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Nanoshell carbon-supported cobalt catalyst for the aerobic oxidation of alcohols in the presence of benzaldehyde: An efficient, solvent free protocol

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ABSTRACT

A versatile, solvent free aerobic alcohol oxidation system has been established in the presence of benzaldehyde based on a heterogenous cobalt catalyst supported on nanoshell carbon (Co/NSC), which was prepared through the pyrolysis of a mixture of Co(II) phthalocyanine and phenol resin. The established system features equal efficiency toward both benzylic alcohols and aliphatic alcohols. The nanoshell carbon has been demonstrated to be a better supporting material for the present reaction than some other carbon materials, e.g., activated carbon. Mechanistic studies suggest that Co/NSC can catalyze the formation of oxidative intermediate peroxybenzoic acid as efficiently as homogeneous cobalt catalyst, and moreover, suppress the undesired Baeyer–Villiger side reaction. Co/NSC also exhibits good reusability, i.e., it can be reused for at least 10 times without significant loss of performance.

1. Introduction

The oxidation of hydroxy group to corresponding carbonyl or carboxylic group is one of the most fundamental transformations in organic chemistry [1,2]. Although numerous methods have been developed over past decades, efficient, cost effective and environment friendly techniques are still highly sought-after [3]. Apparently, such techniques should be conducted in an aerobic and catalytic way [4,5]. And heterogenous catalysts are favored over homogeneous ones in terms of product purification and catalyst recovery [6,7]. Most of the reported aerobic oxidation methods are based on precious metals, however, their rarities and high costs make them impractical for large-scale industrial applications. Furthermore, those methods generally perform less efficiently when being applied to aliphatic alcohols, especially cyclic ones [7]. We herein report a nanoshell carbon-supported cobalt catalyst (Co/NSC) based aerobic oxidation system, which expediently oxidizes benzyl alcohols as well as linear and cyclic aliphatic alcohols at the same level of efficiency under solvent free conditions in the presence of benzaldehdye.

This research was inspired by the process of cobalt-catalyzed autoxidation of aldehydes, in which peracid intermediates are generated [8,9]. We postulated that the peracid intermediate can be utilized to efficiently oxidize alcohols under certain conditions. A similar system with ruthenium–cobalt bimetallic catalyst has been reported by Murahashi et al. [10]. Their method enables rapid oxidation of alcohols under remarkably mild conditions; however, it involves the use of precious metal ($RuCl_3$), high loading of aldehyde (4 eq.), as well as large amount of solvent (0.2 M). Moreover, the catalyst used therein is homogeneous as Co(II) acetate (Co(II)Ac) dissolves in the solution. Our aim is to develop a heterogeneous system that eliminates the use of precious metal and reduces the use of aldehydes and solvents.

2. Experimental

2.1. Materials and characterization methods

All alcohol substrates, activated carbon (NORIT SX Plus), and other chemicals were obtained from commercial suppliers and were used as received. Transmission electron spectroscopy (TEM) was performed with a JEOL JEM-2010F microscope. Elemental analysis (EA) was conducted with a Perkin Elmer 2400 Series II for CHN, and a LECO VTF-900 for oxygen. X-ray photoelectron spectroscopy (XPS) analysis was performed using a Perkin Elmer 5500-MT spectrometer. Electron probe microanalysis (EPMA) was carried out with a JEOL JXA-8200 electron probe micro-analyzer. Oxidation reactions were carried out using a SIBATA Chemist Plaza CP100 multi-reactor equipped with 30×200 mm sized test tubes as reaction vessels and separate magnetic stirrers. Samples were taken with a hypodermic syringe and diluted in acetone, and analyzed by a SHIMAZDU GCMS-QP2010 Plus, using a TC-FFAP capillary column ($30\,m \times 0.25\,mm$). Helium was used as carrier gas with a flow rate of 1.53 mL/min.

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