic acid (to fix the initial pH to a value of 5.0) into the aqueous phase and titanium tetraisopropoxide as precursor. In all composite samples and the WO₃ reference, ammonium tungsten oxide (Alfa Aesar) was introduced in the aqueous phase of a microemulsion. After 30 min of agitation, a stoichiometric (to obtain the corresponding W(VI) hydroxide) quantity of tetramethylammonium-hydroxide (TMAH) was introduced from the aqueous phase of a similar microemulsion. For nanocomposite samples, after 5 min of contact and pH adjustment with acetic acid (pH 5), titanium tetraisopropoxide was introduced into the previously resulting microemulsion drop by drop from a mixture with isopropanol (2:3). Water/Ti and water/surfactant molar ratios were, respectively, 110 and 18 for all samples [40,41]. 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 °C min⁻¹) up to 525 °C, maintaining this temperature for 2 h. Samples names are *T* for the titania reference, and *xW* for the composite ones where *x* is the molar content of WO₃ (in relation to a fixed amount of titania corresponding to 1 mol).

2.2. Characterization details

The BET surface areas and average pore volume and sizes were measured by nitrogen physisorption (Micromeritics ASAP 2010). XRD profiles were obtained with a Seifert D-500 diffractometer using Ni-filtered Cu K α radiation with a 0.02° step and fitted using the Von Dreele approach to the Le Bail method [42]; particle sizes and microstrain were measured with XRD using the Williamson–Hall formalism [43]. Ti/M composition was analyzed by using inductively coupled plasma and atomic absorption (ICP-AAS; Perkin–Elmer, Optima 3300 DV).

Transmission electron microscopy (HTEM) and X-ray energy dispersive spectra (XEDS) were recorded on a JEOL 2100F TEM/STEM microscope. XEDS analysis was performed in STEM mode, with a probe size \sim 1 nm, using the INCA x-sight (Oxford Instruments) detector. Specimens were prepared by depositing particles of the samples to be investigated onto a copper grid supporting a perforated carbon film. Deposition was achieved by dipping the grid directly into the powder of the samples to avoid contact with any solvent.

XPS data were recorded on 4 \times 4 mm² pellets, 0.5 mm thick, prepared by slightly pressing the powdered materials which were outgassed in the prechamber of the instrument at room temperature up to a pressure $<2 \times 10^{-8}$ to remove chemisorbed water from their surfaces. The SPECS spectrometer main chamber, working at a pressure $<10^{-9}$ torr, was equipped with a PHOIBOS 150 multichannel hemispherical electron analyzer with a dual X-ray source working with Ag K α ($h\nu = 1486.2$ eV) at 120 W, 20 mA using C 1s as energy reference (284.6 eV). Surface chemical compositions were estimated from XP-spectra, by calculating the integral of each peak after subtraction of the ‘S-shaped’ Shirley-type background using the appropriate experimental sensitivity factors and the CASA-XPS (version 2.3.15) software.

The microcalorimetric studies of ammonia adsorption were carried out in a differential heat-flow microcalorimeter (Tian-Calvet type C80; Setaram) connected to a conventional volumetric

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