Short communication

Cellulose supported copper nanoparticles as a versatile and efficient catalyst for the protodecarboxylation and oxidative decarboxylation of aromatic acids under microwave heating

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ABSTRACT

Cellulose supported copper-nanoparticles is a versatile catalyst for the protodecarboxylation of aromatic and vinylic carboxylic acids to corresponding arenes and alkenes without using base or ligand is disclosed. The same nanoparticles catalyze the oxidative decarboxylation of phenylacetic acids to aromatic aldehydes in oxygen atmosphere and protodecarboxylation of phenylacetic acid to alkyl benzene in the absence of O_2 atmosphere. Decarboxylation reactions were performed in acetonitrile or water solvent under microwave heating. The conditions are mild enough to tolerate a wide range of different functional groups. The catalyst gives high yield and it is reusable up to four times, and hence green.

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1. Introduction

Decarboxylation of organic acids is one of the most important reactions in organic synthesis, particularly in a multistep reaction sequence [1]. Recently, decarboxylation is also used to trigger the selective C–C and C-heteroatom bond formations [2]. In general, the activated carboxylic acids like β-oxoacids, polyfluorinated aromatic acids, diaryl acetic acids etc. decarboxylate easily even in the absence of any catalyst [3,4]. But, simple nonactivated carboxylic acids require much extreme conditions. There are a number of different methodologies reported which often use stoichiometric or catalytic amount of transition metals for the decarboxylative protonation. Copper has been found to be the most used one starting from the pioneering work by Shepherd [5–7]. Later on the use of other metals like, silver [8], mercury [9], gold [10], palladium [11], rhodium [12] etc. is also reported. As a whole, these reactions are high yielding and quite efficient, but they are not free from drawbacks like, the use of expensive or toxic nitrogen/phosphorous containing ligands, high temperature, long reaction time, toxic solvents, strong basic conditions, lack of metal catalyst recyclability etc. In some cases, the free carboxylic acids are required to be converted to esters or anhydrides for effective decarboxylation to take place [13]. Moreover, few examples of decarboxylation at sp^3-carbon centre are reported [14–16]. Therefore, development of a recyclable metal catalytic system capable of carrying out decarboxylation at both sp^2- and sp^3-carbon centers under ligand and base free condition is essential.

Because of the wide spread natural abundance and environment friendly sustainable resource; cellulose became a green renewable alternative of currently used synthetic templates for metal nanoparticle synthesis [17]. Cellulose with oxygen-rich carbohydrate (polysaccharide) consists of anhydroglucose units joined by an oxygen linkage (β-1,4 glucosidic bond) to form a molecular chain. The intrachain hydrogen bonding between hydroxyl groups and oxygens of the adjoining ring molecules stabilizes the linkage and results in the linear configuration of the cellulose chain. It also contains microfibrils with up to 30 nm width that are three dimensionally connected to each other. The metal particles can be stabilized in the cavities of those microfibrils via oxygen-metal electrostatic interaction. That is how cellulose can act as a support for the metal nanoparticle synthesis [18]. Although the catalytic applications of cellulose supported metal nanoparticles have been widely explored in various diversified areas [19,20] a few reports have been documented in the field of synthetic organic chemistry as an efficient reusable catalyst. In continuation of our research on nanomaterials [21,22], we reported herein the protodecarboxylation of benzoic acids and vinyl carboxylic acids to corresponding arenes and alkenes respectively. We also reported oxidative decarboxylation and protodecarboxylation of phenylacetic acids to the aldehydes and alkyl benzenes respectively. These reactions were performed in water/acetonitrile solvent under microwave heating using cellulose supported copper nanoparticles as a catalyst (Scheme 1).

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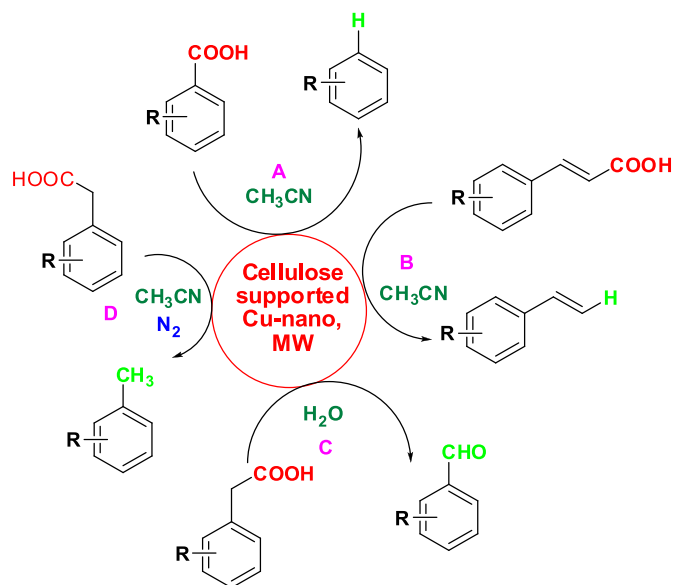
Scheme 1. A, B: Protodecarboxylation of benzoic acid and vinylic carboxylic acids to arene and alkene respectively; C: Oxidative decarboxylation of phenyl acetic acid to benzaldehyde; D: Protodecarboxylation of phenyl acetic acid to alkyl benzene.
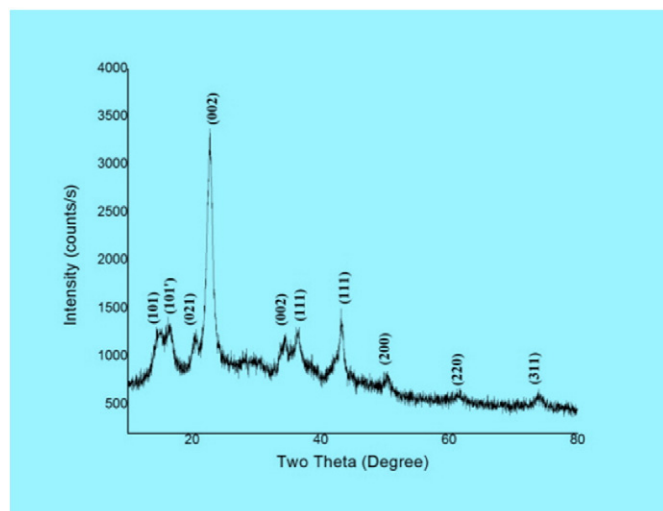
Fig. 1. XRD spectra of cellulose supported copper nanoparticles.
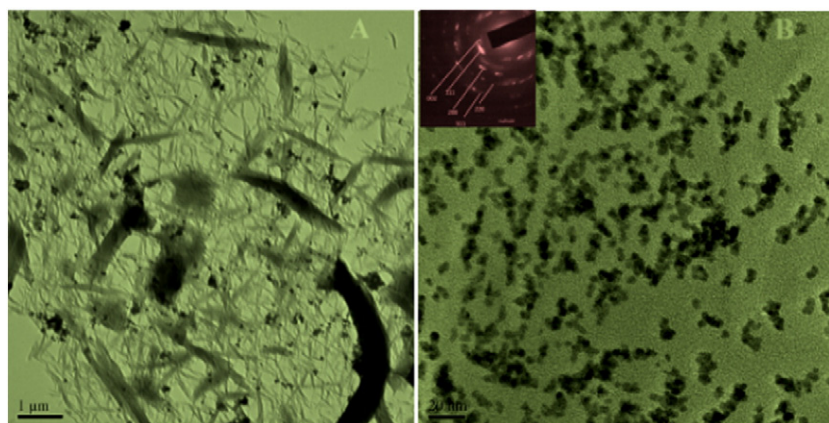
2. Results and discussions

The cellulose supported copper nanoparticles were prepared by the reduction of copper(II) acetate in a mixture with microcrystalline cellulose (powder) using a method reported earlier [22]. The analytical data (XRD, TEM) of the prepared nanoparticles (Figs. 1 & 2) were in good agreement with the reported one. It was observed that there was a mixture of Cu (0) and Cu_2O and the sizes of the metal particles were in the range of 2–10 nm. The prepared nanoparticles were used to study the decarboxylation of p-nitrobenzoic acid (1a). Heating a mixture of 1a with the nanoparticles at 120 °C for 24 h produced a moderate yield of the decarboxylated nitrobenzene (2a) (Entry 1, Table 1). A good yield of the product could be obtained at short time by carrying out the reaction under microwave heating (Entry 3, Table 1). Experiments in the absence of the catalyst confirmed the role of the nanoparticles in the reaction (Entries 2 and 4, Table 1). Acetonitrile was found to be the suitable solvent and stoichiometric amount of metal was required (Entry 3, Table 1). A decrease in the catalyst loading from 1 mmol to 0.2 mmol significantly lowered the product yield (Entry 5, Table 1). On the other hand decreasing the reaction temperature (100 °C) decreased the product yield (55%) significantly (Entry 6, Table 1) and increasing the temperature (150 °C) also did not improve the product yield at all (Entry 7, Table 1). Investigating the reaction in different solvent such as water, toluene, DMF, and DCE did not give any positive result (Entries 8–11, Table 1). Instead of using cellulose supported Cu nanoparticles we tried another reactions using copper acetate, Cu (OAc) $_2$ as a catalyst (Entries 12–13, Table 1). Surprisingly these reactions also found to be failed. This is a clear improvement over most of the reported copper catalyzed decarboxylation processes which usually require the use of nitrogen or phosphorus ligands, strong bases, and toxic solvents like quinoline, NMP, mesitylene, DMSO etc.

A number of different aryl carboxylic acids 1a–k having both electron donating and withdrawing groups were successfully decarboxylated using optimized reaction condition (Table 2). Dicarboxylic acids e.g., 1c provided di-decarboxylated product after completion of the reaction. The reactions were comparatively faster and required less temperature for heterocyclic carboxylic acids like 1h and 1i. The sensitive functional groups like unprotected hydroxyl or amines remained unaffected. The reaction was found to be effective for the alkene systems also. Substituted cinnamic acid derivatives 3a and 3b provided corresponding styrenes in excellent yields. It is to be noted that the 4-vinylphenols, obtained by the decarboxylation of 4-hydroxycinnamic acids, are highly valuable chemicals with wide range of applicability. 4-Vinylguaiacol (4a), the decarboxylated product of ferulic acid (3a), is an antioxidant and flavoring agent [23]. The sinapic acid (3b) provided vinylsyringol (canolol) (4b) which is an antimutagenic compound [24]. The decarboxylation of cyclohexylideneacetic acid (3c) led to the isomerization of the

Fig. 2. TEM images; (A) Cu-nanoparticles dispersed on cellulose template; (B) Size of Cu-nanoparticles on cellulose template with selected area electron diffraction (SAED) diagram.