KENAF CELLULOSE SUPPORTED HIGHLY ACTIVE POLY(AMIDOXIME)PALLADIUM COMPLEX AS A REUSABLE HETEROGENEOUS CATALYST FOR ALLYLIC ARYLATION REACTIONS

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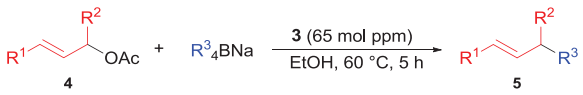
ABSTRACT

A highly active kenaf cellulose supported poly(amidoxime) palladium catalyst was synthesized and characterized with FTIR, UV-Vis, FESEM, XPS and TEM analyses. The catalyst (65 mol ppm to 6.5 mol ppm) was found to promote efficiently the allylic arylation of allylic ester with sodium tetraarylborates in ethanol at 60 °C temperature. Outstanding yields of the corresponding products as well as significant reusability of the catalyst were obtained. The total turnover number (TON) and frequency (TOF) were 144615 and 9641 h^{-1} respectively.



Up to 97% yields, TON: 144615;TOF: 9641 h^{-1}
First Run97%, Sixth Run 90%

Key words: Kenaf, cellulose, poly(hydroxime)Pd-complex, allylic arylation

INTRODUCTION

The use of heterogeneous catalysts for organic synthesis is rapidly growing over homogeneous catalytic systems because of their several advantages such as high stability of the catalyst, tolerant to harsh reaction conditions, reusability and environmental friendliness, easy to purify the products [1,2]. The Tsuji-Trost reaction, an allylic substitution has been accepted as a superior method in the synthesis of natural and pharmaceutical products [3,4]. A number of effective catalysts for the allylic arylation along with boron reagents have emerged [5,6]. These are mostly homogeneous and often suffers from the necessity of comparatively high temperature and high catalyst loading (1-

10 mol %). In addition, purification of products, use of toxic solvents, long reaction time are also associated with these methods. So, development of highly stable and active, cheap and environment-friendly simple heterogeneous catalysts for allylic arylation over a number of substrates of different natures still left over a major challenge. Cellulose is a worldwide available and cheap biodegradable natural polymer and has exceptional characteristics like low density, attractive mechanical properties comparable to glass fibers which have made cellulose a great compelling position as a solid support for catalysts [7]. Cellulose is also fascinating since it can be chemically modified and suitable functional groups can be incorporated into its backbone to coordinate with metal ions [8,9]. Keeping this view, we have attempted to apply cellulose as an anchoring materials for Pd-catalysts and synthesized kenaf cellulose supported poly(amidoxime) palladium(II)complex and applied this complex as the heterogeneous catalyst in the allylic arylation reactions.

MAIN RESULTS

After extraction of kenaf cellulose from kenaf plant followed by subsequent bleaching. graft copolymerization of cellulose as well as synthesis of poly(amidoxime) chelating ligand **2** and cellulose supported palladium complex **3** is shown in the scheme **1**. Pd-content in 3 was 0.65 mmol/g (ICP-AES) [9].

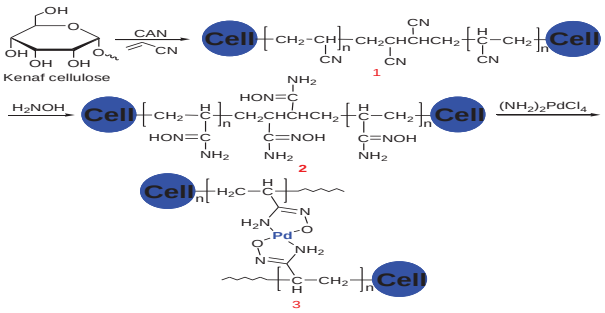


Figure 1. Synthesis of Cellulose supported poly(amidoxime)Pd(II)complex

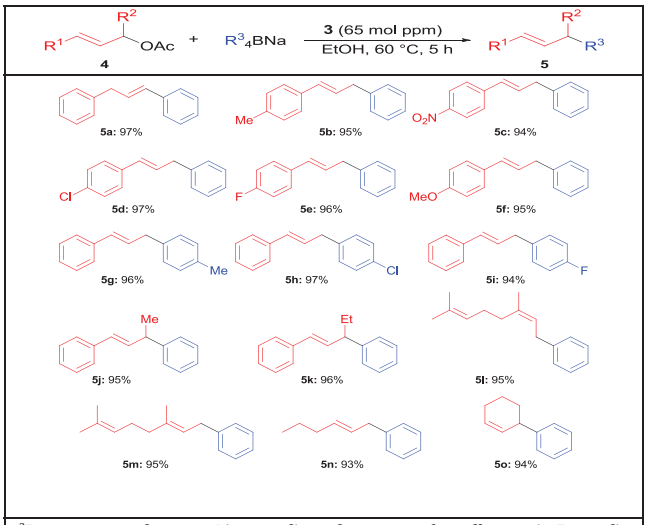
Cellulose, grafted cellulose, ligand and the catalyst were characterized with FTIR, UV-Vis, FESEM, XPS, TEM analyses. The crude arylated products were purified by column chromatography (hexane/ethyl acetate) and were characterized by ^{1}HNMR, ^{13}CNMR, IR and MS. To examine the catalytic activity of cellulose supported poly(amidoxime) palladium complex **3**, the allylic arylation of allylic acetates with sodium tetraarylborates were used in presence of the catalyst **3**(65 mol ppm) in ethanol for 5 h at temperature 60 °C after optimizing the reaction conditions. The reaction progress was monitored by GC analysis. Pd (II) complex **3** efficiently promoted the reactions providing the yields in 94-97% range. When the reaction was completed, the catalyst was filtered, washed with methanol, dried, and reused in the next run. The heterogeneity test was done through hot filtration after 50% completion of reaction.

CONCLUSION

Kenaf cellulose supported poly(amidoxime)Pd(II)complex was sythesized and characterized. The Pd-complex catalyst efficiently (65 mol ppm to 6.5 mol ppm) promoted the allylic arylation of allylic ester with sodium tetraarylborates in ethanol at 60 °C temperature. Excellent yields of the corresponding products with TON144615 and TOF

9641 h^{-1} were obtained. The catalyst was easily recycled and reused for several cycles without significant reduction in its catalytic activity.

Table 1. Allylic arylation of allylic acetates with sodium tetra arylborates[a]



[a]Reaction conditions: **4**(1 mmol), sodium tetraphenylborate(1.5mmol), **3**(0.065 mol%), EtOH (2 mL), 60 °C, 5 h.

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