Catalysis Today xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

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

Photocatalytic CO_2 reduction vs. H_2 production: The effects of surface carbon-containing impurities on the performance of TiO_2-based photocatalysts

Ivan Grigioni, Maria Vittoria Dozzi, Massimo Bernareggi, Gian Luca Chiarello, Elena Selli*

Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milano, Italy

ARTICLE INFO

Article history:
Received 15 April 2016
Received in revised form 30 May 2016
Accepted 31 May 2016
Available online xxx

Keywords:
Photocatalysis
Carbon dioxide reduction
Hydrogen production
Photosteam reforming
Methane production
CO production

ABSTRACT

Photocatalytic CO_2 reduction is a useful way to convert solar energy into fuels, mimicking artificial photosynthesis. The gas phase photocatalytic reduction of CO_2 was investigated with a series of TiO_2-based photocatalysts, either bare or modified by Cu(II) grafting and/or by Pt nanoparticles deposition and the results obtained in this reaction were compared with those obtained in the photocatalytic production of hydrogen by photosteam reforming of methanol-water mixtures employing the same photocatalysts series. The rates of the two reactions largely depend on the type of photocatalyst and exhibit an almost parallel behaviour, both being higher with photocatalysts containing noble metal nanoparticles. However, the yields in CH_4, CO and other products obtained from photocatalytic CO_2 reduction still remain very low and often decline during the runs. Furthermore, methane was found to be produced under irradiation when the photocatalysts were contacted with a gas phase containing water vapour and no carbon dioxide. This points to a major role of carbon-containing impurities on the photocatalyst surface, which may act both as hole scavengers and as carbon source. Two step photocatalytic tests, i.e. a cleaning step in the presence of water vapour followed by purging of the gas phase and a second step after CO_2 addition, allow one to discern between the carbon-containing gaseous products originated from carbon impurities and those produced in the presence of CO_2. In this second step, the presence of copper grafted on the photocatalyst surface favours CO evolution with respect to fully reduced CH_4.

1. Introduction

The rapid depletion of fossil fuel reserves and the environmental impact of the increasing emission and concentration of CO_2 in the atmosphere promoted the search for alternative, clean and renewable energy sources. In this context much interest has been focused in recent years on the development of photocatalytic semiconductor materials allowing efficient conversion and storage of solar energy into chemical energy, in the form of hydrocarbons resulting from CO_2 reduction [1–3] and of hydrogen obtained from water splitting [4,5]. Although the photocatalytic reduction of CO_2 to formaldehyde and methanol in purified water was first reported in 1979 [6], great interest in this reaction has grown only in the last few years. However, the reaction rates are very low, i.e. around 10 $\mu mol\, h^{-1}\, g_{cat}{}^{-1}$ for the major products (usually methanol, formic acid or formaldehyde for the reaction in the liquid phase, methane and carbon monoxide for the gas phase reaction) [7].

Semiconductor photocatalysts, such as SiC, CdS, GaP and Nb- and Ta-based oxides [8–11], having more negative conduction band edges with respect to TiO_2, as well as TiO_2 usually modified by noble or coinage metal co-catalysts [7,12–16], have been employed for this reaction. The electrons photoexcited in these photocatalysts possess large overpotential allowing the otherwise extremely up-hill CO_2 into $CO_2{}^{\bullet-}$ reduction (E° *vs.* RHE = −1.48 V) or the less demanding two electron reactions yielding CO or HCOOH (E° *vs.* RHE = −0.11 V and −0.19 V, respectively) [17]. On the other hand, the prerequisite of a sufficiently high conduction band is often strictly related to the increase of the band gap of photocatalytic materials [18–20] and therefore to the exploitation of the UV portion only of the solar spectrum. Moreover, a reaction rate decrease over time is often encountered due to photocatalysts' deactivation or to the consumption, as hole scavengers, of the previously evolved reduction products [11].

New promising strategies have been recently proposed for CO_2 photoreduction, including for instance the use of H_2 as electron

---

* Corresponding author.
E-mail address: elena.selli@unimi.it (E. Selli).

http://dx.doi.org/10.1016/j.cattod.2016.05.040
0920-5861/© 2016 Elsevier B.V. All rights reserved.

donor in the presence of irradiated nickel supported on silica-alumina [21], the photothermal approach in fluidized bed reactors [22,23], the use of photogenerated pyridinyl radicals [24,25], the use of metal organic frameworks as visible light harvesting materials [26] or of phthalocyanins and porphirins as sensitizers [27,28], the band gap narrowing of photocatalytic materials with high conduction band [29] and the use of sensitized semiconductors in Z-scheme systems [30]. Most recent reports in the photocatalytic reduction of CO_2 concern the use of small band gap materials such as $CuFeO_2$ coupled with CuO [31] and of a novel monolithic assembly based on a triple-junction, exhibiting a promising 4.6% efficiency of solar into chemical energy conversion [32].

However, the rates of products evolution still remain very low [33,34]. The doubt may arise that CH_4 and other carbon-containing species are not obtained from CO_2 photocatalytic reduction, especially when the rate of products evolution declines over time. This holds particularly true if carbon doped or high surface area materials synthesized at low temperature without post annealing treatments are used as photocatalysts [14–16]. Isotopic CO_2 labelling would be one way to demonstrate that the reaction products arise from carbon dioxide reduction and not from other carbon sources, and it has been employed in a few studies so far [24,28,30–32].

In the present work, a series of photocatalysts, including commercial and modified TiO_2-based materials obtained by Cu grafting and/or surface deposition of platinum nanoparticles, were tested in a recirculating gas phase system [35,36], both under the typical experimental conditions of photocatalytic CO_2 reduction (namely in the presence of CO_2 and H_2O in an inert gas) and in the photocatalytic production of H_2 through steam reforming of methanol. Our aim was to verify if the photoactivity of the tested materials in CO_2 photoreduction is correlated to their photoactivity in hydrogen production in the presence of methanol and to ascertain if carbonaceous impurities, mainly present in the form of carboxylates and (bi)carbonates on the photocatalyst surface [7,14], play a role in methane and CO evolution occurring under photocatalytic CO_2 reduction conditions.

2. Experimental

2.1. Photocatalytic materials

The surface-modified photocatalysts were prepared in our laboratory starting from Evonik P25 TiO_2 (84% anatase – 16% rutile), directly employed as supplied. They were obtained either by grafting Cu(II) metal ions on the TiO_2 surface or by Pt nanoparticles (NPs) deposition, or by these two steps in sequence. $Cu(NO_3)_2 \cdot 3H_2O$ was employed as Cu(II) source in the first step. In a typical grafting procedure, 2 g of P25 TiO_2 powder were dispersed in 20 mL of Milli-Q water and sonicated for 10 min in a FALC LBS2 4.5 L bath. Then 76.0 mg of $Cu(NO_3)_2 \cdot 3H_2O$ were dissolved in 1 mL of water and mixed with the aqueous TiO_2 suspension in a vial reactor. The mixture was heated at 90 °C for 1 h under stirring, up to complete solvent removal. The so-obtained material (Cu content 0.1 wt.%) was dried at 110 °C for 24 h and finely ground in an agate mortar.

In the second step, an aliquot of Cu-grafted P25 TiO_2 was further surface modified by deposition of a fixed amount (0.5 wt.%) of Pt NPs according to the deposition-precipitation (DP) method, using urea as the precipitating agent [37]. The proper amount of Cu-grafted P25 TiO_2 was suspended in water, sonicated and added to an aqueous solution containing H_2PtCl_6 (0.1 g L^{-1} of Pt) and urea (0.42 M). The suspension was vigorously stirred for 4 h at 80 °C, until pH 7.5 was reached. The slurry was then cooled down to room temperature and the precipitate was collected by centrifugation, using a CL10 Thermo Scientific centrifuge. The solid product was then re-suspended in 20 mL of Milli-Q water and platinum was reduced by addition of an aqueous $NaBH_4$ solution in slight excess. The colour of the suspension suddenly changed from white to grey. After 20 min stirring, the slurry was centrifuged and the solid recovered and washed at least three times with 20 mL of Milli-Q water, until the residual chloride and nitrate anions content in the surnatant was below 1 ppm, as checked by ion chromatography. The so obtained photocatalyst was named Pt/Cu(0.1)/T.

To check the effects induced by the employed metal deposition procedures and by the single metal or by the co-presence of Cu and Pt on the TiO_2 surface, three more samples were prepared, which were labelled T, Cu(0.1)/T and Pt/T. The T sample was prepared by treating P25 TiO_2 according to the two above described steps, although in the absence of metal precursors. Cu(0.1)/T was produced by the Cu(II) grafting procedure followed by the DP treatment in the absence of Pt precursor. Pt/T was prepared by performing the first step without the Cu(II) source, followed by Pt NPs deposition according to the DP method.

All chemicals employed were purchased from Aldrich. Water purified by a Milli-Q water system (Millipore) was used throughout.

A TiO_2 sample produced by sol-gel synthesis, followed by spray-drying at 150 °C, was also tested. This material was labelled as SD and had a very light brown colour.

2.2. Photocatalysts characterization

Diffuse reflectance (R) spectra of the photocatalyst powders were recorded on a Jasco V-670 spectrophotometer equipped with a PIN-757 integrating sphere; barium sulphate was used as a reference. The reflectance spectra were then converted into absorption (A) spectra (A = 1 – R). Thermogravimetric analysis (TGA) was carried out with a Mettler-Toledo TGA/DSC 2 Star system in flowing air, by heating the sample from 30 up to 800 °C with a 10 °C min^{-1} heating rate. X-ray powder diffraction (XRPD) analysis were carried out with a Philips PW3020 powder diffractometer, by using the Cu Kα radiation (λ = 1.54056 Å). The BET specific surface area (SSA) was measured by N_2 adsorption at liquid nitrogen temperature (77 K) on a ASAP 2020 apparatus, after out-gassing in vacuo at 150 °C for at least 2 h.

2.3. Photocatalytic tests

The photocatalytic activity of the TiO_2-based materials in both carbon dioxide photocatalytic reduction and hydrogen production by photo-steam reforming of methanol was tested using the bench-scale apparatus [35,36], connected to a gas phase closed system, which is sketched in Fig. 1. The gas phase was recirculated by means of a metal Bellows pump and was saturated with the reactants by bubbling it through either pure water (in CO_2 photoreduction), or a 20% methanol solution in deionized water (in H_2 photoproduction). The recirculating system was connected to a gas phase photocatalytic reactor containing the catalyst powder (16 mg) previously immobilized on quartz grains. The photocatalyst was irradiated through a Pyrex window and continuously fed with the reactant vapour phase mixture. The recirculating phase was automatically sampled at regular time intervals and analyzed by an Agilent 6890 N gas-chromatograph equipped with two columns (a MolSieve 5A and a plot-U column), a methanizer and both a flame ionization and a thermal conductivity detector. The irradiation source was an external 300 W Xenon lamp (LOT Oriel LSH 302). Prior to the beginning of irradiation, the system was thoroughly purged with an inert gas, helium or nitrogen, in order to completely remove oxygen from the gas phase and the liquid phase. During the photocatalytic experiment, the temperature of the gas mixture was maintained at 30 °C.

Please cite this article in press as: I. Grigioni, et al., Photocatalytic CO_2 reduction vs. H_2 production: The effects of surface carbon-containing impurities on the performance of TiO_2-based photocatalysts, Catal. Today (2016), http://dx.doi.org/10.1016/j.cattod.2016.05.040