



Application of the polyacrylonitrile fiber as a novel support for polymer-supported copper catalysts in terminal alkyne homocoupling reactions



Xian-Lei Shi^{a,*}, Qianqian Hu^b, Fang Wang^a, Wenqin Zhang^c, Peigao Duan^{a,*}

^a Department of Applied Chemistry, Opening Laboratory of Alternative Energy Technologies, Henan Polytechnic University, Jiaozuo, Henan 454003, People's Republic of China

^b Department of Pharmacy, School of Medicine, Henan Polytechnic University, Jiaozuo, Henan 454003, People's Republic of China

^c Department of Chemistry, Tianjin University, Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, People's Republic of China

ARTICLE INFO

Article history:

Received 1 December 2015

Revised 22 January 2016

Accepted 23 January 2016

Keywords:

Supported catalyst

Fiber catalyst

Homocoupling reactions

Recyclability

Continuous-flow processing

ABSTRACT

A commercially available synthetic polyacrylonitrile fiber, capable of acting as a novel support for polymer-supported copper catalyst in terminal alkyne homocoupling reactions, is presented. Detailed characterization by inductively coupled plasma (ICP) analysis, Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) confirmed the changes and stability of the fiber catalyst during the modification and utilization processes. Moreover, the catalytic reactions proceeded at room temperature using air as a green oxidant to afford nearly quantitative yields (95–99%); the fiber catalyst has shown excellent activity and superior recyclability (over 16 cycles); and the procedure is operationally simple and amenable to the gram scale in continuous-flow processing. Furthermore, the prominent features (high strength, good flexibility, etc.) of the polyacrylonitrile fiber make the fiber-supported catalyst very attractive for fixed-bed reactors in the chemical industry.

© 2016 Elsevier Inc. All rights reserved.

1. Introduction

The utilization of recyclable catalysts for organic synthesis to minimize waste production and maximize catalyst efficiency is one of the key issues in green synthetic strategy [1,2], and with this objective, great efforts in catalysis research have been devoted to the development and application of effective, reusable, and safe supported catalysts [3,4]. Among those, due to their good activity, enhanced stability, and easier handling, the immobilization of metal active sites onto solid supports for more efficient catalytic systems in economical and environmentally benign chemical processes has attracted much attention [5,6]. A variety of supports such as polymers [7–9], silicas [10–12], zeolites [13,14], and some metal particles [15–17] have been tried for the above purpose, particularly for supported copper catalysts [18–20]. In the mainstream of contemporary themes, exploiting new and effective supports for more facile catalytic synthesis, which may quickly move on from the laboratory to the green industrial plant, has received increasing interest [21–23].

Conjugate 1,3-diyne are widely present in natural products and pharmaceuticals with a variety of bioactivities [24–26]. They

also play important roles in the construction of a number of functional polymeric materials [27–29]. Therefore, much attention has been paid to the development of efficient methods for the synthesis of 1,3-diyne derivatives [30–32]. Although significant progress has been made in this area, the exploitation of a new, mild, and effective procedure for the synthesis of 1,3-diyne is still desirable and valuable [33–35]. Polyacrylonitrile fiber (PANF) has been widely applied not only in civilian use but also in industry. Given the many advantages of PANF, such as low cost and simple production technology, high strength and light density, and corrosion and mildew resistance, PANF provides an appealing alternative to many other materials as a support for heterogeneous catalysts. Previously, we have investigated the merits and details of functionalized PANF as a sensor or material for the detection and adsorption of metal ions [36,37], and the results suggested that functionalized PANF possessed good adsorption ability for metallic salts. Based on the above-mentioned studies, we envisaged that the fiber could be used as a support for metal active sites. Inspired by this idea, and in continuation of our interest in the development of novel fiber catalysts and green chemistry [38–41], in the present work, we further apply PANF as a support to develop a new kind of polymer-supported copper catalyst and evaluate it in the terminal alkyne homocoupling reaction for the synthesis of conjugate 1,3-diyne. As expected, the PANF showed good performance as a

* Corresponding authors. Fax: +86 0391 3987811.

E-mail addresses: shixl@tju.edu.cn (X.-L. Shi), pgduan@hpu.edu.cn (P. Duan).

support for metal active sites, and the fiber-supported copper catalyst could mediate homocoupling reactions efficiently at room temperature in air and could easily be recovered and reused over 16 cycles without significant loss of activity. Moreover, the catalytic process of the homocoupling reaction is operationally simple and amenable to the gram scale in continuous-flow processing.

2. Experimental

2.1. Materials

Commercially available polyacrylonitrile fiber (PANF, 93.0% acrylonitrile, 6.5% methyl acrylate, and 0.4–0.5% sodium styrene sulfonate) with a length of 10 cm and a diameter of $30 \pm 0.5 \mu\text{m}$ (from the Fushun Petrochemical Corporation of China) was used. All other chemicals used were analytical grade and employed without further purification. Water was deionized.

2.2. Apparatus and instruments

The copper content of the fibers was measured by inductively coupled plasma (ICP) analysis on a PE5300DV analyzer. Fourier transform infrared (FTIR) spectra were obtained with an AVATAR 360 FTIR spectrometer (Thermo Nicolet), KBr disc. A scanning electron microscope (Hitachi, Model S-4800) was used to characterize the surface morphology of the fibers. ^1H NMR spectra were recorded on an AVANCE III (Bruker, 600 MHz) instrument using TMS as the internal standard. ^{13}C NMR spectra were recorded on an AVANCE III (Bruker, 151 MHz) instrument with complete proton decoupling. Melting points were measured with a Yanagimoto MP-500 apparatus.

2.3. Preparation of the fiber-supported copper catalyst

2.3.1. Step 1

Dried PANF (2.50 g), *N,N*-dimethyl-1,3-propanediamine (35 g), and deionized water (15 g) were introduced into a three-necked flask connected with a condenser. The mixture was refluxed with stirring for 6 h. Next, the fiber sample was filtered off and washed repeatedly with water (60–70 °C) until the pH of the filtrate was 7. Finally, the fiber sample was dried overnight at 60 °C under vacuum to give tertiary amine functionalized PANF (PANF_{TA}, 3.5020 g, with a weight gain of 40%).

2.3.2. Step 2

CuI (3.43 g, 18 mmol) was dissolved in acetonitrile (135 mL), and then the dried PANF_{TA} (3 g, about 9 mmol tertiary amine groups determined by acid exchange capacity) was introduced into the solution. The mixture was stirred at room temperature for 24 h. Next, the sample was filtered out and washed with acetonitrile ($3 \times 50 \text{ mL}$) and AcOEt ($2 \times 50 \text{ mL}$) and then dried overnight at 60 °C under vacuum to give the fiber-supported copper catalyst (PANF_{TA}•CuI, 2.0 mmol g⁻¹ CuI loading by weight, which is consistent with the ICP analysis).

2.4. General procedure for the terminal alkyne homocoupling reactions

The terminal alkyne (1.0 mmol), *n*-butylamine (0.5 mmol), PANF_{TA}•CuI (0.01 g, 2 mol%), and AcOEt (3 mL) were added to a short test-tube open to the air. The mixture was stirred at room temperature for 12 h. After completion of the reaction, the PANF_{TA}•CuI was taken out with common tweezers and washed with AcOEt ($2 \times 10 \text{ mL}$), and the AcOEt solution was combined with the reaction mixture. Then the solvent of the mixture was evaporated under reduced pressure and the residue was purified by col-

umn chromatography over silica gel to afford the corresponding 1,3-diynes. For the recycling process, the washed PANF_{TA}•CuI was conducted to the next cycle without any further treatment.

2.5. Enlargement experiments procedures in continuous-flow processing

A mixture of phenylacetylene (50 mmol, 5.11 g), *n*-butylamine (25 mmol, 1.83 g), and AcOEt (150 mL) in a flask open to the air was stirred at room temperature. The fiber catalyst PANF_{TA}•CuI (0.50 g, 2 mol%) was packed into a silicone column between the flask and peristaltic pump. The catalytic column was kept at room temperature while the reaction solution from the flask was pumped into the system at a flow rate of about 0.22 mL/min. After completion of the reaction, pure AcOEt (20 mL) was added to the flask, which was pumped into the system to wash the fiber catalyst. Finally, the solvent, ethyl acetate, was recovered by simple distillation and about 161 mL of ethyl acetate was obtained (original 150 mL + 20 mL, recovery 94.7%, ignoring the trace *n*-butylamine). The residue was purified by column chromatography over silica gel to afford the product (4.86 g), with an isolated yield of 96%.

3. Results and discussion

3.1. The preparation of the fiber-supported copper catalyst

We started this study to synthesize the designed fiber catalyst. The strategy for preparing PANF_{TA}•CuI was planned by following our previous work and referring to the literature [42], and according to a simple two-step process as shown in Scheme 1. First, the tertiary amine groups were successfully immobilized on PANF by amination with *N,N*-dimethyl-1,3-propanediamine in water, and the extent of immobilization was measured by weight gain (weight gain = $[(W_2 - W_1)/W_1] \times 100\%$, where W_1 and W_2 are the weight of the fiber sample before and after amination, respectively); a weight gain of 40% was obtained. Then the PANF_{TA}•CuI was afforded by chelation with excess CuI in acetonitrile, and the content of the copper loading was 2.04 mmol g⁻¹ as determined by inductively coupled plasma (ICP) analysis, which is consistent with the result calculated by weight (2.0 mmol g⁻¹).

3.2. The characterization of fiber-supported copper catalysts

To avoid any errors during the preparation process and investigate the rangeability and stability of the fiber-supported copper catalyst before and after the catalytic reaction, we performed a detailed characterization of fiber samples at different stages. The original polyacrylonitrile fiber (PANF), the tertiary amine functionalized PANF (PANF_{TA}), the fresh PANF-supported copper catalyst (PANF_{TA}•CuI), the catalyst recovered after the first run in the homocoupling reaction (PANF_{TA}•CuI-1), and the catalyst recovered after the 16th cycle (PANF_{TA}•CuI-16) were all characterized by means of inductively coupled plasma (ICP) analysis, Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM).

3.2.1. ICP analysis

The ICP analysis data of PANF, PANF_{TA}, PANF_{TA}•CuI, PANF_{TA}•CuI-1, and PANF_{TA}•CuI-16 are listed in Table 1. It is obvious that the original PANF and PANF_{TA} did not contain copper. After the chelation with CuI, the amount of copper of PANF_{TA}•CuI was 2.04 mmol g⁻¹. Moreover, after PANF_{TA}•CuI was used as the catalyst in the terminal alkyne homocoupling reaction once and 16 times, as can be seen from the table, there was no significant loss

Download English Version:

<https://daneshyari.com/en/article/6527002>

Download Persian Version:

<https://daneshyari.com/article/6527002>

[Daneshyari.com](https://daneshyari.com)