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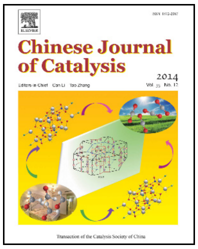

Article

Oyster shell waste supported $CuCl_2$ for aldehyde-alkyne-amine coupling reaction to propargylamines

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ABSTRACT

The development of an economic and simple heterogeneous oyster shell waste supported $CuCl_2$ catalyst for the aldehyde-alkyne-amine (A3) coupling reaction was reported. The waste oyster shell powder (OSP) supported $CuCl_2$ (OSP-$CuCl_2$) catalyst was prepared by a simple method from waste OSPs and $CuCl_2$, which was shown to be a highly active and recyclable catalyst for the A3-coupling reaction. A range of propargylamines were obtained in good to excellent yields (85%–97%) under solvent-free and microwave-heated conditions. The OSP-$CuCl_2$ catalyst can be simply recovered by filtration and reused for at least six runs. Propargylamine can be produced in 87% yield even when the scale of the A3-coupling reaction was increased to 150 mmol.

1. Introduction

Propargylamine derivatives are important materials in organic synthesis, pharmaceutical chemistry and chemical engineering, with a structural motif that is found in many natural products and drug molecules [1–4]. The synthesis of propargylamines is an important topic in modern synthetic chemistry. Therefore, efforts have been made to develop efficient and green strategies for this preparation. The most efficient, convenient and reliable method for the production of propargylamines is the three component aldehyde-alkyne-amine coupling (A3-coupling) reaction [5]. The catalytic A3-coupling reaction gives water as the only byproduct. Gold salts [6,7], silver salts [8,9] and other metal salts [10,11] have been used as homogeneous catalysts to catalyze the A3-coupling reaction. However, most of these homogeneous catalytic systems suffer from the problems of the difficult separation and recycling of the expensive or hazardous catalysts, and environmental pollution.

In order to overcome these drawbacks, the immobilization of the metal salts on a solid support has been applied to the A3-coupling reaction, which allows the straightforward removal of the catalyst from the reaction mixture. Numerous methods have been developed to immobilize metal salts on a large variety of solid supports such as SiO_2 [12], zeolite [13], tungstophosphoric acid [14], polymers [15], and so on [16,17].

However, the disadvantages of these methods are the high price of the catalyst, tedious and time consuming procedure of catalyst preparation, and sensitivity of the Cu(I) compounds. Thus, the development of an efficient and easily available solid catalyst has been an interesting challenge. One way to improve

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synthesis efficiency and reduce the cost of the heterogeneous catalyst is to use naturally available wastes as the support. A number of recent studies have reported using bio-wastes as the support of catalysts, which would reduce the number of synthesis steps, cost and use of hazardous chemicals in the preparation of heterogeneous catalysts [18].

In Fujian province, an enormous amount of oyster shell wastes has been illegally disposed by oyster farms. Therefore, the recycling of these is desirable. Oyster shell powder (OSP) has been used widely as an additive in construction materials, adsorbent of heavy metal ions in sewage treatment and chicken feed in chicken farms in order to reduce the amount of waste oyster shells [19–21]. In addition, oyster shells have medicinal value and have been used as a calcium source [22]. The main component of oyster shells (>95%) is calcium carbonate.

Although OSPs are already widely used in other fields, their application as support of heterogeneous catalysts is less well understood. In addition, microwave (MW) irradiation has proven to be a highly effective heating source for driving chemical reactions in modern organic chemistry [23,24]. It was found that MWs can accelerate the A3-coupling reaction [25,26].

In order to further improve the efficiency and practicability of MW irradiation technology [27–30], we report here a simple, green and scalable process for the synthesis of propargylamines from aldehydes, alkynes and amines catalyzed by a heterogeneous OSP-$CuCl_2$ catalyst under microwave irradiation and solvent-free conditions. OSP-$CuCl_2$ is highly efficient, low cost and easy to make. In addition, the catalyst was easily recovered from the reaction mixture by filtration and was reusable. This work is the first attempt to synthesize propargylamines using a catalyst composed of a bio-waste material support and $CuCl_2$ in a one-pot, three-component and scalable synthesis strategy. It not only produces useful propargylamines at low cost, but also reduces waste and improves environmental conditions.

2. Experimental

2.1. *Materials and instrumentation*

Waste oyster shells used in this study was obtained from a commercial oyster farm in Jimei district, Xiamen city, Fujian province. All reagents and solvents were obtained from commercial sources and used without further purification. All the A3-coupling reactions were carried out in a commercial microwave reactor (MAS-II) manufactured by Sineo Microwave Chemistry Technology (Shanghai) Co.

FT-IR spectra were recorded using KBr on a Thermo Nicolet iS10 FT-IR spectrometer. OSP-$CuCl_2$ was analyzed by atomic absorption spectrophotometry (AAS) using standard methods with a Varian AA275 atomic absorption spectrophotometer (USA). The crystallinity of OSP-$CuCl_2$ was characterized by XRD on a Bruker D8 Advance (Germany) apparatus using Cu K_α radiation. The thermo gravimetric analyzer (TGA) was a TA instrument (USA) DSC2910/SDT2960, and samples were heated from 25 to 800 °C at 10 °C/min under N_2. Scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX) used an Oxford instrument 7021. NMR spectra were acquired in $CDCl_3$ on a Bruker DMX-400 spectrometer at 400 MHz for ^1H NMR. The chemical shifts are given in δ values from TMS as an internal standard.

2.2. *Preparation of OSP-$CuCl_2$ and $CaCO_3$-$CuCl_2$*

In order to remove seaweeds and sands deposited on the shell surface, the waste oyster shells were washed several times in an ultrasonic cleaner and dried naturally. The oyster shells were roughly crushed using a hammer then ground into powder with a pestle and mortar and passed through a 100 mesh sieve. The OSPs were then dried at 100 °C for 2 h and stored in a desiccator.

In a round-bottom flask, OSPs (5.0 g) was mixed with $CuCl_2$ (1.5 g, 0.011 mol) in deionized water (50 mL). The mixture was stirred at room temperature for 8 h. The product was filtered and washed with ethanol, ethyl acetate and water successively. The catalyst was placed in a vacuum oven and dried overnight at 50 °C. The $CaCO_3$ supported $CuCl_2$ catalyst was prepared by the same procedure as described above. The two kinds of Cu(II) heterogeneous catalysts are denoted as OSP-$CuCl_2$ and $CaCO_3$-$CuCl_2$, respectively.

2.3. *The A3-coupling reactions*

OSP-$CuCl_2$ and $CaCO_3$-$CuCl_2$ were used for the preparation of propargylamines by the A3-coupling reaction of aldehydes, amines and alkynes. In a typical procedure, to a mixture of aldehyde (3.0 mmol), secondary amine (3.6 mmol) and alkyne (3.6 mmol) was added OSP-$CuCl_2$ or $CaCO_3$-$CuCl_2$ (10 mg) as the catalyst. The mixture was stirred at 90 °C under MW irradiation (480 W) for 20 min. After complete conversion of the aldehyde (determined by TLC analysis), the mixture was cooled to room temperature and filtered, extracted with EtOAc, and dried over anhydrous $MgSO_4$. After evaporation of the solvent, the crude product was obtained. Purification was performed by silica gel flash column chromatography with a mixture of petroleum ether/ethyl acetate as eluent to afford the desired propargylamines in good to excellent yields.

2.4. *Recycling and reuse of OSP-$CuCl_2$ and $CaCO_3$-$CuCl_2$*

After completion of the A3-coupling reaction, OSP-$CuCl_2$ or $CaCO_3$-$CuCl_2$ was separated by simple filtration from the reaction system, and washed with water and ethanol. After drying under vacuum at 60 °C for 1 h, the recycled catalyst was used for the next run under the same conditions.

2.5. *Spectroscopic data of propargylamines*

4-(1,3-diphenylprop-2-ynyl)morpholine. IR (KBr, ν_{max}, cm^{-1}): 3059 (m), 2956 (s), 2852 (s), 2750 (m), 2690 (w), 2222 (w), 1680 (w), 1559 (m), 1489 (s), 1450 (s), 1317 (s), 1114 (s), 1001 (s), 758 (s), 696 (s). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 7.4 Hz, 2H), 7.57–7.49 (m, 2H), 7.41–7.27 (m, 6H), 4.83 (s,