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Green photocatalytic synthesis of vitamin B_3 by Pt loaded TiO_2 photocatalysts

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Authors dedicate this article to the retirement and to the career of Prof. Vincenzo Augugliaro (Palermo University, Italy).

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ABSTRACT

Selective photocatalytic oxidation of 3-pyridinemethanol to 3-pyridinemethanal and vitamin B_3 by using pristine and Pt loaded home prepared (HP) rutile and commercial TiO_2 photocatalysts, under UV, UV–vis and visible irradiations in water, was performed in friendly environmental conditions. The photocatalysts were characterized by XRD, SEM-EDAX, BET, DRS, XPS and TGA techniques. The influence of pH on reactivity and total selectivity to 3-pyridinemethanal and vitamin B_3 was studied. Under very acidic conditions (pH = 2) no or low activity (depending on photocatalyst) was observed, whereas by increasing the pH from 4 to 12 very high total selectivity was achieved. The Pt loading was beneficial for selectivity whereas the reactivity was positively affected only for crystalline HP sample. This last sample showed good activity under visible irradiation, exhibiting an about 4 times higher conversion than the other samples. The influence of the position of the benzylic group in pyridine (2-pyridinemethanol and 4-pyridinemethanol) was also studied. The results showed that to synthesize vitamin B_3 in green conditions the photocatalyst should be poorly crystalline or Pt loaded.

1. Introduction

Heterogeneous photocatalysis by TiO_2 fulfils the principles of Green Chemistry as the experiments are generally carried out in water at ambient temperature and under sunlight by using oxygen from air as the oxidant [1]. A semiconductor such as TiO_2 is very suitable for green photocatalysis as it is very effective, cheap and stable to photocorrosion [2]. Using oxygen from air without doing any purification is very simple, economic and hazardless. Water is also very cheap, sustainable and un-flammable solvent [3]. By considering that fossil fuels will end near future, using sunlight as energy source becomes a very important challenge for mankind. In addition, working at room temperature and pressure decreases energy requirement and costs for reactor security.

Heterogeneous photocatalysis has been mainly employed to oxidise organic and inorganic pollutants in liquid or gaseous phases [2]. The oxidation reaction in water, due mainly to primary oxidant species as hydroxyl radicals, has been considered unselective and therefore synthesis reactions generally have been carried out in organic solvents [4]. Photocatalytic selective oxidation of benzyl alcohol derivatives [5], 5-(hydroxymethyl)-2-furaldehyde [6], amines [7], piperonyl alcohol [8], *trans*-ferulic acid [9], isoeugenol [10], and glycerol [11] or selective cyclization of aromatic acids [12] are examples of synthetic reactions performed in water.

It is well known that Pt loading of TiO_2 photocatalysts increases the activity both under UV and visible irradiation [7,12]; in fact Pt loading decreases the electron-hole recombination rate and therefore the reaction rate increases. By using metal loaded TiO_2, photocatalytic reactions under visible or sunlight irradiation have been generally performed for degrading harmful compounds [13], some investigations having been also carried out to perform organic syntheses in organic solvents [14]. For instance photocatalytic oxidation of aniline to nitrosobenzene has been selectively (90%) performed by using Pt-loaded TiO_2 in toluene and under visible irradiation [14c].

Vitamin B_3 (pyridine-3-carboxylic acid), whose world production is around 35,000 tons per year [15], is generally used in the

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prevention and treatment of pellagra disease. Industrially vitamin B_3 and other pyridine carboxylic acids are produced at high pressure by oxidation of picolinic isomers using nitric acid, permanganate or chromic acid and vanadia-titania-zirconia oxide supported catalysts [15]. Just three research papers were published on the photocatalytic selective oxidation of 3-pyridine-methanol [16,17] and its derivatives [15] to their corresponding aldehydes and acids. These reactions were performed in water, under acidic conditions (pH 1–4) [15–17] and using commercial TiO_2 [15,17] and TiO_2-graphen-like [16] composite photocatalysts. In addition, the reactions were performed under de-aerated conditions using cupric ions as electron acceptor in order to minimize the electron-hole recombination. pH and temperature influence on 3-pyridine-methanol oxidation was also investigated [15]. It was found that temperature effect was negligible for products yields while, by increasing pH from 1 to 4, both aldehyde and vitamin B_3 yields and Cu^{2+} ions conversion decreased. In these works, high total selectivity values were obtained, being selectivities to aldehyde higher than those to acid. Selective production of pyridinecarboxaldehydes from methylpyridine isomers was also performed under de-aerated conditions in acetonitrile or acetonitrile-water solvents [18]. The obtained results show that the reactivity is strongly dependent on the photocatalyst properties.

In our recent work selective photocatalytic oxidation of 4-methoxybenzyl alcohol and 4-nitrobenzyl alcohol was performed in water under simulated solar light by using Pt, Au, Pd and Ag loaded Degussa P25 TiO_2 catalysts [19]. The best activity and selectivity results were obtained with Pt-loaded (0.5%) TiO_2 and the highest aldehyde selectivities were reached at low pH's. Significant amount of 4-nitrobenzoic acid (*ca.* 50%) was obtained only from 4-nitrobenzyl alcohol at high pH values.

In this work, differently from the previously cited works [15–17,19], Pt-loaded home prepared (HP) TiO_2 photocatalysts were used for selective oxidation of 2, 3 and 4-pyridinemethanol to its corresponding aldehyde and acid in water. Oxygen from atmospheric air was used as oxidant; the influence of different light sources (UV, UV–vis and visible) on substrate degradation rates and products selectivities was also investigated for different pH's (2–12). The optimal amount to be loaded on TiO_2 was already investigated [19] and this amount (0.5%) has been used for the TiO_2 samples of this work.

2. Experimental

2.1. Preparation of photocatalysts

2.1.1. Preparation of HPRT

The precursor solution was obtained by adding 20 mL of $TiCl_4$ to 1000 mL of water contained in a volumetric flask (2 L). At the end of the addition, the resulting solution was stirred for 2 min by a magnetic stirrer and then the flask was sealed and maintained at room temperature (*ca.* 298 K) for a total aging time of 6 days. After that time the precipitated powder was separated by decantation and dialysed several times with deionised water until a neutral pH was reached. Then, the sample was centrifuged and dried at room temperature. The final HP catalyst is hereafter indicated as HPRT [6]. A thermal treated HPRT sample was prepared by calcining it for 3 h at 400 °C (HPRT-400).

2.1.2. Preparation of 0.5% Pt loaded samples: Pt-P25, Pt-HPRT and Pt-HPRT-400

The details of metal loading on TiO_2 by photoreduction method are reported elsewhere [19]. 2 L of water, 500 mL of ethanol (as reductive agent), 10 g of TiO_2 (P25, HPRT or HPRT-400) and a nominal amount of Pt (50 mL of 1 ppm Pt aqueous solution of $PtCl_4$) were mixed together. This suspension was ultrasonicated for 15 min.

A Pyrex batch photoreactor of cylindrical shape, with volume of 2.5 L, was used for photodeposition of Pt on suspended TiO_2 by photoreduction of Pt cations. The photoreactor was provided with ports in its upper section for the inlet and outlet of gases. A magnetic bar guaranteed a satisfactory suspension of the photocatalyst and the uniformity of the reacting mixture. A 700 W medium pressure Hg lamp (Helios Italquartz) was axially immersed within the photoreactor and it was cooled by water circulating through a Pyrex thimble; the temperature of the suspension was about 300 K. The aqueous solution was deaerated by bubbling He at atmospheric pressure for 30 min in the dark and then the lamp was turned on. The gas was continuously bubbled during the photodeposition that lasted 8 h. Then it was waited until the metal loaded TiO_2 was precipitated; the solid phase was separated by decantation. The resulting powder was washed two times by using 2.5 L of deionised water. Lastly the powder was dried at room temperature for obtaining fine powders hereafter called Pt-HPRT and Pt-HPRT-400. Pt-loaded P25 sample was calcined at 400 °C (Pt-P25).

2.2. Characterization

XRD patterns of the powders were recorded by Bruker D8 Advance diffractometer using the Cu Kα radiation and a 2θ scan rate of 1.281°/min.

SEM images were obtained using an ESEM microscope (FEI Nova Nano Sem 650) with Through Lens Detector (TLD) and/or Coherence Backscattering Detector (CBS). BET specific surface areas were measured by the multi-point BET method using a Micromeritics (Gemini 2360 model) apparatus. Before the measurement, the samples were outgassed for 3 h at 250 °C. Thermogravimetric analysis (TGA) was performed by using Shimadzu equipment (model TG60H). The heating rate was 10 °C/min in N_2 atmosphere and the used powder amount was *ca.* 8 mg. Ultraviolet-visible spectra were obtained in the 300–800 nm range by diffuse reflectance spectroscopy by using a Shimadzu UV-2401 PC instrument with $BaSO_4$ as the reference.

X-ray photoelectron spectroscopy (XPS) measurements were carried out by using a Thermo Fischer K-Alpha spectrometer. All the binding energies were referred to the C 1 s peak at 284.6 eV.

^{1}H NMR spectra was recorded on a Varian Mercury-400 High Performance Digital FT-NMR spectrometer. Chemical shifts are reported in ppm. DMSO (δ = 2.50 ppm) was used as a solvent and tetramethylsilane was used as the internal standard.

2.3. Photoreactivity setup and procedure

The details of photoactivity set-up and procedure are reported elsewhere [20]. A cylindrical Pyrex batch photoreactor, containing 150 mL of aqueous suspension, was used to perform the reactivity experiments under UV–vis irradiation. The photoreactor was provided with an immersed lamp and with open ports in its upper section for contacting the suspension with atmospheric air and for sampling. A magnetic stirrer guaranteed a satisfactory suspension of the photocatalyst and the homogeneity of the reacting mixture. A 100 W halogen lamp (Osram, Germany) was axially positioned within the photoreactor; it was cooled by water circulating through a Pyrex thimble surrounding the lamp. In order to perform the experiments under visible irradiation, the circulating liquid was 1 M $NaNO_2$ aqueous solution, which totally prevented UV irradiation from reaching the suspension.

For the runs carried out under UV radiation a continuously stirred beaker (volume: 250 mL; diameter: 6.7 cm) containing 150 mL of aqueous suspension was used as photoreactor. In this case the suspension was irradiated by four fluorescent lamps