

Functionalized Nylon 6 Fabric as an Efficient and Recyclable Catalyst for Knoevenagel Condensation

Zhong Yan,^{*,†} Yuwei Liu,[†] Wenwen Wang, and Dong Wang^{*}Cite This: *ACS Omega* 2022, 7, 33186–33191

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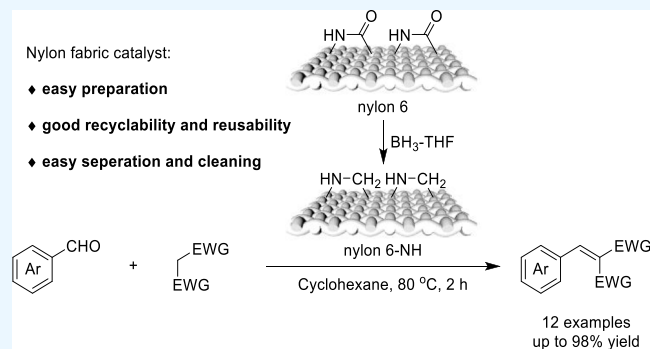


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Supporting Information

ABSTRACT: Nylon 6 fabrics were chemically modified via reduction with BH_3 for being functionalized as heterogeneous base organocatalysts for Knoevenagel condensation. The results of FTIR, XPS, and SEM indicated the successful modification of nylon 6 fabrics. With a low catalytic dosage of 6.6 mol % and a short reaction time (2 h), the fabric catalysts were well applicable to Knoevenagel condensation of a wide range of substrates and up to 98% yield could be obtained. In addition, the fabric catalysts have some beneficial advantages in terms of easy separation, good reusability, and recyclability (up to 10 times).



1. INTRODUCTION

With the development of green chemistry, environmentally friendly catalysts are becoming more and more important in the chemical industry. Knoevenagel condensation, which is a classical means of forming carbon–carbon bonds in organic chemistry, can be catalyzed by a series of homogeneous catalysts, such as organic bases,¹ Lewis acids,² amino acids,³ ionic liquids,⁴ and organometallic catalysts.⁵ However, separation and handling of waste materials generated under these conditions caused additional environmental pollution and an increase in cost. In this regard, heterogeneous catalysts provide an effective solution to the above problems as they entail easier separation of catalysts and avoid the generation of toxic waste.

To prepare heterogeneous catalysts for Knoevenagel condensation, research studies have focused on diverse solid materials such as silicas, zeolites, metal oxides, graphitic carbon nitrides, polymers, and others.^{6–8} Among them, the catalyst carriers are mainly based on powdered materials, and few of them choose fabric materials as supports despite their practical advantages such as easy separation and cleaning, good flexibility, and chemical resistance. In recent years, organic fibers known as textile catalysts have aroused increasing interest among scientists.^{9–17} In 2013, List's group developed a series of nylon-immobilized organocatalysts which display excellent catalytic activity, stability, and recyclability for diverse organic reactions.⁹ Zhang's group chose commercially available polyacrylonitrile fiber as a support, and a variety of efficient Knoevenagel condensation catalysts have been successfully introduced into fibrous carriers and retain excellent catalytic activity.^{11–17} However, despite the above continuing progress, the application of fabric-supported catalysts in organic catalysis

has been still very rare, and developing simple and convenient fabric-supported catalysts is still highly desirable.

Nylon, commonly known as polyamide, contains abundant amide bonds which can be modified or functionalized with various organic reagents.^{18–25} Its outstanding flexibility, mechanical strength, and resistance to organic solvents also lead to increasing interest in its application as a catalyst support. Thanks to the pioneering work of List's group,^{9,10} a series of different nylon-immobilized organocatalysts by using the ultraviolet light-initiated grafting strategy have been prepared, showing high catalytic activity and good reusability for diverse organic reactions. Besides, Opwis's group reported enzyme immobilization on nylon fabrics by photochemical processes in the presence of cross-linking agents, which exhibit excellent activity and recyclability in decomposition reaction of hydrogen peroxide.^{26,27} Noteworthy, chemical transformation of functional groups of fibers can also provide an efficient route for catalyst immobilization,^{11–17} but nylon is rarely chosen as the supporting material. In 2006, Jia's group developed several chemical modification methods for the introduction of functional groups to nylon surfaces.¹⁸ Among them, reduction with borane proves to be an efficient method to convert amide groups to secondary amines. Based on the above background, to prepare an effective heterogeneous base catalyst for

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Knoevenagel condensation, we develop a novel fabric catalyst via reduction of nylon 6 fabric with borane. The newly developed fabric catalyst was found to exhibit good catalytic activity and reusability.

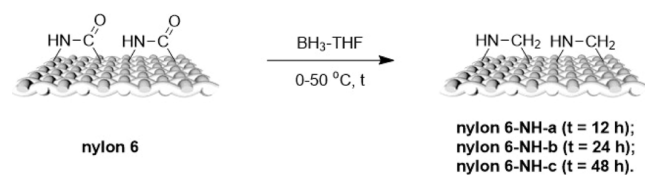
2. EXPERIMENTAL SECTION

2.1. Reagents. Nylon 6 fabric with a diameter of 80–100 μm , an area weight of 50 g m^{-2} , and a weaving pattern of twill weave was purchased from Huanai Mesh Co., Ltd. of China. All aldehydes, malononitrile, and methyl cyanoacetate were analytical grade and purchased from Aldrich. BH_3 -tetrahydrofuran (BH_3 -THF) solution (1.0 M in THF) was purchased from J&K. Commercially available organic solvents were used without further purification. Water was deionized.

2.2. Instruments. FTIR spectra were obtained with a Bruker Tensor 27 FTIR (Germany). XPS was performed on a Thermo Scientific K-Alpha + spectrometer (ThermoFisher). A scanning electron microscope (JEOL JSM-IT 300, Japan) was used to characterize the fabric catalysts.

2.3. Synthesis of the Fabric Catalysts. The fabric catalysts were synthesized as follows: nylon 6 fabric was cut into 3 cm \times 3 cm samples and washed with water, ethanol, 2-propanol, acetone, THF, and hexane (in this order) for 10 min per solvent in a sonicating bath and then dried at 50 $^\circ\text{C}$ for 2 h. To a nitrogen-purged three-necked flask was added the fabric sample (1 g), then BH_3 -THF solution (1.0 M, 40 mL) was added at 0 $^\circ\text{C}$ during the addition. After reaction at 25 $^\circ\text{C}$ for 1 h, the mixture was stirred and heated to 50 $^\circ\text{C}$ for an appropriate time (12, 24 or 48 h). Then the fabric was isolated and washed with water, ethanol, acetone, and hexane. The fabric was dried under vacuum at 50 $^\circ\text{C}$ to give the fabric catalysts (Scheme 1). The fabric catalysts were stored under vacuum before use.

Scheme 1. Synthesis of the Fabric Catalysts



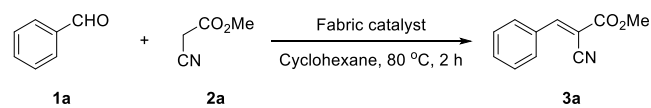
2.4. Base Content Test. The fabric catalyst (0.1 g) was immersed in a solution of HCl (0.01 M, 10 mL) and stirred for 1 h. Then the neutralized fabric was isolated, and the remaining solution was titrated with NaOH (0.01 M). The base content was determined by the amount of acid consumed.

2.5. General Procedure for the Knoevenagel Condensation. To a solution of aromatic aldehyde (1 mmol) and the active methylene compound (1.2 mmol) in cyclohexane or another solvent (5 mL) was added the fabric catalyst (0.1 g), and the mixture was stirred at 80 $^\circ\text{C}$ for 2 h. Then the reaction was cooled to rt, and the fabric catalyst was filtered out and washed with ethyl acetate (3×10 mL). The combined solution was concentrated and purified by column chromatography.

3. RESULTS AND DISCUSSION

3.1. Properties of the Fabric Catalysts. The extents of functionalization determined by base content are listed in Table 1. By prolonging the reaction time, the base content can be effectively enhanced. The base contents of nylon, nylon 6-

Table 1. Properties of the Fabric Catalysts and Their Activity in Catalyzing the Knoevenagel Condensation^a



entry	catalyst	base content [mmol g^{-1}] ^b	yield [%] ^c
1	none		5
2	nylon 6	0.065	21
3	nylon 6-NH-a	0.32	80
4	nylon 6-NH-b	0.66	97
5	nylon 6-NH-c	0.71	97

^aReaction conditions: benzaldehyde (0.1 g, 1 mmol), methyl cyanoacetate (0.12 g, 1.2 mmol), and the fabric catalyst (0.1 g) in cyclohexane (5 mL) stirred at 80 $^\circ\text{C}$ for 2 h. ^bThe base content was calculated by acid–base titration. ^cIsolated yield after column chromatography.

NH-a, nylon 6-NH-b, and nylon 6-NH-c were determined to be 0.065, 0.32, 0.66, and 0.71 mmol g^{-1} , respectively (Table 1, entries 2–5). The catalytic activities of three different fabric catalysts are also listed in Table 1. Noteworthy, Knoevenagel condensation could be effectively catalyzed by base catalysts. The reaction conducted with no catalyst and virgin nylon 6 fabric gave low yields of 5 and 21%, respectively (Table 1, entries 1 and 2). The catalytic activity of virgin nylon could be attributed to the existing terminal amino groups. Furthermore, using nylon 6-NH-b and nylon 6-NH-c as catalysts, the reaction was conducted smoothly with up to 97% yield (Table 1, entries 4 and 5), indicating an efficient catalytic activity of the $-\text{NH}-$ group formed by amide reduction with BH_3 . Moreover, considering the modification time, we chose nylon 6-NH-b as the best catalyst for further condition optimization.

3.2. Characterization of the Fabric Catalysts.

3.2.1. Fourier-Transform Infrared Spectroscopy. The FTIR spectra of virgin nylon 6 fabric and the modified samples are shown in Figure 1. The characteristic adsorption peak of the $-\text{NH}-$ stretching vibration at 3300 cm^{-1} , the stretching vibration of aliphatic groups at 2935 and 2861 cm^{-1} , and the stretching vibration of amide I at 1635 cm^{-1} and amide II at

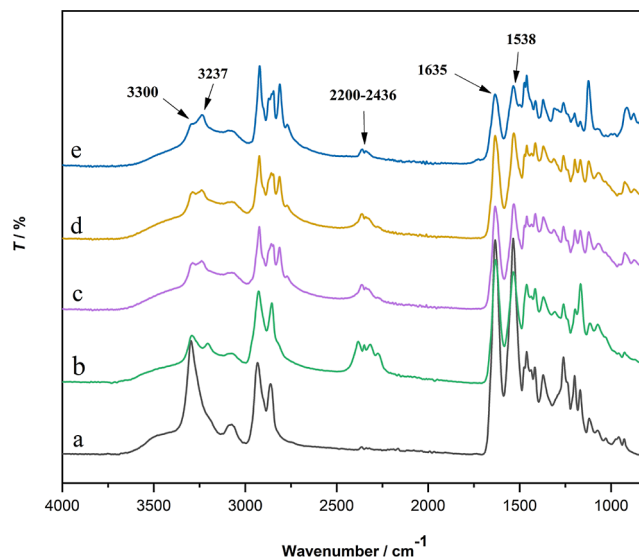


Figure 1. FTIR spectra of (a) nylon 6, (b) nylon 6-NH-a, (c) nylon 6-NH-b, (d) nylon 6-NH-c, and (e) nylon 6-NH-b (run 10).

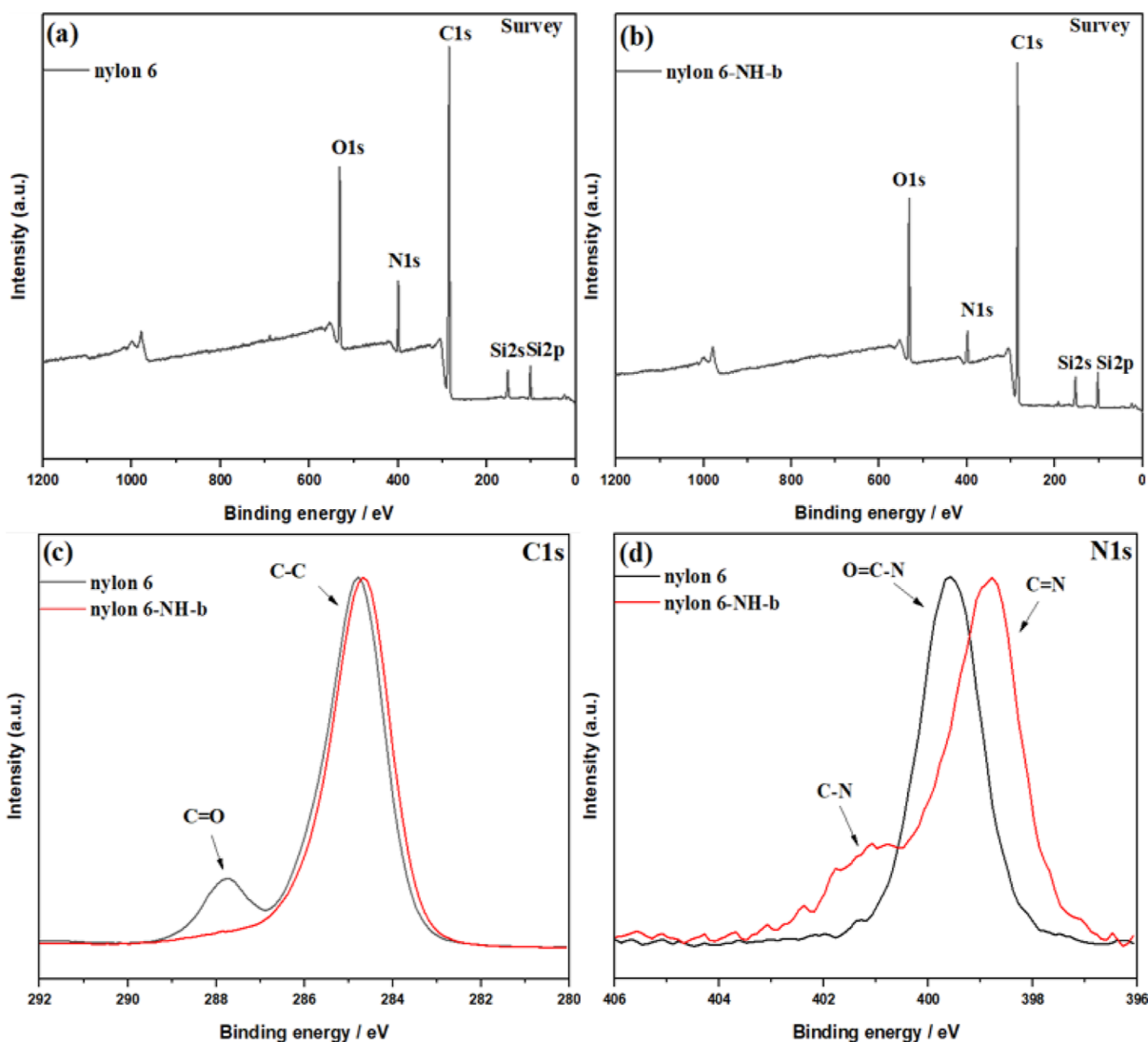


Figure 2. XPS spectra of nylon 6 (a) and nylon 6-NH-b (b), C 1s spectra of nylon 6 and nylon 6-NH-b (c), and N 1s spectra of nylon 6 and nylon 6-NH-b (d).

1538 cm^{-1} are all apparent before and after the reduction with BH_3 (Figure 1a–d). For nylon 6-NH, vibrations of amide I and amide II weakened significantly versus virgin nylon. Meanwhile, we can observe the new peak at 3237 cm^{-1} , which is attributed to the $-\text{NH}-$ vibration of secondary amines, indicating the conversion of amides to amines (Figure 1b–d). The new broad band that appeared at 2200 to 2436 cm^{-1} can be assigned to the imine intermediate or trace $-\text{NH}^+$ salt forms.^{24,25} In addition, the spectra of nylon 6-NH-b (run 10) (Figure 1e) were almost the same as the spectrum of nylon 6-NH-b (Figure 1c), which indicates that the fabric catalyst is still active after being recycled 10 times.

X-ray Photoelectron Spectra. The surface chemical composition of samples was further analyzed by XPS, and the results are shown in Figure 2. For nylon 6 and nylon 6-NH-b, the shifts in the binding energy of C 1s and N 1s spectra clearly demonstrated the conversion of the amide group to secondary amine (Figure 2c–d).^{24,25} The binding energies at 284.8 and 287.8 eV in the spectra of the C 1s region for nylon 6 corresponded to C–C and C=O groups, respectively. After amide reduction, the signal attributed to the C=O group almost disappears, in agreement with the conversion of amide

to secondary amine (Figure 2c). Meanwhile, a new peak at 401.0 eV attributed to the secondary amine and the new binding energy at 398.6 eV corresponding to the C=N group appeared in the high-resolution N 1s spectrum of nylon 6-NH-b. These results further indicated that amide groups were successfully reduced to secondary amines (Figure 2d).

Scanning Electron Microscopy. The SEM images of nylon 6, nylon 6-NH-a, nylon 6-NH-b, and nylon 6-NH-b (run 10) are shown in Figure 3. The surface morphology of nylon 6-NH-a showed no obvious change (Figure 3b). However, after reduction with BH_3 for 24 h, the surface morphology became clearly rougher (Figure 3c). For the surface of nylon 6-NH-b (run 10), the modified layer still remained well, which demonstrated the good physical strength of the fabric catalyst (Figure 3d).

3.3. Condition Optimization of Knoevenagel Condensation. Initially, benzaldehyde and methyl cyanoacetate were chosen as the model substrates. The blank reaction conducted with no catalyst gave a low yield of 5% (Table 2, entry 1). When using the virgin nylon 6 fabric as a catalyst, the yield slightly increased to 21%, which might be attributed to the catalytically active terminal amino group of nylon 6 (Table

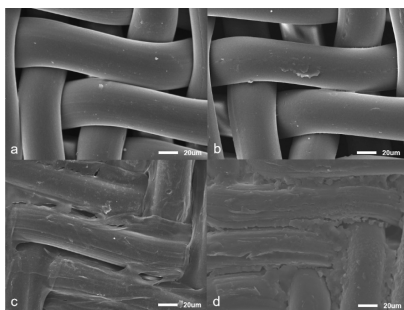


Figure 3. SEM images of (a) nylon 6, (b) nylon 6-NH-a, (c) nylon 6-NH-b, and (d) nylon 6-NH-b (run 10).

Table 2. Optimization of the Knoevenagel Reaction Conditions^a

entry	catalyst	solvent	yield [%] ^b
1	none	cyclohexane	5
2	nylon 6	cyclohexane	21
3	nylon 6-NH-b	cyclohexane	97
4	nylon 6-NH-b	CH ₃ CN	91
5	nylon 6-NH-b	H ₂ O	88
6	nylon 6-NH-b	EtOH	80
7	nylon 6-NH-b	EtOAc	79
8	nylon 6-NH-b	dioxane	69
9	nylon 6-NH-b	ClCH ₂ CH ₂ Cl	70
10	nylon 6-NH-b ^c	cyclohexane	82
11	nylon 6-NH-b ^d	cyclohexane	62
12	nylon 6-NH-b ^e	cyclohexane	5

^aReaction conditions: **1a** (0.1 g, 1 mmol), **2a** (0.12 g, 1.2 mmol), fabric catalyst (0.1 g), solvent (5 mL), 80 °C, 2 h. ^bIsolated yield after column chromatography. ^cFabric catalyst (0.05 g). ^dFabric catalyst (0.02 g). ^eFabric catalyst (0.1 g) was treated with 0.1 M HCl.

2, entry 2). Positively, the yield increased obviously by using nylon 6-NH-b as a catalyst (Table 2, entry 3). A variety of solvents were studied to optimize the reaction conditions, and non-polar cyclohexane gave the best result (Table 2, entries 3–9). To further study the reaction efficiency, we screened the effect of the catalyst dosage. When the amount of fabric catalyst decreased from 0.1 to 0.02 g, there was an obvious decrease in the yield from 97 to 62% (Table 2, entries 3, 10, and 11). Furthermore, a control experiment was conducted with the fabric catalyst treated with 0.1 M HCl to verify the role of basic sites of functionalized nylon 6 fabric, and only 5% yield was obtained (Table 2, entry 12).

After establishing the optimal reaction conditions, we then investigated the substrate scope of the reaction. The results are summarized in Figure 4. Different substituents on the aromatic aldehydes were tested, the substrates bearing electron-donating groups and electron-withdrawing groups all afforded excellent yields (Figure 4, 3a–i). Meanwhile, when methyl cyanoacetate was replaced with malononitrile, the reaction was also conducted smoothly and the reaction time could be reduced to 0.5 h (Figure 4, 3j–l).

3.4. Reusability of the Fabric Catalyst. In order to demonstrate the stability and reusability of the fabric catalyst, further recycling experiments were conducted. Nylon 6-NH-b (0.1 g) was used to catalyze the condensation of benzaldehyde (0.1 g, 1 mmol) with methyl cyanoacetate (0.12 g, 1.2 mmol) in cyclohexane (5 mL) at 80 °C for 2 h in each cycle. The fabric catalyst was then filtered out and directly used for the next cycle. The results are displayed in Figure 5. Pleasingly, the isolated yield only decreased by 5% after 10 runs. This new fabric catalyst exhibits advantages of good stability and reusability.

3.5. Comparison of the Nylon Fabric Catalyst with Reported Catalysts for the Knoevenagel Condensation. The comparison of nylon 6-NH with other amino-functionalized heterogeneous catalysts reported in the earlier literature is listed in Table 3. It is clear that the present work has some

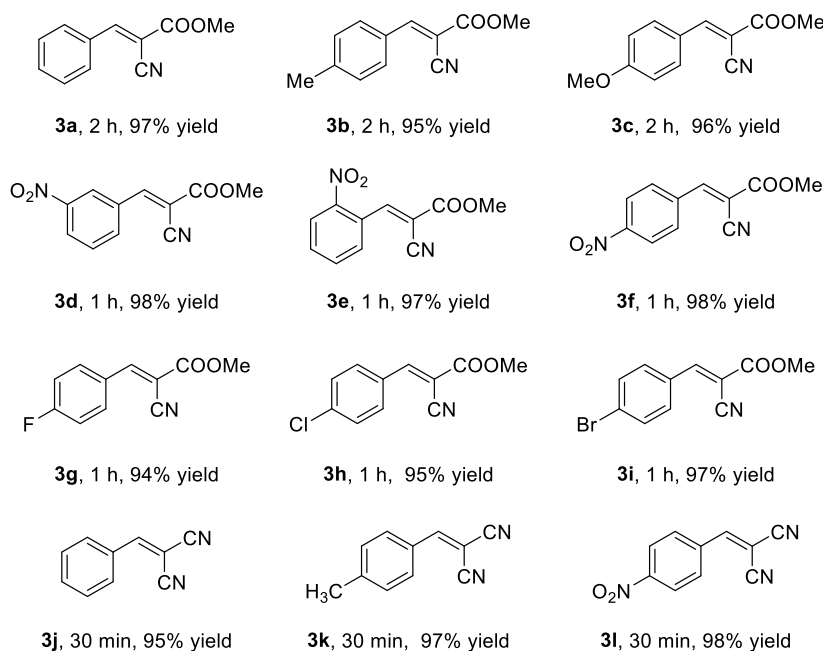


Figure 4. Substrate scope of Knoevenagel condensation.

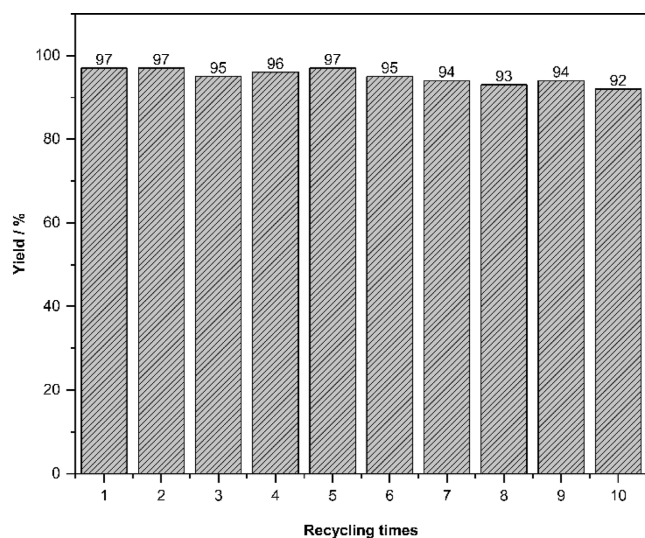


Figure 5. Reusability of the fabric catalyst.

Table 3. Comparison of the Activity of Nylon 6-NH with Those of Other Amino-Functionalized Heterogeneous Catalysts for the Knoevenagel Reaction Between Benzaldehyde and Cyanoacetate

entry	catalyst	reaction conditions	yield [%]	run	refs
1	nano-silica PAMAM Dendrimer	<i>n</i> -hexane, rt, 6 h	90	4	²⁸
2	SBA-NH ₂	Cyclohexane, 82 °C, 1 h	99		²⁹
3	AAPTMS@K10	rt, 12 h	93	6	³⁰
4	Fe ₃ O ₄ @UiO-66-NH ₂	DMF, 80 °C, 2 h	98	4	³¹
5	MPR-NH ₂	H ₂ O, 30 °C, 12 h	100	5	³²
6	MOF-NH ₂	EtOH, 80 °C, 7 h	95	5	³³
7	nylon 6-NH	cyclohexane, 80 °C, 2 h	97	10	this work

beneficial advantages in terms of comparable catalytic activity and reusability. More importantly, contributing to the regularity and flexible structure of the fabric, the fabric catalyst exhibited the advantage of easier separation by filtration over those particle catalysts.

4. CONCLUSIONS

In this work, we have successfully prepared a heterogeneous fabric catalyst based on nylon 6 fabric. The newly developed fabric catalyst was applicable to catalyze Knoevenagel condensation and displayed good catalytic activity and reusability (up to 10 times). This strategy provides an innovative way for the application of functionalized nylon materials, and studies to extend the application are ongoing in our laboratory.

NOVELTY STATEMENT

This work investigates the unique features of nylon fabric as an interesting material for fabrication of heterogeneous base catalysts for catalytic applications. The fabric catalysts exhibit some beneficial advantages in terms of good catalytic activity and reusability. Furthermore, the fabric catalysts exhibit the advantage of easier separation by filtration over those particle catalysts because of the regular and flexible structure of the fabric.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c03401>.

Experimental details and analytical data including compound characterization, ¹H NMR, and ¹³C NMR for all compounds (PDF)

AUTHOR INFORMATION

Corresponding Authors

Zhong Yan – Key Laboratory of Textile Fiber and Products, Ministry of Education, Wuhan Textile University, Wuhan 430200, China; orcid.org/0000-0002-0775-7124; Email: 935432304@qq.com

Dong Wang – Key Laboratory of Textile Fiber and Products, Ministry of Education, Wuhan Textile University, Wuhan 430200, China; orcid.org/0000-0002-8139-8502; Email: wangdon08@126.com

Authors

Yuwei Liu – Key Laboratory of Textile Fiber and Products, Ministry of Education, Wuhan Textile University, Wuhan 430200, China

Wenwen Wang – Key Laboratory of Textile Fiber and Products, Ministry of Education, Wuhan Textile University, Wuhan 430200, China

Complete contact information is available at:

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Author Contributions

[†]These authors contributed equally

Notes

The authors declare no competing financial interest.

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