

Chemicals from Biomass: Aerobic oxidation of 5-hydroxymethyl-2-furaldehyde into diformylfuran catalyzed by immobilized vanadyl-pyridine complexes

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Introduction

5-Hydroxymethyl-2-furaldehyde (HMF), as diformylfuran precursor (DFF), is obtained from fructose or glucose dehydration. DFF is a versatile chemical, and there are numerous reports describing various applications as a monomer, as starting materials for the synthesis of pharmaceuticals and antifungal agents [1]. To date, few reports describe the use of air to oxidize (HMF) with heterogeneous catalysis [2,3]. Basic-type supports are known to be advantageous for the catalytic alcohol oxidation and, besides, metals redox activity (e.g. V, Cu, etc.) may be enhanced by pyridine ligands [4]. We present here the aerobic oxidation of HMF into DFF using catalysts based on metal (Cu, Pd and V)-pyridine coordination adducts, in the form of polymeric materials ((poly(4-vinylpyridine), PVP) and as silica immobilized complexes (organometallic complexes grafted onto organofunctionalized SBA-15 supports).

Materials and Methods

The polymeric catalysts PVP/Cu (8.5 wt%), PVP/Cu-Pd (4.65 wt% Cu, 2.73 wt% Pd), PVP-1/VO (5.1 wt% V) and PVP-2/VO (7.4 wt% V) were prepared by wet impregnation of the support PVP with the corresponding metal salts. The organometallic complexes grafted onto organofunctionalized SBA-15 (SBA-Py-VO-1, 3.65 wt% V, and SBA-Py-VO-2, 7.43 wt% V) were obtained after SBA-15 functionalization with primary amine groups, pyridine-imine formation and further imine reduction. Reactions were carried out in DMSO, toluene and trifluorotoluene (TFT) at 130°C and 10 bar air in an autoclave.

Results and Discussion

The most relevant results are shown in Table 1. PVP-1/VO presents high activity and selectivity (77 mol% Yield to DFF) after 4 hr using TFT as solvent. This result is better than using DMSO (Figure 2), which was up to now the most successful media for the reaction [3]. The homogeneous vanadium salt (vanadyl acetylacetonate) displayed much inferior selectivity than its immobilized analogue, which is ascribed to the strong Lewis acidity of vanadium when it is not coordinated to pyridine. The loss of activity observed in the reused catalyst can be attributed to the gradual leaching of vanadyl, as determined by chemical analysis. When PVP-2/VO was tested under the same conditions, high yields were also obtained, however after prolonged times and without detecting V leaching. This can be explained by the existence of less free pyridines near the redox centre and the impediment of the reactant to accede to such sites.

When SBA-Py-VO-1 (and 2) were used, low yields were obtained after high reaction times. The longer distance between the pyridine (basic site) and V (redox site) may be responsible for this behavior.

Table 1. Catalytic performance in HMF oxidation to DFF at 130°C

Catalyst	Solvent	time (hr)	HMF Conv. (mol%)	DFF Selec. (mol%)
PVP/Cu	Toluene	72	66	72
PVP/Cu-Pd	Toluene	72	48	75
PVP-1/VO	Toluene	24	75	82
PVP-1/VO	TFT	4	77	>99
Homogeneous VO	TFT	10	50	57
PVP-2/VO	TFT	24	78	>99
SBA-Py-VO-1	TFT	24	34	95
SBA-Py-VO-2	TFT	24	33	90

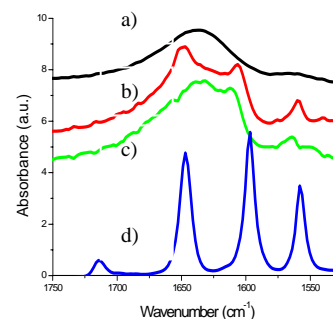


Figure 1. IR spectra between 1750-1870 cm⁻¹ for a) SBA-amine b) SBA-imine c) SBA-reduced-imine and d) pure imine

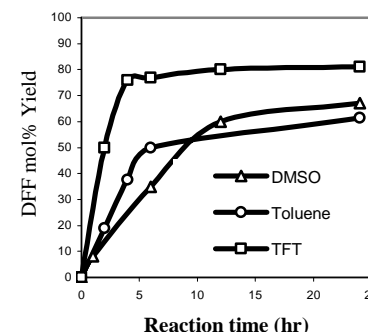


Figure 2. Reaction kinetics for PVP-1/VO catalyst at 130°C, 10 bar air in TFT using DMSO, Toluene and TFT solvents.

Significance

The results shown here enhance the interest in the search for combinations of basic and redox sites within a catalyst to promote the oxidation of alcohol-type biomass derivatives.

References

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