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Revisiting the Knoevenagel condensations: A universal and flexible bis-ammoniated fiber catalyst for the mild synthesis of α,β-unsaturated compounds

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ABSTRACT

A universal fiber catalyst for the Knoevenagel condensations is presented. The detailed characterization by mechanical properties, elemental analysis, FTIR spectroscopy, and SEM confirmed the rangeability of the fiber catalyst during the full-course. Moreover, the mediated condensations proceeded smoothly with lower catalyst amount (1 mol%) in different solvents of varying polarities and the products were obtained in good to excellent yields (95–99%), and even with water as the solvent could also achieve a series of α,β-unsaturated compounds with nearly quantitative yields at room temperature. Furthermore, the catalyst exhibited excellent flexibility and could be easily recovered and recycled with prominent stability over 10 cycles, and the procedure was operationally convenient and effectively amenable to the gram scale on a simple fixed-bed reactor.

Introduction

Environmental concerns associated with organic chemical industry have posed stringent and compelling demands for cleaning processes, and the development of cost-efficient and environmentally benign catalytic systems to maximize reaction efficiency and minimize waste production has become one of the main themes of contemporary green chemistry [1,2]. From this point of view, it is worth mentioning that the innovative and recyclable supported catalytic systems, which have been well investigated and proven to be more crucial to chemical technology [3,4], especially for the heterogeneous catalysts in cheap and environmentally friendly reaction medium of water [5,6], it reduces the reaction-cost and will continue to influence and motivate the development of novel supported catalysts for higher catalytic efficiency [7,8]. And with this objective, more and more materials such as new-types of polymers [9] and zeolites [10], as well as some composite materials (e.g., magnetic nanoparticles [11], carbon nanotubes [12] and metal-organic frameworks [13]) have been used as supports for supported catalytic systems, however, complicated preparation processes and high-cost are normally insurmountable, and strongly hampering their industrial applications. In the main stream of the present research interests, exploiting novel materials with superior stability and high immobilization capacity for more facile catalytic methods, which may quickly move on from the laboratory to the green industrial plant, has received increasing attention [14,15].

The Knoevenagel condensation is one of the most fundamental reactions for the synthesis of α,β-unsaturated carbonyl compounds [16,17], which have been widely used as intermediates or products in fields of fine chemicals [18], drug conjugates [19] and functional polymers [20]. Due to its widely synthetic utility, a large number of catalytic systems for this reaction have been developed [21–24]. However, most of the reported methods suffer from one or more defects, such as the use of unrecyclable catalysts, high reaction temperature, high-power microwaves or the use of toxic metals. Currently, further efforts have focused on making these reactions both substrate-tolerant and operationally simple by using heterogeneous catalysts, which involves metal-organic frameworks [25], functionalized polyvinylamine/SBA-15 [26], mesoporous organosilica [27], and polyoxometalate [28]. Although the reaction efficiency by these catalysts has been improved, there are still some shortcomings including tedious catalyst synthetic

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route, particular organic solvents and poor recyclability should be conquered. Green catalysis is crucial to chemical technology and environmental concerns, it will continue to influence and motivate the development of catalysts for environmental remediation [29]. However, the principles, goals and contents of green chemistry should also be constantly expanded [30], and finding a novel support by effective immobilization for more facile heterogeneous catalysis that provides the desired products in good catalytic activity is very often at the beginning of a long journey. It is worth noting the polyacrylonitrile fiber (PANF), which is well known as "artificial wool" and has been widely utilized not only in civilian but also in industry. Given many merits of PANF, such as corrosion and mildew resistant, excellent mechanical strength and stability, as well as the molecular chains of the fiber contain an abundance of cyano groups which can be easily functionalized [31,32], PANF provides an appealing alternative to other fibers as a support for heterogeneous catalysts. Nevertheless, there are few heterogeneous catalysts based on PANF, so developing a more facile and green catalyst based on PANF for Knoevenagel condensations that holds high catalytic activity and prominent recyclability would be of great interest and value.

In the previous work of our group, two different types of modified amine-functionalized PANFs were used to catalyze Knoevenagel condensations and achieved good results [33,34]. However, the tertiary-amine functionalized PANF for this reaction was only effective in organic solvents with a larger catalyst amount (14.5 mol%), in contrast, the fiber catalyst of polyamine functionalized fiber-mediated Knoevenagel condensations revealed the virtues merely in water, but inoperative in organic solvents. In order to explore a universal fiber catalyst for this reaction, and in continuation of our interest in the development of fiber catalysts [35,36] and green chemistry [37,38], herein, we further apply PANF as a novel support to report a convenient synthesis and detailed characterization of the bis-ammoniated fiber catalyst again for the Knoevenagel condensations.

Experimental

Preparation of fiber catalyst ($PANF_{TSPA}$)

Step 1

N,*N*-Dimethyl-1,3-propanediamine (28 g) and deionized water (12 mL) were introduced into a three-necked flask connected with a condenser, and the mixture was heated to reflux (104–105 °C). Then dried PANF (2.00 g) was immersed into the above refluxing mixture with stirring for 4.5 h. The fiber was filtered out and repeatedly washed with 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 the tertiary amine functionalized PANF ($PANF_{TA}$, 2.4301 g, with a weight gain of 21.5%).

Step 2

Triethylene tetramine (15 g) and deionized water (15 mL) were introduced into a three-necked flask connected with a condenser, and the mixture was heated to reflux (104–105 °C). Then the dried $PANF_{TA}$ (2.00 g) was immersed into the above refluxing mixture with stirring for 2.5 h. Next, the operations as shown in Step 1 and finally to give tertiary, secondary and primary amines functionalized PANF (Bis-ammoniated fiber catalyst, $PANF_{TSPA}$, 2.2907 g, with a weight gain of 14.5%, the acid exchange capacity was 3.75 mmol g^{-1}).

General procedure for Knoevenagel condensations

The aldehyde (5.0 mmol), ethyl cyanoacetate (5.5 mmol) or malononitrile (5.0 mmol), $PANF_{TSPA}$ (0.067 g, 5 mol%, based on the acid exchange capacity) and water (5 mL) were added into a round-bottomed flask. The mixture was stirred at room temperature for the corresponding time. After completion of the reaction, the fiber catalyst was filtered out and washed with ethyl acetate (3 × 10 mL). The filtrate was separated and extracted three times with ethyl acetate. Then the combined organic phases were concentrated and the crude product was purified by column chromatography (petroleum ether–ethyl acetate). For the recycling process, the washed fiber catalyst was conducted to the next cycle without any further treatment.

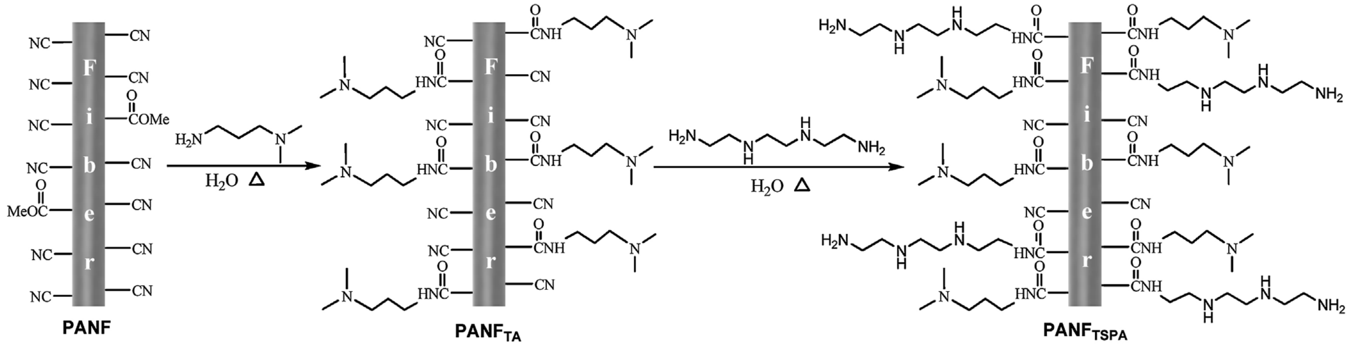
Typical lager-scale procedure for Knoevenagel condensations

A mixture of aldehyde (5.31 g, 50 mmol), ethyl cyanoacetate (6.23 g, 55 mmol), and water (50 mL) was added into the simple fixed-bed reactor (with 0.67 g $PANF_{TSPA}$ intertwined on the stirring paddle, 5 mol%, based on the acid exchange capacity) and stirred at room temperature for 4 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 (9.76 g, with an isolated yield of 97%).

Results and discussion

Preparation of fiber catalyst

We started this study to synthesize the designed bis-ammoniated fiber catalyst, and the strategy for preparing the fiber catalyst was conducted by a simple process of two-step



Scheme 1. Preparation of the bis-ammoniated fiber catalyst.