

Efficient Oxidation of Lignin and Related Aromatics using CoCl_2 /Ionic Liquid and Co-ZIF-9 Catalysts

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Introduction

Lignocellulosic biomass is an attractive, renewable carbon source for the production of fuels and chemicals. The lignin fraction of lignocellulose has the potential to become an alternative feedstock for the production of high-value aromatic chemicals [1]. We have made use of the fact that lignin readily dissolves in ionic liquids and studied the catalytic oxidation of lignin using homogeneous cobalt salts and molecular oxygen [2]. In addition to soda and Alcell lignin, various lignin model compounds containing the salient features of lignin were used to better understand the transformations that occur during lignin oxidation. The reaction mechanism has been elucidated using *in-situ* spectroscopic studies by the detection of various catalytic intermediates [2]. In an effort to circumvent catalyst recovery issues associated with homogeneous catalysts, a series of cobalt zeolitic imidazolate frameworks (Co-ZIF-9) were synthesized and found to be highly active as heterogeneous oxidation catalysts for lignin valorization [3]. Here, we present our results on the cobalt-catalyzed oxidation reactions.

Experimental

The substrates were dissolved in 1-ethyl-3-methylimidazolium diethylphosphate ([EMIM][DEP]) ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) or toluene (Co-ZIF-9) with NaOH, and reactions were conducted in a batch autoclave charged with O_2 . Product analysis was conducted by GC, GC/MS, and LC/MS. *In-situ* experiments were conducted using an autoclave equipped with an ATR-IR probe. The Co-ZIF-9 catalyst was characterized by XRD, TGA and UV-Vis [1-3].

Results/Discussion

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in the ionic liquid [EMIM][DEP] proved a particularly effective catalyst for the oxidation of lignin and its model compounds. The catalyst rapidly oxidized benzyl and other alcohol functionalities in soda and Alcell lignin, but left phenolic functionalities and 5-5', β -O-4 and phenyl-coumaran linkages intact. In the oxidation of veratryl alcohol, for instance, very fast oxidation to veratraldehyde and veratrylic acid was observed, with a maximum turnover frequency of 1440 h^{-1} relative to $10\text{-}15 \text{ h}^{-1}$ for previously described systems [2]. The influence of reaction conditions, such as temperature, oxygen pressure and NaOH loading, were also investigated.

In situ ATR-IR, Raman, and UV-Vis spectroscopic studies provided mechanistic insight and evidence for several species involved in the catalytic cycle. A reaction mechanism is proposed

that explains the role of the ionic liquid and the other reaction conditions necessary to achieve high catalytic activity. Direct spectroscopic evidence for different intermediates, including cobalt-peroxido and superoxido species, was obtained and further confirmed by $^{18}\text{O}_2$ labeling studies. The ionic liquid greatly influences the catalytic activity both by stabilizing reactive intermediates and by favouring coordination of the substrate to cobalt over direct oxidation of the cobalt without substrate.

Co-ZIF-9, a zeolitic imidazolate framework of sodalite topology, has been investigated as heterogeneous alternative in the catalytic oxidation of small aromatic molecules including phthalan, vanillyl alcohol, veratryl alcohol, and cinnamyl alcohol by molecular oxygen. An exemplary reaction is the oxidation of veratryl alcohol in which the benzylic functionality was selectively oxidized to form veratrylaldehyde. Indeed, selective oxidation of the substrates was generally observed, which makes Co-ZIF-9 a promising heterogeneous catalyst for the oxidation of small aromatic substrates. The presence of NaOH in the solution was found to greatly enhance oxidation activity. The heterogeneous nature of the catalyst was established by a hot filtration experiment and ICP analysis of the liquid phase. Importantly, the catalyst could be re-used several times without loss of activity.

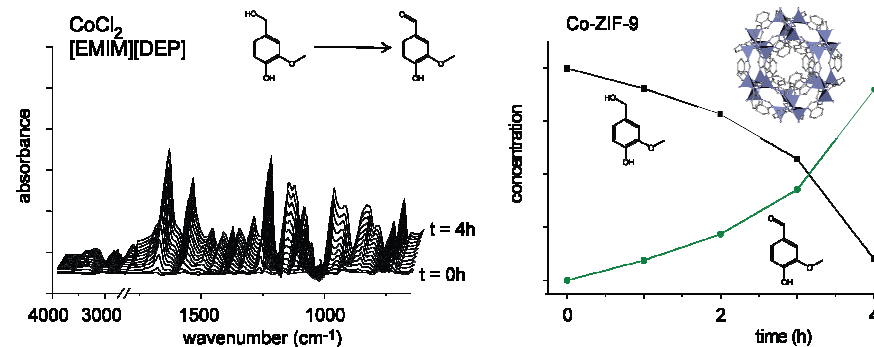


Figure 1. Oxidation of vanillyl alcohol to vanillin. Left: *In situ* ATR IR study of CoCl_2 /[EMIM][DEP] catalyst; Right: Co-ZIF-9-catalyzed oxidation.

References.

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