Solar Energy and Biowaste Conversion into H_2 on CuO_x/TiO_2 Nanocomposites

Claudio Ampelli[a,*], Rosalba Passalacqua[a], Chiara Genovese[a], Siglinda Perathoner[a], Gabriele Centi[a], Tiziano Montini[b], Valentina Gombac[b], Paolo Fornasiero[b]

[a]Department of Electronic Engineering, Industrial Chemistry and Engineering, University of Messina, viale F. Stagno D'Alcontres, 31 - 98166 Messina, Italy
[b]Department of Chemical and Pharmaceutical Sciences, University of Trieste, via L. Giorgieri, 1 - 34127 Trieste, Italy
ampellic@unime.it

The possibility to recover H_2 from waste organic streams in biorefineries using photocatalytic approaches is an attractive option to enhance process sustainability and produce valuable energy products. With respect to the overall photoreforming to obtain H_2 and CO_2, the photo-dehydrogenation of bioethanol leads to the co-production of a valuable chemical (acetaldehyde) together with H_2. Here we report on the synthesis and characterization of low cost CuO_x/TiO_2 nanocomposites and on their photocatalytic evaluation in the process of H_2 production by selective photo-dehydrogenation of ethanol. The methods of sample preparation allowed to maximize the dispersion of copper nanoparticles on TiO_2 surface, improving their photocatalytic performances in H_2 production. CuO_x/TiO_2 materials were tested i) in liquid phase as a powder suspended in a typical slurry-type reactor and ii) in gas phase as a thin film using a novel reactor design. The aim of this contribution is to better understand analogies and differences between gas and liquid phase operations, which are important aspects to take into account in the reactor design. Results showed that gas phase operation allowed high H_2 productivity and high selectivity (about 92 - 93 %) to acetaldehyde. It is remarked that the route of photo-dehydrogenation of ethanol to H_2 and acetaldehyde has an economic value about 3.0 - 3.5 times higher than the alternative route of photoreforming to produce H_2 and CO_2.

1. Introduction

In view of the depletion of fossil fuels, a broad debate has long been opened within both the scientific and political communities about the strategies to be adopted for sustaining the growing world energy demand (Nemet et al., 2012). In this context, hydrogen has attracted great interest not only as the future energy carrier (Armaroli et al., 2011), but also as a sustainable solution if coming from renewable sources (i.e. from sunlight, water and biomass). Hydrogen can be used as a transport fuel (Tollefson, 2010) and is already widely used as a raw material for making products like fertilisers and plastics. Producing hydrogen by water splitting is an extremely promising and environmentally friendly route for the direct conversion of solar energy into fuels (Ampelli et al., 2012a). However, its industrial applicability is still a long way off, due to issues related to i) the need to synthesize a photo-active material capable to absorb efficiently sunlight and catalyze the reaction of water splitting and ii) the very fast back reaction to re-generate water, which occurs too facile on the same catalytic sites active for its dissociation (Ampelli et al., 2011a). All the papers about water splitting refer to the pioneering work by Fujishima and Honda (1972) who first observed water photolysis on TiO_2 semiconductor electrodes. From then on, many efforts have been made to improve TiO_2 performances in H_2 generation, doping the crystalline lattice with heteroatoms, decorating the surface with metal particles, generally noble metals (Ampelli et al., 2010a) or tailoring the structure on a nano-scale level, with the aim to move the bang gap to the visible region (Ampelli et al., 2008). Nonetheless, photocatalytic water splitting is far from an actual implementation and yet we have to wait a long time to

use solar cell devices based on water as the sole input. Conversely, the addition of organic compounds may give rise to H_2 productivity (Gombac et al., 2011). The photo-reforming of organics may represent a good opportunity to recover waste streams coming from biomass processing (agro-food or agro-chemical) which are too dilute to be processed by conventional catalytic routes, i.e. as feed to produce hydrogen by catalytic processes or methane by anaerobic digestion, or to be used as feed in new generation fuel cells (Ampelli et al., 2010b). From a practical perspective, it would also be interesting the possibility of co-production of H_2 and a valuable chemicals rather than carbon dioxide, in order to have better process economics (Cargnello et al., 2011). A good example could be the photocatalytic dehydrogenation of ethanol to H_2 and acetaldehyde, as alternative to the ethanol photoreforming. In terms of product value at actual costs (assuming 100 % selectivity in both reactions), the photo-dehydrogenation has an economic value about 3.0-3.5 times higher than the photo-reforming.

Herein we report on the preparation, characterization and testing of low cost CuO_x/TiO_2 nanocomposites to be used as photocatalysts in the photo-dehydrogenation of ethanol. Three different TiO_2 supports were prepared: i) by sol-gel, ii) by precipitation from titanyl sulphate and iii) by water-in-oil microemulsion procedure. The metal copper nanoparticles were loaded on the supports by photo-deposition technique, which allowed a better control of the particle size and dispersion on TiO_2 surface (Ampelli et al., 2012b).

In the last decade an increasing attention has been devoted to Cu_2O and CuO as photocatalysts, also in combination with TiO_2 (Barreca et al., 2011). The copper oxides show a band gap lower than titania (2.1 eV for Cu_2O and 1.2 eV for CuO), making them as suitable candidates for photo-splitting water and/or photo-reforming to produce hydrogen by using visible light. Unfortunately the copper oxides are unstable in electrolytic solutions because of their facile photo-oxidation, but the interaction with TiO_2 by heterojunction may enhance protection against photo-corrosion (Siripala et al., 2003).

The other aspect to take into account is the reactor design which plays a fundamental role on the process performance. There are various types of photo-reactors used in literature for testing photoactive materials for H_2 production (Minggu et al., 2010), but the current configurations, mostly designed for photocatalysts in form of a slurry, show several drawbacks which strongly limit their performances, such as: light scattering phenomena, difficulties to recover the photocatalytic materials at the end of the process, easy catalyst leaching, difficulty in translating the results to plate-type photo-reactors using solar light, etc. (Ampelli et al., 2011b). In this work we have focused the attention on the development of a novel solar device working in gas phase for the production of H_2 from ethanol. In this innovative configuration the gas phase, abounding in the organic component, is generated directly in situ from the bottom of the reactor by keeping an aqueous ethanol solution in evaporation. The same photocatalytic samples were also tested in a conventional liquid photo-reactor, in the form of a powder suspended in an aqueous ethanol solution. Differences and analogies between gas and liquid phase operation in the photo-production of H_2 were discussed in terms of productivity and selectivity.

2. Experimental

2.1 Preparation

All the reagents were of analytical grade and were used without further purification. Bidistilled water was used in all the preparations. TiO_2 supports were synthesized by three methods: i) sol-gel (SG), ii) precipitation from titanyl sulphate (PS) and iii) by water-in-oil microemulsion (ME) procedure. The descriptions of the preparation methods are reported elsewhere (Gombac et al., 2007). Copper nanoparticles were loaded on the titania supports by photo-deposition technique. Usually 1 g of TiO_2 (SG, PS or ME) was suspended in a water/methanol 1:1 by volume solution containing copper nitrate. The amount of $Cu(NO_3)_2 \cdot 3H_2O$ was changed in order to obtain the desired Cu loading (1.0 or 2.5 wt. %). After stirring for 30 min, the suspension was irradiated with a 125 W medium pressure Hg lamp for 2 h. The samples were finally filtered and dried. In the presence of light, a rapid change from green to black in the colour of the suspension is observed, indicating that the copper is easily reduced to Cu(0) and deposited on the support (Montini et al., 2011). All the samples showed a stable evolution of H_2 during the catalyst preparation. The nature of TiO_2 and the loading of Cu affect the H_2 evolution rate.

In order to obtain a thin film of photoactive substrate, we prepared a paste by mixing 1 g of CuO_x/TiO_2 (SG, PS or ME, 1.0 or 2.5 wt. %) with 10 ml of a solution consisting of water (H_2O, 51 wt. %), ethanol (EtOH, 47 wt. %) and polyethylene glycol (PEG 2000, 2 wt. %), which was then deposited on a conductive substrate (Ti plate) by doctor-blade technique. After deposition, the substrate was annealed at 200 °C to eliminate all the organic. The photocatalyst film area is about 10 cm^2, with at thickness of about 50 μm, and a total photocatalyst loading of about 100 mg.

2.2 Characterization

The materials were characterized by Brunauer-Emmet and Teller (BET) surface area analysis using a Micromeritic ASAP2020 after degassing the samples overnight at 350 °C. Powder X-Ray Diffraction (XRD) patterns were recorded with a computer-controlled Philips X'Pert diffractometer using Cu Kα radiation (λ = 0.154 nm), while UV-visible diffuse reflectance spectra were recorded by a Jasco V570 spectrometer equipped with an integrating sphere for solid samples using $BaSO_4$ as reference and in air. Transmission Electron Microscopy (TEM) measurements were performed on a JEOL2010F instrument, with 0.21 nm spatial resolution at Scherzer defocus conditions. High Angle Annular Dark Field-Scanning Transmission Electron Microscopy (HAADF-STEM) images were recorded on the same microscope by using an electron probe of 0.5 nm of diameter and a diffraction camera length of 12 cm.

2.3 Testing in gas-phase

The photo-active thin films were tested in H_2 production by solar irradiation. The apparatus for the photocatalytic experiments consists of i) a solar illuminator source, ii) a photo-reactor and iii) a gaschromatograph. The light source is a Xe-arc lamp (ORIEL, 300 W), installed within a lamp housing with a set of lenses for light collection and focusing and a water filter to eliminate the infrared radiation. Moreover the possibility to use filters to select the wavelength band allows simulating sunlight under standard terrestrial solar spectral irradiance distributions (i.e. Air Mass 1.5G). The photo-reactor is homemade. It is made in Pyrex and equipped with a quartz window which allows irradiating a photocatalytic area of ~10 cm^2. The CuO_x/TiO_2-based substrate, prepared as thin film, was suspended within the reactor headspace and irradiated perpendicularly by light coming from the external lamp. A liquid phase (aqueous ethanol solution), having controlled temperature (60 °C) and composition, was present on the bottom of the reactor and maintained the gas phase in equilibrium with the liquid phase. A small continuous flow of inert gas (10 ml/min) was fluxed to the reactor to monitor composition. A gas chromatograph (GC) with a Thermal Conductivity Detector (TCD) was used to analyze the permanent gases (H_2, O_2, CH_4 and CO) by a molecular sieve column (5A Plot). Carbon dioxide, ethanol and acetaldehyde were instead analyzed by a fused silica column (Rt-Qbond). The total incident solar irradiance at a distance of 20 cm from the lamp was estimated to be 100 mW·cm^{-2}.

2.4 Testing in liquid-phase

Results of H_2 productivity were also compared with those obtained by using a conventional slurry photo-reactor. Even though the two reactor configurations are quite different, we have expressed the rates of H_2 productions per units of photocatalyst weight and area of irradiation, in order to have comparable results. The photocatalytic activity was evaluated using 125 mg of catalyst suspended in 80 mL of aqueous solution (ethanol 1:1 by volume) and irradiating the suspension using a solar simulator (LOT-ORIEL) equipped with a 150 W Xe lamp and an Atmospheric filter to cut-off UV photons below 300 nm. Ar flow (15 mL/min) was employed to remove air from the reactor and as carrier for the reaction products. Gaseous products were analyzed by a GC analysis using a TCD for the quantification of H_2 and a Flame Ionization Detector (FID), couple with a methanator, for the quantification of the C-containing compounds (CO, CO_2, CH_4, etc.). The by-products present in the liquid phases after catalytic activity were analyzed by GC-MS using a HP 7890 GC equipped with a DB-225ms column (J&W) and a HP 5975C mass spectrometer.

3. Results and discussion

The photo-catalytic substrates, prepared as thin films, should have well designed characteristics, such as efficient light harvesting, long lifetime of excited states, good adsorption of reactants, and relatively easy desorption of products; but in order to enhance the photocatalytic activity, a correct design of the photo-reactor should be adopted, in terms of geometrical configuration and operating mode (Ampelli et al., 2009). Starting from an aqueous solution of ethanol, the process is likely governed by the formation of surface ethoxide and OH groups by dissociative adsorption at the interface between metal particles and TiO_2 (Cargnello et al., 2011), which evolves in the production of large amounts of acetaldehyde both under slurry and gas phase conditions. The presence of small metal particles deposited on TiO_2 surface is fundamental to perform the photo-process because i) they act as electron attractive sites for H_2 production and ii) their light absorption bands positively interact with those of titania with the result of a shift moving from the ultraviolet to visible region. Noble metals are the most studied doping agents for titania, but issues related to their high cost ant toxicity have induced scientists to investigate other more accessible metals (Montini et al., 2011). In this context, we have evaluated the effects of copper nanoparticles on titania in the process of H_2 production by photo-dehydrogenation of ethanol.

3.1 Characterization

Table 1 summarizes the results of the textural (by BET method) and structural (by XRD method) characterization of CuO_x/TiO_2 samples.

Table 1: Textural and structural characterization of CuO_x/TiO_2-based samples

Sample	Composition[a] (%)	XRD Mean crystallite size (nm)	BET Surface area (m^2/g)
TiO_2-SG	A (72) R (10) B (18)	A (11) R (32) B (11)	67
TiO_2-PS	A (100)	A (7)	108
TiO_2-ME	A (92) R (3) B (5)	A (14) R (9) B (13)	63

[a] The labels A, B and R refer to *anatase, brookite* and *rutile* polymorphs

The samples showed relatively high surface area with good pore volume (0.15 mL·g^{-1}) and medium average mesopore size distribution (7-8 nm). Powder X-ray diffraction was employed to estimate the relative content of the different TiO_2 polymorphs by the integrated intensity of the anatase (101), rutile (110), and brookite (121) reflections. The XRD pattern evidenced the presence of a mixture of polymorphs for TiO_2-SG and TiO_2-ME, and pure anatase phase for TiO_2-PS, with a mean crystallite size of 7 nm.

In order to determine the copper particle size distribution, high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) was used in combination with X-ray energy dispersive spectrometry (XEDS) chemical analysis. Results for CuO_x/TiO_2-ME samples show a relatively narrow distribution of copper particles in the 0.5 - 3.0 nm range. CuO_x/TiO_2-SG shows also the presence of relatively small copper oxide nanoparticles in the 0.5-3.5 nm range, with an average diameter only slightly higher than that of CuO_x/TiO_2-ME samples (1.7 vs. 1.5 nm). CuO_x/TiO_2-PS sample instead shows larger particles in the 3.0 - 6.0 nm range, with an average size of 4.3 nm. For all the samples, no significant changes in particle size distribution were noted on increasing the copper loading from 1.0 to 2.5 wt. %.

Figure 1 reports the UV-Visible diffuse reflectance spectra of CuO_x/TiO_2 samples prepared according with the three studied modalities and with 1.0 and 2.5 wt. % copper loading. The spectra of the bare TiO_2 samples (without deposited copper) are also shown in Figure 1. Bare TiO_2 exhibits a strong absorption band centred at about 350 nm related to the lowest energy charge transfer $Ti^{4+} \rightarrow O^{2-}$ and thus associated to the band gap which could be estimated to be in the 3.0-3.1 eV range, consistent with expectations for a mixture of anatase, brookite and rutile TiO_2 polymorphs (see Table 1). Their modification by copper shifts the band gap, up to about 2.5 eV depending on the copper loading and method of preparation. Copper-doped TiO_2 may thus extend its absorption in the visible region enhancing the photocatalytic response, but at the same time the increase of the oxygen vacancy concentration at the higher copper loading also increases the presence of trap sites for the photogenerated electrons and holes.
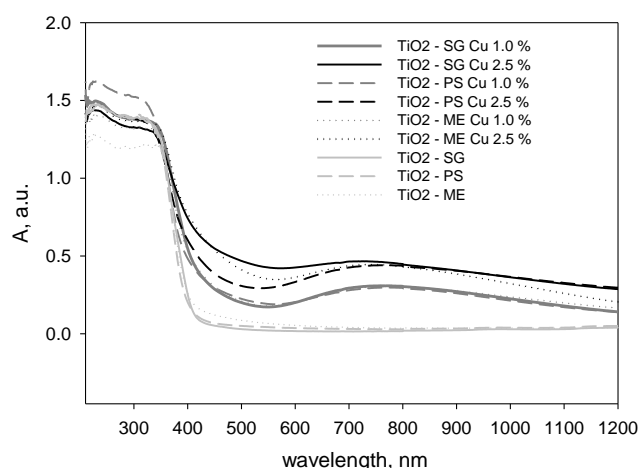

Figure 1: UV-Visible diffuse reflectance spectra of CuO_x/TiO_2 samples and of their corresponding TiO_2 samples without deposited copper
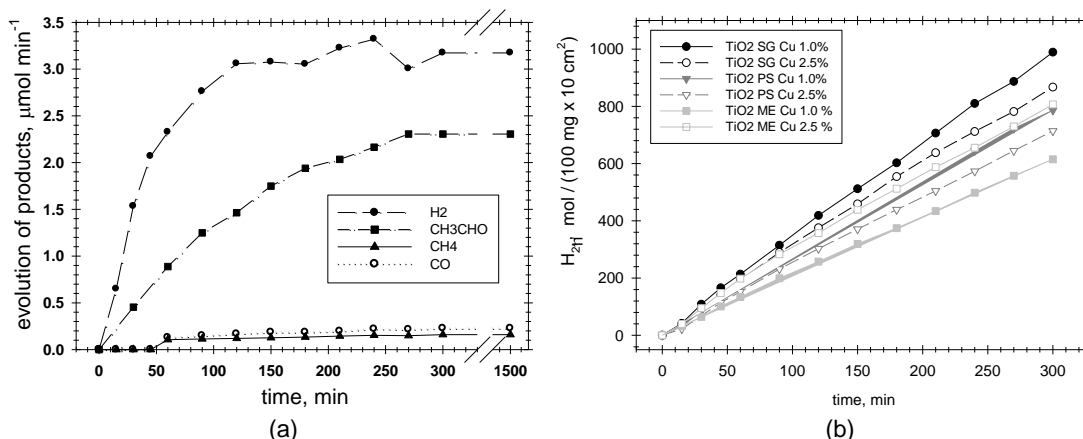
3.2 Hydrogen production

Figure 2: a) Rate of production vs. time profiles for a gas phase experiment with CuO_x/TiO_2-SG (Cu 1 %) as photo-catalyst; b) Cumulative H_2 production for all the gas phase experiments (until 5 h)

Starting from an evaporating aqueous solution of 10 vol. % of ethanol and flowing with inert gas into the solution at 10 ml min^{-1}, the feed vapour composition (in vol. %) consists of 1.5 % of ethanol and 19 % of water (the remaining part is the inert gas). The main reaction pathway is the dehydrogenation of ethanol to acetaldehyde which leads to the production of H_2 in a stoichiometric ratio of 1:1. The overall photoreforming process, instead, allows the production of 6 molecules of H_2 and 2 of CO_2 per one of ethanol. The acetaldehyde produced by dehydrogenation may either decompose to form CH_4 and CO or continue photo-reforming process to CO_2, while CO and CO_2 may be converted each to other through water-gas shift reaction. The selectivity to H_2 by dehydrogenation was high (about 92 - 93 %), depending on the nature of the photocatalytic thin film used. Figure 2a shows the typical profiles of the rates of product formation for a gas phase experiment (CuO_x/TiO_2-SG with Cu 1 wt. %). The initial transient increase of productivity is due to the activation of photocatalysts and to the accumulation of the products in the reactor volume. Usually, about four-five times the residence (holding) time is required to reach a constant value in transient CSTR-type reactor experiments, e.g. about 2 h in our case. However acetaldehyde's profile increases slower than H_2 reaching a plateau after 300 min of irradiation. The possible explanations are multiple: H_2 is produced not only by dehydrogenation but also by other pathways, as already discussed above; while acetaldehyde may initially interact with water decomposing itself. Acetaldehyde may also further convert to form heavier products but they probably remain adsorbed on the photocatalyst. By a comparison between all the CuO_x/TiO_2 substrates (see Figure 2b), the samples prepared by SG method demonstrated the best performances in terms of H_2 production. This may be ascribed to the longer lifetime of the electron/hole pair of multiphasic TiO_2 materials and particularly to the higher quantity of rutile with respect to anatase. Slightly worse results were obtained increasing Cu loading from 1.0 to 2.5 % for samples prepared by SG and PS, while the situation is reversed for the sample prepared by ME.

From the photoreforming in liquid phase, all the catalysts containing 1.0 % of Cu showed, under the present conditions, comparable H_2 production rates close to 2.5 μmol min^{-1}, irrespectively from the type of TiO_2 used as support. The most part of the acetaldehyde produced was accumulated in the solution, where it reacts with excess ethanol forming 1,1-diethoxyethane. Nevertheless, significant leaching of the Cu to the solution was observed, corresponding to ~ 15 % of the total amount of metal. This is a major drawback of liquid phase photo-assisted dehydrogenation of ethanol, that is not affecting the performances of reactor working in gas phase.

4. Conclusions

In this work the ethanol photodehydrogenation to H_2 and acetaldehyde using CuO_x/TiO_2 nanocomposites was investigated under different operation modes. High selectivity (>90%) to acetaldehyde was observed in gas phase, while liquid phase operations was affected by a significant leaching of the metal phase. CuO_x/TiO_2 nanocomposites represent also a valid alternative to the most investigated titania catalysts doped with noble metals. Samples prepared by copper photodeposition on TiO_2 prepared following three

different routes were investigated. The best performances were obtained by using TiO_2-SG with Cu 1 % in gas phase operation.

The potential industrial applicability of such kinds of systems depends on some issues related to i) the synthesis of films with bigger size (in order to obtain an irradiation surface area of at least 20 x 20 cm) and ii) the stability of the photocatalytic material (avoiding detachment of the powder from the electron collecting substrate and leaching of Cu). The ability to prepare nano-structured TiO_2 thin films prepared by anodization method may improve the photo-stability and minimize problems of contact to the electron collector material (Passalacqua et al., 2012).

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