Applied Catalysis B: Environmental 163 (2015) 248–257

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

# Production of pyridinecarboxy aldehydes, nicotinic and isonicotinic and picolinic acids by $TiO_2$-sacrificial photocatalysis at ambient conditions and in aqueous solution through artificial solar radiation

Danilo Spasiano[a], Raffaele Marotta[a,*], Ilaria Di Somma[b], Giuseppe Mancini[c]

[a] Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università di Napoli "Federico II", p.le V. Tecchio, 80, 80125—Naples, Italy
[b] Istituto di Ricerche sulla Combustione, Centro Nazionale delle Ricerche (IRC-CNR) —P.le V. Tecchio, 80, 80125—Naples, Italy
[c] Dipartimento di Ingegneria Industriale, Università di Catania, v.le A. Doria, 5, 95125—Catania, Italy

## ARTICLE INFO

*Article history:*
Received 1 May 2014
Received in revised form 15 July 2014
Accepted 2 August 2014
Available online 12 August 2014

*Keywords:*
Vitamin B3
Picolinic acid
Pyridinecarboxy aldehydes
Sacrificial photocatalysis
Solar chemical productions

## ABSTRACT

The conversion of pyridinemethanol isomers into their respective aldehydes and carboxylic acids has been attempted in aqueous solution through sacrificial $TiO_2$ photocatalysis in the presence of cupric ions, at ambient temperature, under acidic and deaerated conditions, using artificial sunlight.

The presence of a nitrogen atom in the aromatic ring, with respect to benzylic alcohol and its derivatives, affects the photocatalytic behavior of the substrate. The influence of both pH and temperature has also been investigated. The position of the methanolic group on the aromatic ring leads to slight changes in the selectivities, yields and the oxidation rates. Under the adopted conditions, the yields and selectivities to aldehydes are always higher than those of the respective carboxylic acids.

The photocatalytic process can be carried out in consecutive copper reduction/oxidation steps in order to reuse the catalyst. In this way greater yields and selectivities to the desired product than 60% can be achieved.

The process can be considered interesting as it concerns the eco-green production of valuable fine chemicals, using water as a solvent at ambient conditions, a cheap heterogeneous catalyst and solar radiation.

## 1. Introduction

Nicotinic, isonicotinic and picolinic acids are valuable intermediates for pharmaceuticals, dyes, agriculture products, and in the production of cosmetics and food additives [1–3].

Nicotinic acid (niacin, vitamin PP or B3) is an important vitamin in the B group: it is particularly used in the prevention and treatment of pellagra disease. The annual worldwide production of nicotinic acid is around 35,000 tons [4].

Pyridinecarboxylic acids are industrially produced through the oxidation of the respective picolinic isomers with nitric acid, permanganate or chromic acid under high pressure in the liquid-phase or by means of vapor-phase oxidation with oxygen or air over supported catalysts, such as vanadia–titania–zirconia oxides [5,6,59].

Pyridinecarboxylic acids are also formed via the hydrolysis of pyridinecarboxynitriles, which are produced by the ammoxidation of picoline isomers in the presence of solid catalysts [7,8] or using nitrile hydratase–amidase enzymatic systems [58]. However, some of these processes suffer from substantial drawbacks. The main disadvantages of liquid-phase processes include problems due to the handling of nitric acid at elevated temperatures and pressures, and to the production of mother-liquors, caused by the neutralization of nitric acid, together with the purity of the end-products [9]. On the other hand, catalyzed vapor-phase processes suffer from problems due to the necessity of obtaining a selective and efficient reaction, because of the existence of undesired competitive total oxidation reactions of the reagents and intermediates, and catalyst regeneration [4]. Moreover, from a safety point of view, both the liquid and vapor of picoline derivatives, which are used as reagents, are highly flammable and spread quite readily over an operating system [10,11].

These problems have led to the search for alternative routes and manufacturing processes that are less expensive and dangerous and no-polluting for pyridine carboxylic acids [12].

For example, the one-pot synthesis of nicotinic acid by air oxidation of 3-picoline over a $V_2O_5$-$TiO_2$ catalyst has been proposed

---

* Corresponding author. Tel.: +39 0817682968; fax: +39 0815936936.
*E-mail address:* rmarotta@unina.it (R. Marotta).

http://dx.doi.org/10.1016/j.apcatb.2014.08.002
0926-3373/

[13–15]. 3-picoline can also be oxidized with oxygen, in the gas-phase, to nicotinic acid, with high yields on mixed oxide catalysts, such as $Cr_{1-x}Al_xVO_4$ or $CrV_{1-x}P_xO_4$ [16,17]. These processes produce little solid or liquid waste and no harmful gas exhaust, and thus meet all the requirements of "green" technology, although operative temperatures equal to or higher than 250 °C are required.

Moreover, it has been reported that methylpyridine isomers are stable at high temperatures, but pyridine-carboxylic acids, pyridine-carboxaldehydes and pyridylmethanol intermediates all undergo cleavage and form pyridine with the release of carbon dioxide, formic acid and formaldehyde, respectively [18].

Cobalt-doped catalysts and selenium dioxide also exhibit very high picoline conversion and good selectivity towards to pyridinecarboxylic acids in organic solvents [6,19]. In this case, the main disadvantage is the handling of highly toxic poisonous and expensive metals. It has been demonstrated that methylpyridine isomers can be effectively converted to pyridinecarboxaldehyde isomers through a photocatalytic oxidation process using $TiO_2$ as the catalyst under deaerated conditions [20]. The pyridinecarboxaldehyde production rate depends on which $TiO_2$ powder is used and on the position of the methyl group in the pyridinic ring.

In recent years, $TiO_2$ photocatalysis has also been successfully proposed in a selective oxidation process of aromatic alcohols to aldehydes and carboxylic acids, and high yields have been obtained [21–25,60]. Among the photocatalytic processes that have the aim of partially oxidizing aromatic alcohols, "sacrificial photocatalysis", in which oxygen is replaced by cupric ions dissolved in the solution to prevent the mineralization to $CO_2$, is particularly interesting [26,27]. The cupric ions are reduced to a lower oxidation state by capturing the photo-generated electrons on $TiO_2$, whereas the alcohol is oxidized, through a direct reaction with the positive holes [28].

Among the $TiO_2$ commercial samples that were investigated, the catalysts in which $TiO_2$ is present in rutile form, either prevalently or totally, showed less activities than the samples that prevalently contain anatase [45], probably because the more negative redox potential (−0.27 V vs NHE) of the anatase conduction band makes it more competitive than the rutile one (−0.15 V vs NHE) for cupric ion reduction.

At the end of the process, the solid $TiO_2$ photocatalysts can easily be recovered and recycled, while the cupric ions, after reduction to zero-valent copper, can be regenerated by means of air oxidation of metal copper under dark conditions.

In the present paper, the authors propose sacrificial photocatalysis as a green innovative method to produce pyridinecarboxy aldehydes and pyridinecarboxylic acids, starting from their respective pyridinemethanol isomers.

The technique proposed can also be considered useful to produce pyridinecarboxy aldehydes, which are used as precursors for the synthesis of chemical agents with pharmacological or biological activities, such as antineoplastics, antivirals, antifungals, antibacterials and antimalarials [29–32].

Moreover, 2-pyridinecarboxyaldehyde is a precursor of pralidoxime, which is used to treat poisoning by organophosphates [33], while 4-pyridinecarboxyaldehyde is a chemical intermediate for the preparation of Donepezil [34], a drug used for the treatment of mild to moderate Alzheimer type dementia [35].

## 2. Experimental

### 2.1. Equipment

Photocatalytic runs have been carried out in a batch cylindrical glass jacketed reactor (280 ml) equipped with a high-pressure UV lamp (UV 12F-Helios Italquartz model, nominal power 125 W), mainly emitting at 305, 313 and 366 nm (manufacturer's data). The measured powers of the lamp were $4.85 \times 10^{-5}$, $8.34 \times 10^{-5}$ and $2.71 \times 10^{-4}$ E min$^{-1}$ at 305, 313 and 366 nm, respectively.

**Fig. 1.** Image showing the mixture before the photocatalytic process (A) and after 3 h of oxidation (B).

The reactor was thermostated at the desired temperature. The pH was regulated with perchloric acid and monitored by means of an Orion 420A+ pH-meter (Thermo).

Before starting each experiment, the solution was preventively purged with nitrogen to remove the oxygen present in the reactor. During the experimental runs, nitrogen gas was continuously sparged to the irradiated and magnetically stirred solution, thus preventing contact with the oxygen.Fig. 1.

Before the photocatalytic process, the solution and catalyst exhibited a slightly skyblue/white color due to the presence of titania and cupric aquo-complexes (A, Fig. 2). After the photocatalytic run, the mixture had a brown/red color (B, Fig. 2), thus indicating the presence of zero-valent copper.

### 2.2. Analytical methods

The 2-pyridinemethanol (2-PMA), 3-pyridinemethanol (3-PMA), 4-pyridinemethanol (4-PMA), 2-pyridinecarboxyaldehyde (2-PCA), 3-pyridinecarboxyaldehyde (3-PCA), 4-pyridinecarboxyaldehyde (4-PCA), nicotinic (NA), isonicotinic (INA) and picolinic