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A potential industrialized fiber-supported copper catalyst for one-pot multicomponent CuAAC reactions in water

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ABSTRACT

A potential industrialized fiber catalyst for “click chemistry” *via* the one-pot multicomponent Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC) for the synthesis of 1,2,3-triazoles in water, is reported. Detailed characterization by appearance, mechanical properties, elemental analysis, FTIR spectroscopy, and SEM confirmed the rangeability of the fiber catalyst during the preparation and utilization processes. Moreover, the fiber catalyst-mediated reactions proceeded smoothly to afford triazoles with nearly quantitative yields in short time (15 min). Furthermore, the fiber catalyst has shown tandem activities and superior recyclability (over 10 cycles), and the procedure is operationally simple and amenable to the gram-scale on a simple fixed-bed reactor.

Introduction

With the implement of sustainable development strategy, the concept of green chemistry has been deeply into the human mind, and the significant progress in the studies of interdiscipline has been providing many new materials for the green objective, however, the principles, goals and contents of green chemistry should also be constantly enriched and expanded [1,2]. In all these efforts, and given that the majority of chemical processes involve the utilization of catalysts, employing green catalysts for greener procedures to maximize reaction efficiency and minimize waste production in chemical and pharmaceutical industry still holds a significant position [3,4]. Therefore, it is worth noting that the recyclable supported catalysts, which have been well investigated and proven to be more crucial to chemical science [5,6], especially for the supported catalyst with tandem effects, it simplifies the operation steps and will continue to influence and motivate the development of catalysts toward milder reaction conditions [7,8]. Nowadays, the commonly-used objects for supports are inorganic solids (e.g. silica [9], grapheme [10] and zeolite [11]), organic polymers (e.g. resin [12], PEG [13] and cellulose [14]) and some composite materials (e.g. magnetic nanoparticle [15], carbon nanotube [16] and metal-organic framework [17]), and in the contemporary stream of the present research hotspots, exploiting stable and effective catalytic materials for more facile reaction processes, which may quickly apply to green industrial plant from the laboratory is currently of great interest [18].

“Click chemistry” is a term that was introduced by Sharpless to describe reactions which are of wide scope, high yielding, simple to perform, and use highly energetic reactants to form irreversible carbon-carbon or carbon-heteroatom bonds [19,20]. This concept was developed in parallel with the interest within the materials, pharmaceutical and other industries in capabilities for generating large libraries of compounds for screening in discovery research [21,22]. It is worth mentioning that the copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) reaction, is a representative example of click chemistry, which proceeds with high regioselectivity to provide 1,2,3-triazoles with 100% atom efficiency [23]. This important reaction has attracted a considerable amount of attention in the field of organic synthesis, Bio- and medicinal chemistry [24–26]. The general homogeneous copper salts for the CuAAC reaction suffering from the problem of separation procedures or the requirement of adding reducing agents and

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stabilizing ligands. Therefore, a variety of heterogeneous copper-catalysts such as copper zeolites [27], amphiphilic tris(triazolyl)-PEG supported copper(I) [28], copper-in-charcoal [29], and copper NPs supported on functionalized silica [30] have been tried for this reaction. However, most of the catalytic processes were relatively slow and requires organic solvents, and the exploitation of a new, mild and rapid procedure without organic solvents for the synthesis of 1,2,3-triazoles is still a worthwhile practice.

Due to the excellent flexibility, the fibrous catalysts have been applied to several reactions ranging from pollutant control to fuel processing and were found to be one of the most promising forms of catalysts from the reaction engineering point of view [31,32]. Among those, the commonly used support materials were inorganic fibers such as metal-fiber [33], glass-fiber [34], ceramic-fiber [35], activated carbon fiber [36] and other nanofibers [37]. As one of the man-made organic polymer materials, polyacrylonitrile fiber (PANF) has been widely used in textile industry and our daily life. It has good mechanical strength and light density, and the molecular chains of the fiber contain an abundance of cyano groups which can be easily functionalized [38–40], and as such, PANF is very attractive for serving as the starting material in supported-catalysis. In our previous work, we have investigated the merits and details of the functionalized PANFs as effective and reusable acid-base catalysts for organic synthesis [41,42], and following the pioneering studies on fiber catalysts and in continuation of our interest in green chemistry [43–45], herein, we further apply PANF as a novel support to report a new types of supported-copper catalyst with tandem effects, which was evaluate in click chemistry *via* the one-pot multicomponent CuAAC reaction for the synthesis of 1,2,3-triazoles in water. Moreover, the structure-activity relationship of the catalyst was verified, and the fiber catalyst with long-chains ($PANF_{PTA}$@CuI, which derived from polyethylene polyamine functionalized PANF) was more effective than the relatively short-chains one ($PANF_{TTA}$@CuI, which derived from triethylene tetramine functionalized PANF). Furthermore, the fiber catalyst could easily be recovered with common tweezers and reused over 10 cycles, and the procedure is operationally reliable and amenable to the gram-scale on a simple fixed-bed reactor.

Experimental section

Preparation of fiber-supported poly(tertiary amine)@Cu catalyst ($PANF_{PTA}$@CuI)

Step 1, Amination

Polyethylene polyamine (30 g) and deionized water (30 mL) were introduced into a three-necked flask, and the mixture was heated to reflux (104–105 °C). Then the dried PANF (3.05 g) was immersed into the above refluxing mixture and stirred for 22 h. The fiber was filtered out and repeatedly washed with hot water (60–70 °C) until the pH of the filtrate was 7, and next the sample was dried to constant weight at 60 °C under vacuum to give polyamine functionalized PANF ($PANF_{PA}$, 4.03 g, with a weight gain of 32%).

Step 2, Salinization

Bromoethane (10 g) was dissolved in acetonitrile (100 mL), and then the dried $PANF_{PA}$ (3.79 g) was introduced to the solution. The mixture was refluxed with stirring for 12 h. Next, the fiber sample was filtered out and washed with acetonitrile (2 × 50 mL), and then dried overnight at 60 °C under vacuum to give PANF-supported poly(ethylammonium bromide)s ($PANF_{PA}$[EtBr], 5.10 g, the content of ethylammonium bromide was 2.36 mmol g^{-1}).

Step 3, Neutralization

$PANF_{PA}$[EtBr] (4.69 g) was immersed and stirred in a 5% sodium carbonate solution (100 mL) at room temperature for 2 h, afterwards, the fiber sample was filtered out and washed with water (2 × 50 mL), and then dried overnight at 60 °C under vacuum to give poly(tertiary amine) functionalized PANF ($PANF_{PTA}$, 3.78 g, the content of tertiary amine group was 2.98 mmol g^{-1}).

Step 4, Chelation

CuI (3.43 g, 18 mmol) was dissolved in acetonitrile (135 mL), and then the dried $PANF_{PTA}$ (3.00 g) was introduced into the solution. The mixture was stirred at room temperature for 12 h. Finally, the fiber sample was filtered out and washed with acetonitrile (3 × 50 mL), and then dried overnight at 60 °C under vacuum to give the polymer-supported copper catalyst ($PANF_{PTA}$@CuI, 4.57 g, 1.8 mmol g^{-1} CuI loading by weight, which was consistent with the ICP analysis).

General procedure for CuAAC reaction

The terminal alkyne (1.0 mmol), sodium azide (1.0 mmol), primary halide (1.05 mmol), $PANF_{PTA}$@CuI (0.0056 g, 1 mol%) and water (5 mL) were added into a round-bottomed flask. The mixture was heated and stirred at 60 °C for 15 min. After completion of the reaction, the reaction mixture was cooled to room temperature, the fiber catalyst and the product were removed by filtration to recover the solvent. The fiber catalyst was taken out with common tweezers and washed with water (10 mL), and then the filter cake (product) was rinsed with the above water solution. Finally, the solid was collected (filter cake) and dried under vacuum to obtain the pure product. For the recycling process, the washed fiber catalyst was conducted to the next cycle without any further treatment.

Typical lager-scale procedure for CuAAC reaction on a fixed-bed reactor

A mixture of phenylacetylene (50 mmol, 5.11 g), sodium azide (50 mmol, 3.30 g), benzyl chloride (52.5 mmol, 6.65 g), and water (75 mL) was added into the simple fixed-bed reactor (with 0.28 g fiber catalyst intertwined on the stirring paddle, 1 mol%) and stirred at room temperature for 6 h. After completion of the reaction, the mixture was pumped out, then ethanol (20 mL) was added to the flask, which was pumped off the system to wash the fiber catalyst and the reaction vessel. Finally, the combining mixture was concentrated for recrystallization, the white solid was collected and dried under vacuum to obtain the pure product (11.07 g, with an isolated yield of 94%).

Results and discussion

Preparation of the fiber catalysts

On the basis of our previous work [43,45], we started this study to synthesize the designed fiber catalysts. The strategy for preparing the fiber catalysts was planned according to a simple four-step process as shown in Scheme 1. The first step is an amination procedure in water, triethylene tetramine and polyethylene polyamine were used respectively to prepare the incipient amine-functionalized PANFs. The degree of immobilization was detected by weight gain (weight gain = $[(W_2 - W_1)/W_1] \times 100\%$, in which W_1 and W_2 are the weight of the fiber sample before and after amination, respectively). The weight gain of amination