

Aerobic oxidation of secondary aromatic alcohols in the presence of carbon-supported noble metal catalysts

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Introduction

The oxidation of primary and secondary aromatic alcohols to the corresponding carbonyl compounds in the presence of heterogeneous catalysts and air is of significant importance in organic synthesis. While many reports concerned the selective oxidation of benzyl alcohol derivatives to either aldehydes or acids[1], the oxidation of secondary aliphatic or aromatic alcohols to the corresponding ketones has been less studied[2]. More specifically, the aerobic oxidation of pyridine derivatives is still challenging. In this paper we wish to present our contribution in this field.

Experimental

The supported metallic catalysts were prepared on a synthetic carbon from MAST Carbon Technology Ltd by impregnation with an aqueous solution of H_2PtCl_6 (to obtain Pt loadings of 3-5 wt%) followed by liquid phase formaldehyde reduction. The Pt-Bi catalysts were prepared by redox surface reaction from an aqueous $BiONO_3$ glucose solution.

The reaction tests were performed in a stirred Hastelloy autoclave reactor in batch mode. In a typical oxidation reaction, the reactor was loaded with a mixture of alcohol (15 mmol), solvent (150 ml) and the supported catalyst (1 mol% Pt). After purging with argon, the reactor was heated to the desired temperature, and then air was introduced up to 10 bar. Liquid samples were periodically withdrawn from the reactor and analysed by GC.

Results/Discussion

Previously we have reported the influence of water in the aerobic oxidation of 2-octanol in the presence of Pt/C catalyst: with increasing water contents in dioxane/water mixture, a dramatic enhancement of the catalytic activity was observed. We investigated the oxidation of aromatic-substituted alcohols with the same catalyst. Phenylethanol behave similarly: the higher concentration of water, the more rapid the reaction (Fig 1a). The positive influence of water was also clearly detected for pyridine derivatives substituted by either a phenyl or a methyl group (Fig 1b). However, these substrates exhibited lower reactivity under similar reaction

conditions, particularly 2-pyridinyl methyl methanol. Moreover, in pure water, low selectivity toward the ketone was achieved.

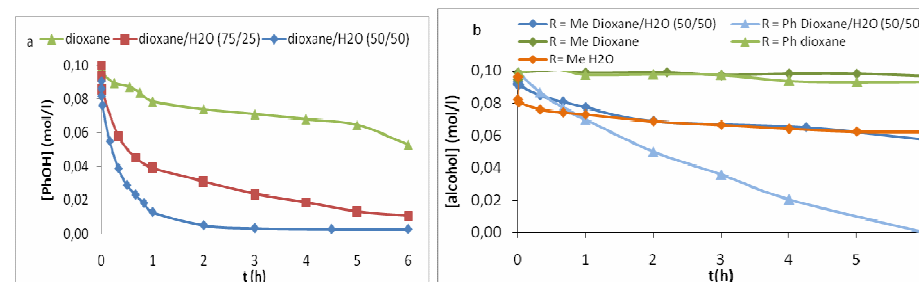
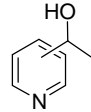
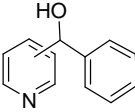


Figure 1. Oxidation of a) 1-phenylethanol; b) Pyridinyl derivatives (Py-CH(OH)-R with R = Me or Ph)

The reaction rate was dramatically affected by the nature and the position of the substituent on the heteroaromatic moiety.

Table 1 Oxidation of substituted pyridinol in dioxane/ H_2O (1/1), 100°C, 10 bar air, 6h.

substrate	catalyst	conversion/% (selectivity/%)		
		<i>o</i>	<i>m</i>	<i>p</i>
	Pt/C	38 (90)	17 (82)	22 (50)
	PtBi/C	76 (97)	42 (83)	31 (77)
	Pt/C	100 (95)	19 (70)	30 (95)
	PtBi/C	100 (95)	47 (95)	53 (95)

The derivatives substituted with a phenyl group are more active whatever the catalyst. As a general rule, the reactivity is the following $m < o < p$. A promoting effect of bismuth is observed.

The role of each parameter on the activity and selectivity will be discussed.

References

- [1] M. Besson, P. Gallezot, *Catal. Today*, **57**, 127 (2000); T. Mallat, A. Baiker, *Chem. Rev.*, **104**, 3037 (2000).
 [2] A. Frassoldati, C. Pinel, M. Besson, *Catal. Today*, (2011), accepted