



A comparative study of Bi₂WO₆, CeO₂, and TiO₂ as catalysts for selective photo-oxidation of alcohols to carbonyl compounds

F.J. López-Tenllado^a, S. Murcia-López^{b,1}, D.M. Gómez^c, A. Marinas^{a,*}, J.M. Marinas^a, F.J. Urbano^a, J.A. Navío^b, M.C. Hidalgo^b, J.M. Gatica^c

^a Organic Chemistry Department, Campus de Excelencia Internacional CeIA3, University of Córdoba, Campus de Rabanales, Marie Curie Building, E-14014 Córdoba, Spain

^b Institute of Materials Science of Seville, Joint Center CSIC-Universidad de Sevilla, C/ Américo Vespucio 49, E-41092 Sevilla, Spain

^c Department of Material Science, Metallurgy Engineering and Inorganic Chemistry, Faculty of Sciences, University of Cádiz, E-11510 Puerto Real, Cádiz, Spain

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ABSTRACT

Several semiconductors based on ceria or bismuth tungstate were tested for selective oxidation of alcohols to carbonyl compounds in a search for photocatalysts more selective than TiO₂. Gas-phase selective photo-oxidation of propan-2-ol to acetone and liquid-phase transformation of 2-buten-1-ol (crotyl alcohol) to 2-butenal (crotonaldehyde) were studied as test reactions. In both processes the highest selectivities were achieved with Bi₂WO₆-based solids. Further studies on crotyl alcohol transformation evidenced the lower adsorption of the aldehyde on these systems which could minimize the decrease in crotyl alcohol yield observed for TiO₂ or CeO₂ at high conversions. Incorporation of titania (5% molar) to the Bi₂WO₆ system increased the reaction rate significantly whereas the aldehyde yield remained high.

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1. Introduction

Partial oxidation of alcohols is an important process for the production of fine and specialty chemicals. The process can be carried out in different ways: (i) with strong oxidizing agents, for instance Jones reagent (a solution of chromic and sulfuric acids in water) which can oxidize primary allylic alcohols to aldehydes. Special care must be taken to prevent further oxidation of aldehydes to carboxylic acids. One possibility is distillation of aldehyde as it is produced. Alternatively, there are some other selective oxidizing reagents such as dimethyl sulfoxide or pyridinium chlorochromate, just to cite some of them. (ii) A second approach is the use of dehydrogenation catalysts, typically copper chromite. (iii) A third alternative is the utilization of the Oppenauer oxidation in which a ketone (typically acetone, butanone or cyclohexanone) in the presence of a base is used as the oxidizing reagent (and it

is reduced to a secondary alcohol). (iv) Using TEMPO and related reagents. (v) Utilizing hypervalent iodine reagent, and (vi) resorting to N-bromosuccinimide or in the case of primary alcohols N-chlorosuccinimide [1].

Nevertheless, when talking about environmentally-benign oxidants, H₂O₂ and specially O₂ are preferred to the above-mentioned oxidants since they give either no byproduct or water as byproduct. However, the use of oxygen as oxidant in heterogeneous catalyzed organic reactions is typically associated with substrate total oxidation and/or to the formation of byproducts [2].

One alternative is the use of heterogeneous photocatalysis which can provide a new synthetic method since it requires milder conditions with respect to thermal activation and allows shorter reaction sequences minimizing side processes [3]. Several selective photo-oxidation processes have been reported in the literature (e.g. aromatic hydroxylation, hydrocarbon oxidation, alkene epoxidation, and alcohol oxidation) [4–10]. Focusing on alcohols, the most studied substrates are aromatic, typically benzyl alcohol. One interesting example is oxidation of 4-methoxybenzyl alcohol to the corresponding aldehyde of application in organic synthesis and Fine Chemistry [11]. In comparison to aromatic alcohols, aliphatic require longer irradiation times. The heterogeneous

* Corresponding author. Tel.: +34 957218622; fax: +34 957212066.

E-mail address: alberto.marinas@uco.es (A. Marinas).

¹ Present address: Catalonia Institute for Energy Research (IREC), Jardins de les Dones de Negre 1, E-08930 Sant Adrià de Besòs, Barcelona, Spain.

catalyst of choice is TiO₂ typically, though some other such as ZnO [12], CdS/TNTs nanocomposites [13], Fe-g-C₃N₄, and titanium silicate zeolite hybrid materials [14] or encapsulated polyoxometalate [15] have been described.

In a previous paper [16] 24 different titania-based systems were tested for gas-phase selective photo-oxidation of propan-2-ol to acetone and liquid-phase transformation of 2-buten-1-ol (crotyl alcohol) to 2-butenal (crotonaldehyde). In general, selectivities to acetone with all the systems were very similar (ca. 50–60%) and quite constant with conversion, the exception being platinum-containing solids which showed quite high selectivity values to acetone (in the 78–80% range at 22–28% conversion). As for the crotyl alcohol transformation, the catalysts differed on the time required to achieve a certain conversion level but for the same conversion values all systems exhibited similar selectivities to crotonaldehyde, the highest crotonaldehyde yield being, under our experimental conditions, ca. 35%. This suggests that selectivity is somehow associated to the semiconductor of choice. With a view to increase the carbonyl compound yield, in the present manuscript the study is expanded to two other semiconductors: Bi₂WO₆ and CeO₂. Though comparatively less explored than TiO₂, both systems have been successfully used in photocatalytic processes. Therefore, for instance, Bi₂WO₆ has been described in photocatalytic mineralization of rhodamine B [17–19], methyl orange [20] or 4-chlorophenol [21] as well as selective photo-oxidation of glycerol to dihydroxyacetone [22] or several benzylic alcohols to the corresponding carbonyl compounds [23]. As for CeO₂, some examples of its photocatalytic application include degradation of halogenated herbicides [24], organic acids [25] or dyes [26], propylene epoxidation [27], and selective oxidation of benzylic alcohols [28,29].

2. Experimental

2.1. Synthesis and characterization of the solids

The synthesis and characterization of the different bismuth tungstate solids was described previously [17,18]. Briefly, the Bi₂WO₆ solids were obtained from a mixture of a solution of Bi(NO₃)₃ in glacial acetic acid and an aqueous solution of Na₂WO₄ at pH 2. The resulting suspension was submitted to hydrothermal treatment (140 °C for 20 h) followed by filtration, washing, and drying overnight at 120 °C. The solid was then calcined at 300 °C for 4 h, thus obtaining the system labeled as Bi₂WO₆ (2). Solid named as Bi₂WO₆ (9) was synthesized in a similar way but adjusting the pH of the Bi(NO₃)₃–Na₂WO₄ mixture at a value of 9. Incorporation of titanium was carried out through addition of TiO₂ sol (formed from titanium isopropoxide in isopropanol) [17] before the hydrothermal method at the required level as to obtain a final composition 5% molar TiO₂/Bi₂WO₆.

The incorporation of gold was carried out by a photodeposition method. For this purpose, solutions of HAuCl₄ in isopropanol (0.3 M) with the corresponding Au content were prepared (0.25 wt% nominal). Suspensions of 1 g of catalyst in 250 mL of the previous solution were prepared and sonicated, after which the pH value was adjusted to 9 by KOH addition. Then, the suspensions were irradiated by visible light for 2 h, under a N₂ atmosphere and, finally, the powder material was filtered, repeatedly washed, and dried overnight.

Catalyst nomenclature includes the pH of the synthesis in brackets. Moreover, when applicable, a suffix indicates the presence of gold (Au) or the incorporation of 5% molar TiO₂ (Ti5).

As regards ceria-based systems, they were prepared from a CeO₂ sample supplied by Rhodia with ≥99.5% and 118 as purity and BET specific surface area, respectively. This ceria was previously studied

in [30]. It was separated in three portions and submitted to three different calcination treatments at 500 (2 h), 800 (2 h) or 900 °C (4 h), respectively, with the aim of obtaining samples with different textural properties. Platinum was then incorporated for obtaining different nominal loadings (0.02%, 0.04% or 0.06%, respectively) by incipient wetness from an aqueous solution of [Pt(NH₃)](OH)₂. Solids were dried at 105 °C for 12 h and finally calcined at 500 °C for 4 h. Nomenclature includes a suffix (5, 8 or 9) referring to ceria calcination temperature (500, 800 or 900 °C, respectively) and the Pt weight % in the case of the metalized samples.

Finally, Degussa P25 titania was used as a common reference material for photocatalysis.

Some of the features concerning characterization of the solids are given in Table 1.

2.2. Photocatalytic experiments

2.2.1. Gas-phase selective photo-oxidation of propan-2-ol to acetone

Experimental device and reaction conditions were described elsewhere [16]. Basically, 15 mL min⁻¹ of O₂ previously bubbled through propan-2-ol at 0 °C was allowed into the photocatalytic reactor, in which 30 mg of catalyst had been placed. The fix bed of the catalyst was in contact with the gas flow. UV light (UV Spotlight source Lightningcure™ L8022, Hamamatsu, maximum emission at 365 nm) was focalized on the sample compartment through an optic fiber. Radiant flux in the catalyst compartment was measured to be 1 W cm⁻² (Newport UV-meter 818P-015-19 Model) and the spot area 1.33 cm². Reactor was on-line connected to a HP6890 chromatograph equipped with a six-way valve, a HP-PLOTU column (30 m long, 0.53 mm ID, 20 mm film thickness) and a Ni methanator (Agilent Part Number G2747A) which allowed us to determine the percentage of CO₂ resulting from mineralization. Temperature at the photoreactor was controlled by water thermostated at 10 °C. The reaction lasted for 5 h.

2.2.2. Liquid phase selective photo-oxidation of 2-buten-1-ol (crotyl alcohol) to 2-butenal (crotonaldehyde)

Experimental device and optimization of reaction conditions were described in a previous study [16]. Under standard conditions, 3 mL of a stock solution 0.01 M of crotyl alcohol (97% *trans*) in acetonitrile was introduced in the 30 mL double-mouthed heart-shaped reactor. After 5 min bubbling through the solution pure oxygen (10 mL min⁻¹), 0.15 mL were sampled, filtered, injected in the GC and taken as initial concentration (C₀). The catalyst 18 mg (6 g/L) was then added, the system closed and stirred (900 rpm) and after 15 min of adsorption in the dark, light was allowed into the reactor. UV light (UV Spotlight source Lightningcure™ L8022, Hamamatsu, maximum emission at 365 nm) was focalized on the sample compartment through an optic fiber. Radiant flux in the catalyst compartment was set up at 500 mW cm⁻² (measured with a Newport UV-meter 818P-015-19 Model) and the spot area on the liquid surface was 2.54 cm². Water used for cooling was thermostated at 10 °C. Reaction profiles were obtained for the same stock solution, each point corresponding to one individual reaction. Once the system had been irradiated for the selected time, the whole suspension was filtered (15 mm diameter, 0.45 μm pore size, Sartorius re. 17559) and analyzed by GC (HP6890 chromatograph equipped with an automatic injector and a HP-PLOTU column –30 m long, 0.53 mm ID, 20 mm film thickness). The main reaction products identified in the liquid phase were crotonaldehyde (*cis* and *trans*) and acetaldehyde. Moreover, some other very minor species (e.g. formaldehyde and methanol) were detected at trace levels.

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