



# Aerobic oxidation of secondary pyridine-derivative alcohols in the presence of carbon-supported noble metal catalysts

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## ABSTRACT

Pt/C and PtBi/C catalysts prepared on a synthetic mesoporous carbon were evaluated in the oxidation of secondary aromatic alcohols (1-phenylethanol,  $\alpha$ -methyl or phenyl pyridinemethanol) with air in different dioxane/water mixtures at 100 °C under 10 bar air. The observed activity for all substrates over both types of catalysts was strongly improved with the addition of water to the dioxane solvent as a result of different interactions of the alcohols with the metallic surface in the apolar dioxane solvent or polar aqueous medium. A promoting effect of bismuth was observed for all substrates. However, the reaction rate was also dramatically influenced by the nature of the aromatic moiety, the nature of the  $\alpha$ -group, and the position of the substituent on the pyridine moiety. As a general rule the reactivity was *meta* < *para* < *ortho* and the pyridine derivatives with a phenyl group were more reactive.  $\alpha$ -Phenyl-2-pyridinemethanol was totally converted to 2-benzoylpyridine with a selectivity of 96% in dioxane/water 50/50 vol% in the presence of a 2.7% Pt–0.9% Bi/C. Nevertheless, platinum leaching was detected, which could be limited with the promotion by bismuth.

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## 1. Introduction

The development of clean, selective and atom-efficient reactions remains an area of intense interest in organic synthesis. This is particular the case for oxidation of primary and secondary alcohols to carbonyl compounds; the challenge is the oxidation with molecular oxygen in the presence of heterogeneous catalysts. A substantial effort has been devoted to this type of reaction and noble metal-catalyzed oxidation with air or pure oxygen is a clean alternative. Platinum, palladium, ruthenium, and more recently gold are proposed as efficient catalysts under mild conditions [1–4]. Whilst many reports concerned the selective oxidation of benzyl alcohol derivatives to either the corresponding aldehydes or acids [2,5–7], the oxidation of secondary aliphatic or aromatic alcohols to the corresponding ketones has been less studied [8,9]. The heterocyclic carbonyl derivatives are interesting synthons in pharmaceutical industry [10–16]. For instance, heterocyclic thiosemicarbazone derivatives represent an important series of compounds with potentially beneficial pharmacological properties [11]. As examples, different metal complexes with 2-formyl and 2-acetylpyridine thiosemicarbazones showed antiviral and antitumor activity [13,14]. Using a polymer incarcerated gold or gold–platinum bimetallic catalyst, 58% and 80% yields to the desired

ketone were obtained respectively, after 48 h in the oxidation of  $\alpha$ -methyl-2-pyridinemethanol in water/trifluorobenzene under ambient conditions [15,16]. 1-Phenylethanol was completely converted to acetophenone under the same conditions within 3 h or 5 h, respectively. Consequently, the aerobic oxidation of pyridine derivatives is still challenging.

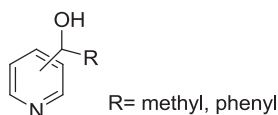
In this work, we investigated the oxidation with air of different  $\alpha$ -methyl or  $\alpha$ -phenyl pyridinemethanols in the presence of Pt/C catalyst. Preliminary experiments were performed with 1-phenylethanol to examine the impact of the nature of the aromatic ring. Previously, we reported on the positive influence of water in the aerobic oxidation of 2-octanol; with increasing water contents in 1,4-dioxane/water solvent, a dramatic enhancement of the catalytic activity was observed [8]. In line with our previous work, this parameter, as well as the nature and the position of the substituents on the heteroaromatic moiety were examined.

## 2. Experimental

### 2.1. Catalysts preparation and characterization

The supported catalysts were prepared on a synthetic carbon from MAST Carbon Technology Ltd. The carbon was prepared by carbonisation at 800 °C of a porous polymeric resin prepared from a phenolic resin and hexamethylenetetramine in ethyleneglycol, washing, and activation by treatment with CO<sub>2</sub> at 850 °C with 30% burn-off. Different batches of platinum catalyst were prepared by

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**Scheme 1.**  $\alpha$ -Substituted pyridinemethanol derivatives.

impregnation of the carbon with an aqueous solution of  $\text{H}_2\text{PtCl}_6$  to obtain a metal loading of 3–5 wt.%, followed by liquid phase reduction with formaldehyde in alkaline medium, as described in [8]. The Pt catalyst was also used as the precursor for preparing a bimetallic Pt–Bi/C catalyst via a redox surface reaction from an aqueous  $\text{BiONO}_3$  solution, using glucose as the reductant, according to previously reported procedure [17]. By this way, Bi is directly and preferentially deposited on the noble metal. A molar Bi/Pt ratio of 0.35 was chosen, since this composition has been shown to be often the optimum in the oxidation of a series of alcohols [1,2] (Scheme 1).

The metal content of the samples were determined by using ICP-OES (inductively coupled plasma-optical emission spectroscopy). Surface area and pore volume of the carbon sample were measured by nitrogen adsorption experiments at 77 K, using a Micromeritics ASAP 2020 automated system. The sample was degassed for 3 h at 623 K before the measurement. Transmission electron microscopy (TEM) was performed using a JEOL 200EX microscope operating at 200 kV. The samples were first suspended in ethanol and agitated in an ultrasonic bath. A drop of the suspended catalyst was applied to a copper mesh grid with a carbon film, and the ethanol was allowed to evaporate.

## 2.2. Catalytic tests

The reaction tests were performed under a set of realistic conditions in a stirred autoclave reactor of 300 mL made of Hastelloy in batch mode equipped with a magnetically driven stirrer set. In a typical oxidation reaction, the reactor was loaded with a solution of alcohol (15 mmol) in solvent (150 mL), and the supported catalyst, to get a 1 mol% Pt with respect to the alcohol. This ratio corresponds to ca. 27 mg Pt introduced in the reactor. After sealing and purging with argon, the reactor was heated to the desired reaction temperature of 373 K, and then air was introduced up to the pressure of 10 bar. Efficient stirring was started and this time was considered to be zero time for the reaction.

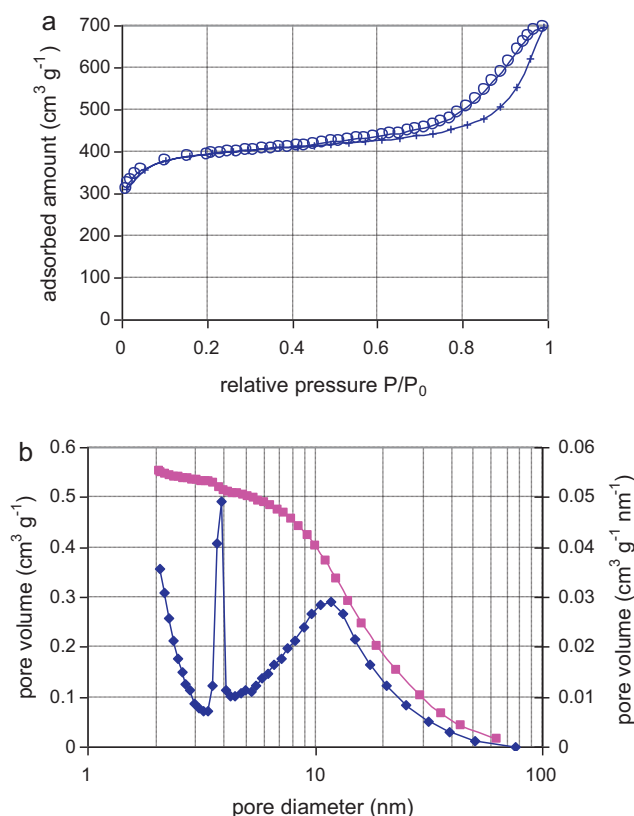
Liquid samples were periodically removed from the reactor via a sample diptube. The samples from the reaction were filtered and then analyzed via gas chromatography (GC) equipped with a flame ionisation detector (FID) and a HP5 column (30 m  $\times$  0.25 mm, 0.25  $\mu\text{m}$  film thickness). The external calibration method was used to quantify reactant and products.

The metal analysis in samples was carried out using a ICP-OES Horiba Jobin Yvon (Activa) instrument.

## 2.3. Synthesis of the heteroaromatic alcohols

Except  $\alpha$ -methyl-4-pyridinemethanol which was commercial (Sigma–Aldrich), the other  $\alpha$ -heteroaromatic alcohols were synthesized from the commercial corresponding ketones, according to the procedure described in [18].

**Synthesis of  $\alpha$ -methyl-2-pyridinemethanol. General procedure.** 20 g (0.17 mol) of 2-acetyl-pyridine were dissolved in 250 mL of EtOH. 12.5 g (0.3 mol) of  $\text{NaBH}_4$  were added slowly. After 1 h at room temperature, the conversion of the substrate was complete. 250 mL of water were added and the solution was heated at 90 °C for 15 min. After cooling, the product was extracted with AcOEt. The combined organic solutions were dried over  $\text{MgSO}_4$ , the solvent was evaporated to give 13 g (70%) of  $\alpha$ -methyl-2-pyridine methanol as a pale green oil.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):



**Fig. 1.** Characterization of the carbon support: (a)  $\text{N}_2$  sorption isotherm (+ adsorption,  $\circ$  desorption), (b) pore size distribution ( $\blacksquare$  cumulative pore volume,  $\blacklozenge$  desorption  $dV/dD$  volume).

$\delta$  (ppm) = 1.49 (3H, d,  $J$  = 6 Hz); 4.94 (1H, q,  $J$  = 6 Hz); 7.21 (1H, m); 7.28 (1H, m); 7.73 (1H, m); 8.48 (1H, m). Purity = 99% (NMR).

**$\alpha$ -Methyl-3-pyridinemethanol.** Using similar procedure, 92% of colourless oil was obtained.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 1.47 (3H, d,  $J$  = 7 Hz); 3.78 (1H, s); 4.92 (1H, q,  $J$  = 7 Hz); 7.23 (1H, m); 7.71 (1H, m); 8.36 (1H, m); 8.44 (1H, m). Purity = 99% (NMR).

**$\alpha$ -Phenyl-2-pyridinemethanol.** Using similar procedure, 86% of white solid was obtained.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 5.76 (1H, s); 7.17–7.37 (7H, m); 7.62 (1H, m). m.p. = 74 °C. Purity = 99% (NMR).

**$\alpha$ -Phenyl-3-pyridinemethanol.** Using similar procedure, 93% of white solid was obtained.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 5.92 (1H, s); 7.17–7.42 (6H, m); 7.70 (1H, m); 8.30 (1H, m); 8.50 (1H, m). m.p. = 54 °C. Purity = 99% (NMR).

**$\alpha$ -Phenyl-4-pyridinemethanol.** Using similar procedure, 86% of white solid was obtained.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 5.76 (1H, s); 7.29–7.34 (7H, m); 8.46 (2H, m). m.p. = 116 °C. Purity = 98% (GC).

## 3. Results and discussion

### 3.1. Catalyst characterization

Fig. 1a shows the dinitrogen adsorption–desorption isotherm of the support with a hysteresis loop at a relative pressure  $0.7 < P/P_0 < 1.0$ . Correspondingly, the resulting carbon was shown to be mesoporous with the main pore sizes centered at 11 nm in diameter (Fig. 1b). Moreover, a BET surface area of 1265  $\text{m}^2 \text{g}^{-1}$  was calculated. Elemental analysis revealed that the carbon was poorly functionalized, and that it was rather hydrophobic.

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