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An efficient, recyclable and large-scalable fiber-supported Fe(III) catalytic system on a simple fixed-bed reactor verified in the Biginelli reactions

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ABSTRACT

An efficient, recyclable and large-scalable fiber-supported Fe(III) catalytic system verifed in the one-pot multicomponent Biginelli reactions, is presented. The fiber catalyst was prepared conveniently from commercially available polyacrylonitrile fiber according to a simple two-step procedure by amination and chelation in water, and characterized detailedly with ICP analysis, morphology, mechanical properties, elemental analysis, FTIR spectroscopy, and SEM during the modification and utilization processes. Moreover, the fiber catalyst-mediated reactions showed broad applicability and proceeded smoothly to afford a series of substituted 3,4-dihydropyrimidin-2-(1*H*)-ones/-thiones (yields 81–94%) in ethanol under mild conditions. Furthermore, the newly developed fiber catalyst held high strength, good flexibility and exhibited excellent stability and recyclability (over 10 cycles), and the procedure was operationally concise and effectively amenable to the gram-scale on a simple fixed-bed reactor with potential industrialization prospect.

Introduction

New types of catalyst for high-efficiency synthetic methodologies have the potential to greatly impact fine chemical and pharmaceutical manufacturing, which, in turn, can have a positive effect on economic and environmental value. Although there is no shortage of new catalysts being reported each year, the likelihood of any of these being adopted in an industrial application remains low. Indeed, chemists in practical work often rely on a handful of common catalysts that proceed reliably and efficiently, and, intrinsically, the barrier for adopting a new catalytic system in a large-scale manufacturing process can be substantial [1]. There are many hurdles lay in practical gaps between the typical academic methodology and an economical manufacturing process. For instance, the pressures of manufacturing deadlines may prohibit industrial optimization of published academic methodologies. As such, the earlier a catalyst can be rendered efficient and scalable, the more likely it is to be implemented in industry. It is worth noting that the innovative and recyclable supported catalysts, which reduce the reaction-cost and simplify the separation operation, and proven to be more crucial to chemical technology [2,3]. Especially for the immobilization of common used homogenous metal salt catalysts, on the one hand, this gives a new concisely catalytic system, and on the other hand, which will greatly reduces the emission of metal ions. Among those, the supported iron catalyst has received increasing interest due to its high catalytic efficiency, low cost, wider range of application and easier to be made. Various materials such as silica [4–6], activated carbon [7,8], Al_2O_3 [9,10], zeolite [11], graphite [12], resin [13], and nanosheets [14] have been used as supports for supported iron catalysts in all kinds of different types of reactions, good catalytic performance is often obtained, however, the large-scale tests are frequent missing. That is, most of the supported iron catalysts in reports are only merit advantages in academic laboratories, and the well-suited for large-scale manufacturing of supported iron catalytic system is still need to pay more attention. Thus, the development of synthetic strategies to supported iron catalysts with the use of high stable and easy to scale-up support materials, which lead to better chances of such methodologies being adopted

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industrially is more appealing because it combines the advantages of the robust catalyst support with one of the most abundant and inexpensive metals.

The century-old Biginelli reaction [15,16], one of the most fundamental multicomponent reactions, which involves a one-pot condensation of an aldehyde, β-keto ester and urea or thiourea under strongly acidic conditions to afford 3,4-dihydropyrimidin-2-(1*H*)-ones/thiones (DHPMs). In recently years, DHPMs derivatives are of considerable interest in academia as well as in industry because of their promising biological activities [17,18]. Now, the utilization of the Biginelli reaction for the synthesis of DHPMs has attracted renewed attention, and several improved methods using supported catalysts with the materials such as silica [19,20], alumina [21,22], resin [23], PEG [24], magnetic nanoparticle [25], carbon nanotubes [26] or metal-organic framework [27] have been reported. However, to the best of our knowledge, whether traditional materials or new type composites for supported catalysis in the Biginelli reactions were normally out of practical use, and strongly hampering its industrial application. In the main stream of the present research interest, developing effective support materials with high stability and better applied performance for more practical catalytic methods, which may quickly move on from the academic laboratory to industrial plant, has received increasing attention [28].

In our previous work, we have investigated the details of two different sets of fiber-supported Brønsted acid catalysts for Biginelli reactions [29,30], although excellent applicability and prominent recyclability of catalyst were observed, the practical application in large-scale were inadequate. Given the excellent mechanical strength and easy functionalization of polyacrylonitrile fiber (PANF) [31], and so as to explore a practical supported catalyst for Biginelli reactions, as well as, in continuation of our objective to design novel fiber catalysts [32–34], herein, we further take advantage of PANF as an effective support to report an efficient and large-scalable PANF-supported Lewis acid catalytic system again for the Biginelli reactions.

Experimental

Materials

Commercially available 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 ± 0.5 μm (from the Fushun Petrochemical Corporation of China) was used. The polyethylene polyamine (MW, typical 275, from Aladdin) and all other chemicals used were analytical grade and employed without further purification. Water was deionized.

Apparatus and instruments

The copper contents of the fiber samples were measured by inductively coupled plasma (ICP) analysis on a PE5300DV analyzer. The mechanical properties of different fiber samples were tested with an electronic single fiber strength tester (Laizhou Electronic Instrument Co., Ltd., of China, model LLY-06E). Elemental analyses were performed on a thermo scientific flash 2000 auto-analyzer. Fourier transform infrared (FTIR) spectra were obtained with an AVATAR 360 FTIR spectrometer (Thermo Nicolet), KBr disc. A scanning electron microscope (Phenom G2 pro) 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.

Preparation of the fiber-supported Fe(III) catalysts

Step 1, amination

Polyethylene polyamine (30 g) and water (30 mL) were introduced into a three-necked flask with a condenser, and the mixture was stirred and preheated to reflux. Next the dried PANF (3.00 g) was immersed into the above refluxing mixture (105 °C) and stirred for 24 h. The fiber was filtered out and repeatedly rinsed with hot water (60–70 °C) until the pH of the filtrate was 7, and then the sample was dried to constant weight at 60 °C under vacuum to give polyamine functionalized PANF ($PANF_{PA}$, 4.05 g, with a weight gain of 35%).

Step 2, chelation

Dried $PANF_{PA}$ (1.00 g) and Fe(III) aqueous solution (1 mmol mL^{-1}, 30 mL) were added into a flask. The mixture was stirred at room temperature for 24 h. Then, the fiber sample was filtered out and rinsed with water until the filtrate no color change in KSCN solution, and finally the sample was dried to constant weight at 60 °C under vacuum to give the fiber-supported Fe(III) catalyst ($PANF_{PA}$@Fe(III)).

General procedure for the Biginelli reactions

A mixture of aldehyde (5 mmol), urea or thiourea (6.0 mmol), 1,3-dicarbonyl compound (5.5 mmol) and $PANF_{PA}$@Fe(III) (5 mol% Fe(III) content based on the aldehyde) in ethanol (15 mL) was stirred under refluxing for 4 h. After completion of the reaction, the fiber catalyst was just taken out with common tweezers and rinsed with ethanol (15 mL) which was combined to the reaction mixture. The whole mixture was concentrated and the purified products were obtained from crystallization (ethanol and water, 10 mL, v/v = 1:1).

Typical gram-scale procedure for the Biginelli reactions

A mixture of anisic aldehyde (6.81 g, 50 mmol), urea (3.61 g, 60 mmol), ethyl acetoacetate (7.26 g, 55 mmol), and ethanol (150 mL) was added into in the simple fixed-bed reactor (500 mL, with the catalyst $PANF_{PA}@FeCl_3$ intertwined on the stirring paddle, 5 mol% Fe(III) content based on the aldehyde) and stirred under refluxing for 4 h. After completion of the reaction, the mixture was let out through the discharge spout, then ethanol (100 mL) was added to the reactor feedstock port, which was discharge from the system to wash the fiber catalyst and the reaction vessel. Finally, the combining mixture was concentrated for recrystallization (ethanol and water, 100 mL, v/v = 1:1), the white solid was collected and dried under vacuum to obtain the pure product.

Results and discussion

The preparation of the fiber-supported Fe(III) catalysts

The study was started with the preparation of the fiber catalyst, and the tactics for synthesizing the fiber-supported Fe(III) catalysts were conducted by a simple two-step of amination and chelation procedures as shown in Scheme 1.

The first step is polyamine immobilization, that is, using the polyethylene polyamine as the aminating reagent in water to afford a polyamine functionalized PANF ($PANF_{PA}$). According to our previous work [30], the polyamine groups were successfully immobilized on the fiber with a 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) of 35%. Then the fiber-supported Fe(III) catalysts were obtained through