Catalysis Today xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

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

ZrO_2 Based materials as photocatalysts for 2-propanol oxidation by using UV and solar light irradiation and tests for CO_2 reduction

E. García-López[a,*], G. Marcì[a], F.R. Pomilla[a], M.C. Paganini[b], C. Gionco[b], E. Giamello[b], L. Palmisano[a]

[a] *"Schiavello-Grillone" Photocatalysis Group, Dipartimento di Energia, Ingegneria dell'informazione e modelli Matematici (DEIM), Università di Palermo, Viale delle Scienze, 90128 Palermo, Italy*

[b] *Dipartimento di Chimica, Università di Torino, Via Giuria 7, 10125 Torino, Italy*

ARTICLE INFO

Keywords:
Photocatalysis
ZrO_2
Ce doped ZrO_2
Er doped ZrO_2
2-Propanol oxidation
CO_2 reduction

ABSTRACT

Bare ZrO_2, Ce doped ZrO_2 and Er doped ZrO_2 samples have been prepared by a hydrothermal process and have been used as photocatalysts for 2-propanol oxidation reaction in gas solid regime. Moreover, some preliminary tests have been carried out for CO_2 reduction. The samples were physico-chemically characterized and both bare and doped ZrO_2 based materials resulted active for oxidation and reduction reactions by using UV and solar irradiation. The reactivity results have been correlated with the compositional, structural and morphological features of the photocatalysts.

1. Introduction

Photocatalysis has been extensively used in the last thirty years in environmental chemistry to remove pollutants [1] or more recently for synthetic purposes [2,3]. TiO_2 has been one of the most investigated and active photocatalyst for environmental applications giving rise to mineralization of pollutants under UV irradiation, but it is poorly effective under solar irradiation. The search of new heterogeneous photocatalysts active under visible light has been the object of intense effort. Modifications of TiO_2 via doping with transition-metal ions, non metal *p*-block elements or supported metal nanoparticles having plasmonic effects, constitute the second-generation photoactive materials, resulting in many cases more active than the pristine TiO_2. The continuous pursuit of active photocatalysts under visible light has addressed the research to a third generation of materials not based on TiO_2 [4]. ZrO_2 has been seldom applied in photocatalysis because of its wide band gap (ca. 5.0 eV), although some reports are available concerning photo-oxidation of chemicals [5], water photo-splitting [6] and CO_2 photoreduction [6–8]. The band energy levels of ZrO_2 are suitable for photocatalytic applications because the lowest potential of the conduction band (CB) is ca. -1.0 V (vs. NHE, pH 0), i.e. much more negative than that of TiO_2 anatase (-0.1 V), whereas the highest potential of the valence band (VB) is ca. $+4.0$ V, more positive than that of TiO_2 ($+3.1$ V). Introduction of new electronic states in the high band gap by doping with rare earth elements modifies the optical properties of the ZrO_2 giving rise to an active photocatalyst which can absorb also a fraction of the visible light. For instance, the presence of Ce(IV) ions in the bulk of ZrO_2 improved the photocatalytic activity of the oxide [9]. The activity of this third generation photoactive material, as Ce-ZrO_2, is based on the double excitation through localized intra-band-gap states [10,11]. The intra band gap Ce 4f empty states, which could act as a bridge between the VB and the CB of the ZrO_2, allows low-energy photons to excite electrons from the VB to the CB. A first type of photons provides the excitation of the electrons from VB to the Ce intra band gap states, a second one promotes the excited electrons into the CB, analogously to what occurs in the visible light active N-doped TiO_2 photocatalyst [12]. Also the role of Er in ZrO_2 has been studied. Ce and Er-doped ZrO_2 samples resulted photoactive in methylene blue removal in aqueous solution [13]. The TiO_2 doping 3d metal ions has been very much explored in the past to obtain visible light active photocatalysts, however the results obtained are very scarce because the metals act generally as recombination centers of the photogenerated carriers [14]. This phenomenon is due to the partial population of the 3d states introduced at mid gap of TiO_2. The introduction of empty 4f states creates a different situation; indeed, the empty states as mid gap levels seem to be essential to obtain a photoactive material [15]. In the present paper ZrO_2 doped with Ce and Er with different loadings have been prepared giving rise to materials with different physico-chemical features. Their photocatalytic activity was tested in gas-solid regime for 2-pronanol oxidation under UV and solar (artificial or natural) irradiation and for

---

* Corresponding author.
E-mail address: elisaisabel.garcialopez@unipa.it (E. García-López).

https://doi.org/10.1016/j.cattod.2018.01.030
Received 14 July 2017; Received in revised form 18 January 2018; Accepted 27 January 2018

Please cite this article as: Garcia-Lopez, E.I., Catalysis Today (2018), https://doi.org/10.1016/j.cattod.2018.01.030

some preliminary tests for CO_2 reduction under simulated solar irradiation.

2. Experimental

2.1. Preparation and characterization of the photocatalysts

The samples have been prepared by means of a hydrothermal process, starting from an aqueous solution containing the zirconium precursor ($ZrOCl_2{\cdot}8H_2O$) in 1.0 M concentration and the rare earth (RE) precursor, ($Ce(SO_4)_2$ or $Er(NO_3)_3{\cdot}5H_2O$). The pH of the solution was then adjusted to 11 by using a 4.0 M NaOH aqueous solution. The solution with the precipitates was then transferred into a 125 ml Teflon-lined stainless steel autoclave, 70% filled, which was heated at 175 °C overnight in an oven. The precipitates were hence centrifuged and washed three times with deionized water, then dried at 60 °C. For comparison pure ZrO_2 was prepared by the same procedure, without the presence of the RE. Finally, the prepared powders were calcined at 500 °C for 2 h. For each dopant (Ce or Er) four samples with different RE content, namely 0.5%, 2.0%, 5.0% and 10% molar percentage, were prepared. Samples will be labeled throughout the paper by using C for cerium and E for erbium, followed by a figure indicating the molar percentage of the dopant. For example: Z stands for pure zirconia, C05Z stands for the 0.5% mol Ce doped zirconia. For the sake of comparison, a sample of bare CeO_2 was also prepared by starting from $Ce(SO_4)_2$ and following the same methodology used for the preparation of the other samples.

X-Ray Diffraction (XRD) patterns were recorded with a PANalytical PW3040/60 X'Pert PRO MPD using a copper Kα radiation source (0.15418 nm) and a Bragg Brentano geometry. X'Pert High-Score software was used for data handling. Rietveld refinement was performed to determine the crystallite size and relative abundance of phases, using the MAUD 2.26 software and a NIST Si powder to determine the instrumental broadening. Raman measurements were performed on pure powdered samples and recorded by a micro Raman Mediatek i-Plus with a 785 nm laser diode. Surface area measurements were carried out on a Micromeritics ASAP 2020 using the BET model at five P/P^0 points. The photoluminescence spectra were recorded by using a Jobin-Yvon spectrometer (Fluorolog 320) equipped with a 450 W Xenon lamp as the excitation source. Electron Paramagnetic Resonance (EPR) spectra were recorded at room temperature and at liquid nitrogen temperature (77 K) on a X-band CW-EPR Bruker EMX spectrometer equipped with a cylindrical cavity operating at 100 kHz field modulation. The effect of light on EPR spectra was investigated by using a 1600 W Mercury/Xenon lamp (Oriel Instruments) and an IR water filter. A 400 nm cut off filter was used to eliminate part of the UV radiation, leaving a 5–8% of UVA component comparable to that present in the solar spectrum. Diffuse Reflectance Spectroscopy (DRS) data were recorded in the 200–800 nm range using a Varian Cary 5000 spectrometer, coupled with an integration sphere for diffuse reflectance studies, using a Carywin-UV/scan software. A sample of PTFE with 100% reflectance was used as the reference. The optical band gap energy has been calculated from the Tauc plot.

2.2. Photocatalytic experiments

The photoreactivity of the powders was studied for an oxidation model reaction in gas-solid regime. Moreover, some tests for CO_2 photoreduction were carried out. The photocatalytic oxidation of 2-propanol was carried out in a cylindrical Pyrex batch photoreactor (V = 25 ml, ø = 45 mm, height = 15 mm) provided with a silicon/teflon septum. For the oxidation runs, the photocatalyst (0.06 g) was dispersed in the bottom of the photoreactor and O_2 was fluxed for ca. 0.5 h to ensure saturation. 1 μl of liquid 2-propanol was introduced and vaporized in the batch reactor (C_o = 0.54 mM). Irradiation started when the steady state conditions had been achieved, i.e. after that the system was maintained under dark conditions at room temperature to achieve the adsorption equilibrium of the substrate on the catalyst surface. All of the samples were studied by illuminating the photoreactor, horizontally positioned, by an UV-LED IRIS40 at 365 nm (first set-up) or by a SOLARBOX apparatus (CO·FO.ME·GRA.), simulating the solar light, equipped with a 1500 W high pressure Xenon lamp (second set-up). The irradiance reaching the reactor, measured by a Delta Ohm DO 9721 radiometer equipped with a 315–400 nm sensor, resulted 45 W/m^2 in the first set-up and 10 and 1000 W/m^2 in the range 315–400 nm and 400–950 nm, respectively in the second set-up. Additional experiments were carried out under visible light irradiation by using a KNO_2 1 M solution as filter which cut off the UV radiation with wavelength lower than 400 nm. The runs were also carried out by using natural solar light as the irradiation source. The photon flux was measured every 5 min throughout the runs to estimate the energy impinging on the photoreactor. The reacting fluid was analysed by withdrawing gaseous samples from the photoreactor by means of a gas-tight syringe. The concentrations of 2-propanol and of its degradation organic compounds were measured by using a GC-17A Shimadzu GC equipped with a HP-1 column kept at 40 °C and a FID.

The second set of photocatalytic tests, devoted to the photocatalytic reduction of CO_2 was carried out by using the same previously described batch photoreactor and the SOLARBOX apparatus. 0.06 g of photocatalyst were dispersed in the bottom of the photoreactor and N_2 was flushed for 2 h inside the system under irradiation in order to photodesorb possible impurities and/or carbon residues from the catalyst surface. Subsequently, the photoreactor was saturated with CO_2 containing the vapor pressure of water at 298 K. In order to start the experiment in the presence of humid CO_2, the stream of CO_2 was continuously flushed for at least 1 h inside the reactor, after bubbling it in a flask containing water. Then the reactor was closed and the lamp was switched on. The possible presence of products deriving from C impurities was checked by treating the photocatalysts under irradiation (before the photoactivity experiments in the presence of CO_2) with a flow of humid He according to Strunk et al. [16,17], which allowed also to clean the surface. Notably no organic species were observed during the treatment.

Aliquots of the gaseous reaction mixture were withdrawn at fixed irradiation times by using a gas-tight microsyringe. The evolution of the formed organic products was followed by a GC-2010 Shimadzu equipped with a Phenomenex Zebron Wax-plus column by using He as the carrier gas and a FID. CO was analysed by a HP 6890 GC equipped with a packed column GC 60/80 Carboxen-1000 and a TCD.

3. Results and discussion

3.1. Physico-Chemical characterization

XRD patterns of some selected prepared samples (those with the lowest and the highest content of dopant) are reported in Fig. S1. A mixture of both monoclinic (m-ZrO_2) and tetragonal (t-ZrO_2) polymorphs of zirconia was observed in all of them. In agreement with previous studies [13], the increasing of RE dopant amount led to the stabilization of the tetragonal polymorph.

A Rietveld refinement was performed on the XRD patterns and the results are reported in Table 1. The weight percentages of phases obtained are in agreement with the qualitative considerations. The cell parameters of the m-ZrO_2 phase are poorly influenced by the insertion of the RE dopant, while the lattice constants of t-ZrO_2 undergo a distortion which increases with the RE content. Moreover, the m-ZrO_2, both in the bare and doped oxides, presents some degree of anisotropy. Indeed, the peaks broadening is not constant; for this reason we have used the Popa model [18] for the refinement of this phase and we have listed in Table 1 the maximum (D) and minimum (d) crystallite sizes obtained from the Rietveld refinement, along with the (11 0) and (-11 1) plans, respectively. The maximum crystallite sizes for the monoclinic