Contents lists available at ScienceDirect



Applied Catalysis A, General



journal homepage: www.elsevier.com/locate/apcata

Surface wettability modification of amine-functionalized polyacrylonitrile fiber to enhance heterogeneous catalytic performance for aldol reaction in water



Hai Zhu^a, Chenlu Zhang^a, Ning Ma^{a,*}, Minli Tao^a, Wenqin Zhang^{a,b}

^a Department of Chemistry, School of Science, Tianjin University, Tianjin, 300072, PR China

^b Key Laboratory of Inorganic-Organic Hybrid Functional Materials Chemistry, Ministry of Education, Tianjin Key Laboratory of Structure and Performance for Functional Molecules, Tianjin Normal University, Tianjin, 300387, PR China

ARTICLE INFO

Keywords: Polyacrylonitrile fiber Wettability Surface modification Heterogeneous catalysis Aldol reaction

ABSTRACT

Heterogeneous catalytic aldol reaction has widely focused on tethering multiple functional groups upon support that can act together (for example, acid-base cooperation) to improve reaction rate beyond individual moiety alone. Here, a series of amine-functionalized fibers with additional surface wettability modification were prepared to promote aldol reaction in water. The result showed that an enhanced catalytic activity was achieved by introducing hydroxyl group to fiber. Hydrophilic prolinamide-functionalized fiber (PAN_EF-PLA) exhibited the best catalytic performance, and its activity proved to be higher than those of hydrophobic-modified fiber and even the small molecule prolinamide. This enhancement is attributed to that the favorable hydrophilic microenvironment consisting of hydroxyl group, residual cyano group and prolinamide facilitates the accessibility of reactants to catalytic sites and increases the rate of mass transfer in water for promoting reaction. This work provides an effective protocol to maximize performance of fiber-supported catalyst by appropriate wettability modification.

1. Introduction

Organocatalysis has attracted continuous attention over the past few decades as it provides an alternative paralleling enzyme and transition-metal catalysis for the production of valuable fine chemicals [1-4]. The use of small organic molecule catalysts has gained tremendous growth within the domain of synthetic chemistry because of their distinct activity and selectivity [5,6]. Nevertheless, such homogeneous catalysts are difficult to separate from the reaction system and reuse for consecutive cycles, which limits their practical applications, especially in continuous flow process. To achieve greener, more economical and sustainable chemical process and solve above problems, immobilization of a homogeneous catalyst by tethering it onto solid materials via covalent bond has been prosperously developed. These heterogeneous catalysts, characterized as chemically homogeneous but physically heterogeneous feature, are highly desired in organic synthesis since the convenience of recycling of catalysts and reducing of waste [7-9]. Despite much effort to the introduction of diverse functionalities onto support, in some cases, it's difficult to attain the level of catalytic efficiency that homogeneous counterparts exhibited, which

was correlated with the intrinsic interfacial effects, complicated competitive absorption and changed chemical microenvironment around active sites in heterogeneous catalytic process [10-13]. In this concern, several strategies based on tailoring catalyst by modulating support surface microenvironment were implemented [14-17]. Importantly, recent advances in regulating surface wettability for efficient oil-water separation gave inspiration for heterogeneous catalytic system [18-20], in which the controlled hydrophilic/hydrophobic properties of support surface may finely tune the interactions of substrates with catalytic sites and then facilitate the subsequent catalytic conversion [21-24]. For example, Shank et al. reported silica material decorated by both sulfonic group and hydrophobic alkyl group displayed much higher activity than the one containing only acid sites in esterification reaction [25]. Xiao et al. reported that hydrophilic TS-1 zeolite with rich hydroxyl group showed increased activities in oxidation of hexene and hexane as compared with conventional TA-1 [26]. Therefore, the construction of heterogeneous catalyst with specific surface wettability is in definite demand with the aim of maximizing catalytic performance, in which rational design and controllable synthesis are crucial.

Heterogeneous catalysis of aldol reaction has been intensively

E-mail address: mntju@tju.edu.cn (N. Ma).

https://doi.org/10.1016/j.apcata.2020.117842

Received 20 December 2019; Received in revised form 12 September 2020; Accepted 19 September 2020 Available online 22 September 2020 0926-860X/ © 2020 Elsevier B.V. All rights reserved.

^{*} Corresponding author.

investigated in chemical industry, and satisfactory results are achieved using silica-supported acid-base bifunctional catalysts [27-33]. Its reaction mechanisms are well understood by combining molecular dynamic simulation [34], quantum mechanical and molecular mechanical calculations [35], and kinetic examination [36]. Further detailed studies show that the modulation of chemical and physical properties [37-41] significantly affects cooperative catalysis. Apart from typical silica support, some new solid materials such as polymer [42] and cellulose nanocrystal [43] were successfully applied to graft organocatalysts for aldol reaction through similar cooperative mechanism. Such acid-base cooperative reaction pathway that imitates enzyme catalysis is becoming a popular strategy for promoting reaction, however, accurate control of spatial distribution of acid- and base-sites is generally required but still remains a challenge. In addition to positioning two incompatible functionalities at a suitable sequence for mimicking enzyme upon support material, we envision that delicate arrangement of two functionalities, in which one could help to modify surface wettability and provide H-donor for constructing tunable microenvironment around catalytic sites, would improve catalytic performance in aldol reaction.

Polyacrylonitrile fiber (PANF), for its unique properties, such as excellent durability, good mechanical and thermal stability, and high solvent resistance [44], has recently emerged as a promising polymer support for absorption and catalysis. Cyano group of PANF surface is generally capable of reacting with specific functional molecules to offer novel functionalities through aminolysis and hydrolysis. The modified PANFs have been used as absorbents to remove dyes [45], heavy metal ions [46,47] and organic pollutants [48] from waste water effectively and selectively. Moreover, several research groups including us confirmed that the functionalized fibers were excellent catalysts in desymmetrization of *meso*-anhydride [49], Knoevenagel reaction [50], mutilcomponent reactions [51,52], cycloaddition of CO₂ [53] and ring-opening reaction [54].

In continuation of our research on green application of fiber in sustainable organic synthesis, herein, various amine-functionalized polyacrylonitrile fibers were prepared to investigate the effect of surface wettability modification on catalytic activity in aldol reaction. The obtained fiber catalysts were characterized by mechanical strength, FT-IR, solid state ¹³C NMR, TGA, XRD, elemental analysis, SEM and water contact angle. The surface wettability of the functionalized fiber was tuned by introducing hydroxyl group into fiber support. Due to its high activity in aldol reaction, prolinamide-functionalized fiber was chosen as a template catalyst to further investigate the influence of hydrophilic/hydrophobic surface properties on aqueous catalytic reaction. Additionally, its catalytic performance was compared with the reported conventional acid-base bifunctional aminosilica catalysts, and the results showed that fiber catalyst exhibited superior catalytic activity and selectivity under mild conditions.

2. Experimental

2.1. Chemicals and materials

Commercially available polyacrylonitrile fiber (PANF, 93% 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 µm was obtained from Fushun Petrochemical Corporation of China. Ethanolamine, propane-1,3-diamine, *N*,*N*-dimethylpropane-1,3-diamine, ethane-1,2-diamine, *L*-proline methyl ester hydrochloride, 1,3-diaminopropan-2-ol, ethylene glycol, *p*-nitrobenzaldehyde, acetone, ethyl acetate, dichloromethane, methanol, xylene, Na₂SO₄, petroleum ether were analytical grade and used without further purification. Deionized water was commercially obtained.

2.2. Catalyst characterizations

The Fourier transform infrared spectra (FT-IR) of fibers were collected on AVATAR360 FT-IR spectrometer (Thermo Nicolet). The sample of fiber was cut to pieces and compressed into KBr pellets before measurement. Solid-state ¹³C CP-MAS NMR spectra were recorded on Infinityplus 300 (Varian Company, America). Thermogravimetric analysis (TGA) was performed on a STA409PC TGA/DSC simultaneous thermalanalyzer (Netzsch Company, Germany) under nitrogen atmosphere, and the sample of fiber was analyzed in the temperature range of 35-800 °C with a heating rate of 10 K min⁻¹. The mechanical property of fiber was measured using electronic single fiber strength tester YG(B) 001A (Wen zhou Da Rong Textile Instrument Corporation, China) with a clamping length of 10 mm and an elongation rate of 20 mm min⁻¹ at 25 °C. Each sample was tested ten times in parallel and the average data was calculated to afford breaking strength of fiber. D/MAX-2500 X-ray diffractometer (Rigaku Corporation) was used to determine the crystallinity of fiber. Elemental analysis was carried out using a Vario Micro Cube instrument (Elementar, Germany). Scanning electron microcopy (SEM) experiments were carried out with Hitachi S-4800 field emission scanning electron microscope. Water contact angle (WCA) test was conducted with a POWEREACH-JC2000DI contact angle system. The sample of fiber was cut to pieces and dissolved in DMSO under heating at 100 °C for 20 min. The sticky liquid was spread onto the glass slide and then dried under vacuum at 80 °C for 3 h to give fiber membrane before measurement. ¹H NMR (400 MHz) and ¹³C NMR (101 MHz) of the products were measured with BRUKER-AVANCE III instruments in CDCl₃ using TMS (tetramethylsilane) as the internal standard.

2.3. Synthesis of functionalized fibers

PANF is one of the most common synthetic fibers and its surface contains abundant cyano groups and ester groups which can be converted partially through the formation of amide bonds. As depicted in Scheme 1, the preparation of functionalized fiber was typically achieved by introducing functional molecule onto PANF surface. Hydroxyl-modified amine fibers (PAN_EF-PMA, PAN_EF-PLA and PAN_EF-TTA) were synthesized by a simple two-step approach. First, hydroxylfunctionalized fiber PAN_EF was prepared by anchoring of ethanolamine onto fiber via the formation of amide bond. Next, the resultant PAN_EF was allowed to react with different alkylamines to give the corresponding hydroxyl-modified amine fibers. In comparison, mono-functionalized amine fibers (PANPMAF, PANTTAF and PANPLAF) and PAN_{HPP}F were prepared directly by adding PANF into a mixture of solvent and alkylamines according to our previous work [50]. Schematic diagram for the synthesis of PAN_EF-PLA and PAN_{PLA}F is shown in Scheme S1. The modified extent of fiber in this work was measured by weight gain and acid-base exchange capacity, and the results are summarized in Table 1.

2.3.1. Synthesis of hydroxyl-modified amine fibers (PAN_EF -PLA, PAN_EF -PMA and PAN_EF -TTA)

Hydroxyl-modified amine fibers were synthesized through a twostep approach using PANF as the precursors. As a typical experiment for the synthesis of PAN_EF-PLA, first, 2.10 g of dried PANF was added to 50 mL of water solution containing 20 mL of ethanolamine and the mixture was heated to reflux for 3 h. After being cooled to room temperature, the fiber was collected by filtration, rinsed repeatedly with deionized water (60-70 °C), and then dried overnight at 60 °C under vacuum to give fiber PAN_EF (2.284 g, 1.29 mmol/g).

Next, dried PAN_EF (0.25 g) was added to the solution of prolinamide (*S*)-*N*-(2-aminoethyl)pyrrolidine-2-carboxamide (4.0 g) dissolved in ethylene glycol/H₂O (4:1, 6 mL) and the mixture was stirred at 130 °C for 4 h. After being cooled to room temperature, the fiber was collected by filtration, rinsed repeatedly with deionized water (60-70 °C) and dried overnight at 60 °C under vacuum to give fiber PAN_EF-PLA



Scheme 1. Preparation of functionalized fibers.

 Table 1

 The weight gain of the functionalized fibers and their function loading, basicity and mechanical properties.

Entry	Fiber	Weight gain (%) ^a	Function loading (mmol/ g) ^b	Basicity (mmol/ g) ^c	Mechanical properties	
					Breaking strength (cN)	Retention breaking strength (%) ^d
1	PAN _E F	8.76	1.29	0	9.74	95
2	PAN _E F-PMA	7.46	0.92	1.05	8.60	84
3	PAN _E F-PLA	22.40	1.16	1.21	8.05	78
4	PAN _E F-TTA	11.79	1.02	1.08	8.23	80

^a Weight gain = $(w_2 \cdot w_1)/w_1 \times 100\%$, where w_1 and w_2 are the weights of original fiber and modified fiber, respectively.

^b Function loading = $[(w_2 \cdot w_1)/\Delta Mw]/w_2$, where w_1 and w_2 are the weights of original fiber and modified fiber, ΔMw is the changed molecular weight between original fiber and modified fiber.

^c Basiciy is calculated according to acid-base titration.

^d Based on PANF.

(0.306 g, 1.16 mmol/g).

The synthesis of PAN_EF-PMA and PAN_EF-TTA is similar to that of PAN_EF-PLA. Typically, PAN_EF-PMA (0.533 g, 0.92 mmol/g) was prepared from PAN_EF (0.496 g) with a mixture of water (5 mL) and commercial available propane-1,3-diamine (5 mL) under reflux for 0.5 h. And PAN_EF-TTA (0.474 g, 1.02 mmol/g) was prepared from PAN_EF (0.424 g) with a mixture of water (3 mL) and commercial available *N*,*N*-dimethylpropane-1,3-diamine (6 mL) under reflux for 1 h.

2.3.2. Synthesis of mono-functionalized amine fibers (PAN_{PMA}F and PAN_{TTA}F)

As a typical synthesis of $PAN_{PMA}F$, 0.98 g of dried PANF was added to 20 mL of water solution containing 10 mL of propane-1,3-diamine and the mixture was heated to reflux for 1 h. After being cooled to room temperature, the fiber was collected by filtration, rinsed repeatedly with deionized water (60-70 °C) and dried overnight at 60 °C under vacuum to give fiber PAN_{PMA}F (1.166 g, 2.13 mmol/g). The synthesis of PAN_{TTA}F is similar to PAN_{PMA}F. And fiber PAN_{TTA}F (1.179 g, 1.08 mmol/g) was prepared from PANF (1.05 g) with a mixture of water (6 mL) and *N*,*N*-dimmethylpropane-1,3-diamine (14 mL) under reflux for 2.5 h.

2.3.3. Synthesis of amine-functionalized fiber PAN_{HPP}F

As a typical synthesis of PAN_{HPP}F, 0.301 g of dried PANF was added to a solution of (2*S*)-*N*-(3-amino-2-hydroxypropyl)pyrrolidine-2-carboxamide (5.5 g) dissolved in ethylene glycol/H₂O (4:1, 6 mL) and the mixture was heated at 130 °C for 10 h. After being cooled to room temperature, the fiber was collected by filtration, rinsed repeatedly with deionized water (60-70 °C) and dried overnight at 60 °C under vacuum to give fiber PAN_{HPP}F (0.367 g, 0.96 mmol/g).

2.4. The measurement of basicity

Dried amine functionalized fiber (0.1 g) was immersed into 10 mL of 0.02 M HCl for 12 h. After that, the fiber was fetched out using tweezers and rinsed with water. The filtrate was combined with remaining HCl solution and the concentration of the mixture was titrated by 0.02 M NaOH. The basicity of amine-functionalized fiber was determined by the amount of acid consumed.

2.5. General procedure for aldol reaction

To a round-bottom flask containing fiber catalyst (10 mol% compared to aldehyde, based on functional loading) added with *p*-nitrobenzaldehyde (0.151 g, 1 mmol), acetone (0.581 g, 10 mmol) and water (8 mL). The reaction mixture was stirred with a magnetic bar for a period of time at 40 °C. Reaction kinetics was studied by stirring the eight parallel reaction mixtures at 40 °C for different time (0.5 h, 1 h, 2 h, 3 h, 4 h, 5 h, 6 h and 7 h, respectively). After that, the fiber was taken out, rinsed with ethyl acetate (3 × 5 mL), and used directly for next run (recyclability test). The ethyl acetate solution was combined with water solution and the obtained mixtures were then extracted with ethyl acetate (3 × 8 mL). The organic layers were dried over Na₂SO₄. Pure product was obtained by flash column chromatography on silica gel (petroleum ether/ethyl acetate) and the yield of product was calculated.

3. Results and discussion

3.1. The characterization of fiber catalyst

Mechanical properties of different fibers were evaluated by breaking strength and the results are displayed in Table 1 and Table S1. The breaking strength of PANF, PAN_EF and PAN_EF-PLA are 10.27 (Table S1, entry 1) [52], 9.74 and 8.05 cN, respectively (Table 1, entries 1 and 3). Evidently, the mechanical strength of fiber gradually decreased after modification with hydroxyl and amine groups onto fiber surface. This phenomenon can be attributed to the swelling and the changes of partial crystalline region of fiber material during covalent modification. Similarly, the break strength of PAN_EF-PMA and PAN_EF-TTA declined to 8.60 and 8.23 cN, that is, 84% and 80% of original PANF strength were retained, respectively. Mono-functionalized amine fibers can keep more than 83% of pristine PANF strength, which shows their good mechanical properties (Table S1, entries 2-4). Importantly, after being applied in aldol reaction for consecutive seven times, the break strength of PAN_FF-PLA-7 was only 0.7 cN loss compared to fresh PAN_FF-PLA, namely 92% of strength is still maintained (Table S1, entry 7). This result reveals that fiber material possesses good strength and can be used as a promising support in heterogeneous catalysis.

The FT-IR spectra of different fibers are shown in Figs. 1 and S1. Adsorption peaks at 2942, 2868, 2245 and 1738 cm⁻¹ in the original PANF can be assigned to the stretching vibrations of $-CH_2$, C = N and C = O, respectively [52]. After modification, the intensity of peaks at 2245 and 1738 cm⁻¹ in the spectra of PAN_EF, PAN_EF-PMA, PAN_EF-PLA and PAN_FF-TTA slightly decreased compared with original PANF, which is attributed to the consumption of ester moiety and cyano group during aminolysis process (Fig. 1a-c and f). Additional two new peaks appearing at approximately 1660 and 1545 cm⁻¹ correspond to the amide I (C = O stretching vibration in CONH) and amide II (N-H bending vibration in CONH). As expected, the $C \equiv N$ stretching vibration further attenuated after introduction of alkylamines to PAN_EF but still existed, which indicates only partial cyano groups were reacted to form amide moieties and the inner ones hardly participated in the modification. Visibly, the appearance of broad band at around 3670-3130 cm⁻¹ is due to O-H stretching vibrations in the spectra of PAN_EF, PAN_EF-PMA, PAN_EF-PLA and PAN_EF-TTA (Fig. 1a-c and f). Because of overlapping with O-H stretching, the N-H stretching bands of primary amine and prolinamide (pyrrolidine) are not quite distinguishable (Fig. 1b, c). Notably, after PAN_EF-PLA was applied in aldol reaction for successive cycles, the spectrum of PAN_EF-PLA-7 was nearly the same as PAN_EF-PLA-1 and both of them showed a new peak centered at around



Fig. 1. The FT-IR spectra of (a) PAN_EF , (b) PAN_EF -PMA, (c) PAN_EF -PLA, (d) PAN_EF -PLA-1, (e) PAN_EF -PLA-7 and (f) PAN_EF -TTA.



Fig. 2. The solid-state ¹³C CP-MAS NMR spectra of the fibers.

856 cm⁻¹ which can be assigned to C-H in-plane bending vibrations of benzene ring arising from the minor product adsorbed on fiber surface (Fig. 1d, e). Furthermore, the fiber was characterized by ¹³C CP-MAS NMR. After attaching ethanolamine onto PANF, a new peak appearing at 60.8 ppm can be assigned to methylene carbon adjacent to hydroxyl group of ethanolamine molecule, and the peak at 176.8 ppm is ascribed to amide carbon (Fig. 2a) [52]. Compared to fresh PANF, the ¹³C CP-MAS NMR spectrum of PAN_{PLA}F exhibits a new signal at 61.5 ppm related to the NCH of pyrrolidine (Fig. S2c). After the introduction of various alkylamines to PAN_EF, the carbon signal in the wide range of 16.9-50.8 ppm is the superposition of methylene carbon of fiber backbone and alkyl linker (Fig. 2b–d).

The thermostability of the fibers was investigated by TGA and the results are displayed in Figs. 3 and S4. After grafting ethanolamine onto PANF, the initial decomposition temperature of resultant fiber PAN_EF slightly declined to 300 °C, evidencing its high thermal stability [52]. The main weight losses of PAN_EF -PMA, PAN_EF -PLA and PAN_EF -TTA are observed from 300 to 430 °C. As the temperature rose beyond 600 °C, these weight losses tend to be stable and their decompositions are accomplished. In addition, $PAN_{HPP}F$, $PAN_{PMA}F$, $PAN_{PLA}F$ and $PAN_{TTA}F$ exhibit similar decomposition patterns in the range of 35-800 °C and their major weight losses start from 300 °C (Fig. S4). According to the TGA, the amine loadings of the hydroxyl-modified amine fibers were calculated and the results are shown in the Supporting Information



Fig. 3. The TGA curves of the fibers.



Fig. 4. The XRD patterns of the fibers.

(Table S2, 0.61 mmol g⁻¹ for PAN_EF-PLA; 0.84 mmol g⁻¹ for PAN_EF-PMA; 0.77 mmol g⁻¹ for PAN_EF-TTA). It can be seen that the amount of amine group determined from TGA are lower than the function loadings based on weight gain, which is due to that the actual weight loss of amine segment is not accurately acquired from the TGA curve. Although the thermal stabilities of all modified fibers are lower than that of original PANF, it is sufficient for their application in catalytic process.

The XRD patterns of PANF, PAN_EF, PAN_EF-PMA, PAN_EF-PLA and PAN_EF-TTA are shown in Figs. S5a and 4 . Original PANF shows two diffraction peaks at 29.2° and 17.0° which are related to the hexagonal lattice planes of (1 1 0) and (1 0 0), respectively [52,55]. The intensity of these two peaks maintain well after direct modification by ethanolamine (Fig. 4a) and alkylamines (Fig. S5b–e), indicating such surface modification does not significantly distorted the original crystal lattice and the polar interaction between molecular chains. Compared with mono-functionalized amine fibers, the characteristic peaks of PAN_EF-PMA, PAN_EF-PLA and PAN_EF-TTA are almost not shifted or broadened

Table 2	
The elemental analysis data of the fibers.	

Entry	Fiber	C (%)	H (%)	N (%)
1	PAN _E F	60.72	6.56	20.73
2	PAN _E F-PLA	57.20	6.85	19.88
3	PAN _E F-PLA-1	58.06	6.35	18.02
4	PAN _E F-PLA-7	58.10	6.74	18.58
5	PAN _E F-PMA	53.69	7.65	18.33
6	PAN _E F-TTA	56.44	7.77	18.47

but slightly weakened in intensity because of the decrease in crystallinity arising from the further grafting reaction (Fig. 5b–d), which agrees well with the mechanical strength test results. Moreover, according to earlier research [56], these amorphous regions resulting from the reduction in crystallinity could make fiber material quite soft and elastic.

The chemical compositions of different fibers were investigated by elemental analysis and the results are presented in Table 2 and Table S3. It can be seen that PAN_EF (Table 2, entry 1), PAN_{PMA}F, PAN_{PLA}F, PAN_{TTA}F and PAN_{HPP}F (Table S3, entries 2-5) have lower carbon content and higher hydrogen content in comparison with original PANF [52], which is due to the corresponding ethanolamine and alkylamine molecules have less carbon and more hydrogen contents than those of PANF. Whereas, the decrease of nitrogen content of these fibers was caused by the fact that cyano groups partially reacted with alkylamine [50]. Similarly, further decline in carbon and nitrogen contents and increase in hydrogen content were observed for PAN_FF-PLA, PAN_FF-PMA and PAN_EF-TTA. These results demonstrate the successful surface modification of PAN_EF by alkylamine. It is worth noting that there were some changes in the composition of PAN_EF-PLA-7 compared to fresh PAN_EF-PLA after being used in aldol reaction for consecutive seven runs (Table 2, entries 2 vs 4), and its color turned from the original bright vellow to red-brown and retained this color even additional stirring in ethyl acetate. This change in chemical composition upon recycling may be due to the minor product attached to fiber surface, which is consistent with the aforementioned FT-IR analysis.

In addition, the surface morphology of the fibers was observed by SEM and the respective images are shown in Figs. 5 and S6. The original



Fig. 5. The SEM images of (a) PAN_EF, (b) PAN_EF-PLA, (c) PAN_EF-PLA-1 and (d) PAN_EF-PLA-7.



Fig. 6. The water contact angle images of the fibers.

PANF has a smooth, uniform and neat surface (Fig. S6a) [52]. After functionalization, the resultant fiber surfaces are dense with few beads and their integrity remains intact (Figs. 5a, b and S6b–f). When PAN_EF -PLA was used in aldol reaction, the surfaces of the recycled PAN_EF -PLA-1 and PAN_EF -PLA-7 became increasingly wrinkled and rough compared to parent PAN_EF -PLA but did not show any collapse or degradation (Fig. 5c–d). This observation is in agreement with the mechanical strength test results, revealing fiber catalyst can be reused multiple times with good structure stability.

The wettability (hydrophilicity/hydrophobicity) of different fibers was quantitated by water contact angle test and the results are shown in Fig. 6. The contact angle of water droplets on original PANF is 62.9°, while it notably rises to 75.2° upon direct introduction of prolinamide. indicating that the decoration of alkylamine makes fiber more hydrophobic relative to pristine PANF. Likewise, the contact angles of PAN_{PMA}F and PAN_{TTA}F slightly rise to 68.1° and 67.7°, respectively. After modification with hydroxyl group, the water contact angles of PAN_EF-PMA, PAN_EF-PLA and PAN_EF-TTA were observed to drop to 55.8°, 58.4° and 53.5°, respectively, indicating that hydroxyl moiety can effectively tune surface wettability of fiber and improves its hydrophilicity compared with corresponding mono-functionalized amine fiber. Additionally, when fiber were placed in a water-ethyl acetate biphasic mixture, hydrophilic prolinamide fiber (PAN_EF-PLA) can move from organic phase (upper) to aqueous phase (bottom) and be well spread in water (Fig. S7), which further supports the good hydrophilicity of such fiber. This result combined with water contact angle experiment clearly suggests the successful surface wettability modification upon amine-functionalized fiber.

3.2. Catalytic Performance

The catalytic performances of different amine-functionalized fibers were examined in aldol reaction of *p*-nitrobenzaldehyde with acetone and the related results are displayed in Table 3. As expected, blank control and original support material PANF had low yields of addition product as the reaction proceeded in water at 40 °C for 6 h (Table 3, entries 1-2). Meanwhile, hydroxyl-functionalized fiber PAN_EF, the precursor used to graft amine moiety, also showed inferior activity (Table 3, entry 3). Above results exclude the catalytic ability of fiber support itself, and indicate the base centers are required to ensure the completion of reaction. When the reaction was conducted in the presence of mono-functionalized amine fiber PAN_{PMA}F, 37.5% yield of addition product was gained without the formation of enone product (Table 3, entry 4). The fiber PAN_{TTA}F provided a low yield of 30.5% (Table 3, entry 6). With prolinamide fiber PAN_{PLA}F as catalyst, the yield of addition product could reach up to 79.3% under the same conditions (Table 3, entry 5). Moreover, when hydroxyl group was introduced to the mono-functionalized amine fibers, the resultant hydrophilic fibers PAN_EF-PMA, PAN_EF-PLA and PAN_EF-TTA gave the desired addition

Table 3			
The optimization	of reaction	conditions ^a	

Entry	Catalyst	Time (h)	Yield of $2 (\%)^{b}$	Yield of 3 $(\%)^{b}$
1	-	6	28.0 ± 1.1	0
2	PANF (100 mg)	6	21.9 ± 1.7	0
3	PAN _E F	6	20.0 ± 1.3	0
4	PAN _{PMA} F	5	37.5 ± 1.2	0
5	PAN _{PLA} F	5	79.3 ± 0.8	0
6	PAN _{TTA} F	5	30.5 ± 1.1	0
7	PAN _E F-PMA	5	45.8 ± 0.6	4.3 ± 0.6
8	PAN _E F-PLA	5	90.8 ± 0.9	1.6 ± 0.2
9	PAN _E F-TTA	5	36.5 ± 1.3	0
10	PLA	5	67.2 ± 0.9	0
11	PAN _H F-PLA	5	60.8 ± 1.2	trace
12	PAN _E F/PAN _{PLA} F	5	78.5 ± 1.0	trace
13	PAN _E F/PAN _{PMA} F	5	34.5 ± 1.6	0
14	PAN _E F/PAN _{TTA} F	5	29.7 ± 0.6	0
15	PAN _{HPP} F	5	83.6 ± 0.5	0

 $^{\rm a}$ Reaction conditions: ${\it p}\mbox{-nitrobenzaldehyde}$ (1 mmol), acetone (10 mmol), 40 °C, H2O (8 mL).

 $^{\rm b}$ Isolated yield, the error bar is calculated based on three parallel experiments..

product in 45.8%, 90.8% and 36.5% yields, respectively (Table 3, entries 7-9). Compared to other amine structure functionalized fibers, prolinamide fiber provided a better catalytic activity which is in agreement with the observations of Marin [40] and Asefa [57]. They intensively investigated the impact of different type of organoamine immobilized upon silica on cooperatively catalytic aldol reaction. Such dramatic difference in activity is probably related with the formation of active intermediate from amine sties with acetone (Scheme S2). PAN_{PMA}F (primary amine) may form stable inhibiting imine species that would block catalytic sites during the reaction process (Scheme S2a and Fig. S8), and the generation of crucial enamine intermediate was not available for $PAN_{TTA}F$ (tertiary amine) without any hydrogen atom bonded to nitrogen atom [57,58]. The crude products obtained from above fiber-mediated catalytic systems were analyzed using ¹H NMR spectroscopy (Figs. S19-34 in the Supporting Information) and the results showed that a little of olefin product could be produced in the case of PAN_EF-PMA or PAN_EF-PLA. And almost no enone product was detected with other type of fiber-supported catalysts, which demonstrates their high selectivities for aqueous aldol reaction.

It is worth noting that hydrophilic amine-functionalized fibers showed enhanced catalytic activities as compared to their mono-functionalized counterparts under the identical conditions. For instance, despite it had similar pyrrolidine catalytic sites, hydrophilic prolinamide fiber $PAN_{E}F$ -PLA was more active than the corresponding mono-functionalized fiber $PAN_{PLA}F$ and the yield of addition product visibly increased to 90.8% (Table 3, entry 5 *vs* entry 8). Kinetic profiles showed that $PAN_{E}F$ -PLA exhibited high initial rate relative to $PAN_{PLA}F$ as



Fig. 7. Kinetic profiles for aldol reaction over fiber catalyst PAN_EF -PLA, PAN_EF -PMA, PAN_EF -TTA, $PAN_{PLA}F$ and $PAN_{HPP}F$.

reaction proceeded rapidly in the first two hours, after which slow yet gradual increase of the yield was observed over the remaining time (Fig. 7). The initial reaction rate of PAN_EF -PLA reached up to 0.113 mol $L^{-1} h^{-1}$ while the initial reaction rate of PAN_{PLA}F was lower at 0.076 mol L⁻¹ h⁻¹. These results clearly indicate that the decoration of hydroxyl group upon fiber support has important impact on catalytic performance. For PAN_EF-PLA, its good wettability endows fiber material with good spreading in water that helps to increase the accessibility of catalytic sites on fiber. The presence of hydroxyl group together with residual cyano group both adjacent to catalytic sites create a favorable hydrophilic microenvironment in the surface layer of fiber that allows the organic substrates (acetone) to go easily in. A high concentration of active sites along with reactants located in the confined microenvironment make their interactions more sufficient. Meanwhile, the hydrogen bond formed between available hydroxyl group of fiber surface and carbonyl moiety of reactant helps the facile generation of enamine from the reaction of acetone with pyrrolidine moiety of prolinamide, thus turning PAN_EF-PLA into a highly efficient catalyst for aldol reaction. The iminium species formed from hydrophobic aromatic aldehyde with prolinamide is believed to be inhibited owing to the lack of strongly acid sites on fiber surface (Scheme S2b and Fig. S10). Since PAN_EF-PLA exhibits efficient catalytic performance in aldol reaction, its homogeneous counterpart (prolinamide) was prepared and used in the reaction. It was found that small molecule organocatalyst PLA offered a moderate yield of addition product (67.2%) (Table 3, entry 10). The increased activity with the employment of PAN_FF-PLA suggests the advantage of functionalized fiber as heterogeneous catalyst for this transformation.

To further understand the fiber surface property in aqueous catalytic aldol reaction, the incorporation of hydrophobic group in vicinity of catalytic sites would be an alternate way to tune surface microenvironment from the opposite. Following this idea, the long alkyl chain n-hexyl group was grafted onto fiber surface (PAN_HF-PLA) and its water contact angle was notably improved to 86.4° (Fig. S11). When we placed the fiber in a water-ethyl acetate biphasic mixture, PAN_HF-PLA can stay in organic phase (upper) and be well spread in ethyl acetate (Fig. S12). These observations confirm the successful hydrophobic modification upon fiber material. The catalytic experiment showed that reaction yield dramatically dropped from 79.3% to 60.8%, which imply enhancing surface hydrophobicity is detrimental to the reaction (Table 3, entry 11). This might be due to that the formed hydrophobic microenvironment surrounding the catalytic sites would repel watersoluble acetone from prolinamide moiety, which decreases the effective contact of acetone with catalytic sites, thereby turning PAN_HF -PLA into a lowly active catalyst. On the other hand, higher hydrophobicity

makes the hydrophobic reaction products difficult to leave from the surface layer of fiber which leads to the encapsulation of catalytic sites and prevents the accessibility of reactants to catalytic sites. From above results and analysis, we can conclude that the catalytic efficiency of functionalized fibers mainly relies on two aspects: one is the existence of amine group and the other is the surface property of fiber. The amine moiety provides catalytic sites and the appearance of wettability group together with residual cyano group would construct a favorable microenvironment that facilitates the accessibility of reactants to catalytic sites, thus enhancing the rate of mass transfer in water.

Interestingly, when PAN_{PLA}F was combined with hydroxyl-functionalized fiber PAN_EF in the reaction, the yield of addition product was found to be reduced to 78.5% (Table 3, entry 12), which was lower than that of PAN_EF-PLA. Similar results were obtained when PAN_{PMA}F and PAN_{TTA}F was physically mixed with PAN_EF, respectively (Table 3, entries 13-14). These results reveal that hydroxyl group and amine moiety should be located on the same fiber chain, and the generated hydroxylamine pairs in this case could form a hydrophilic microenvironment around the catalytic sites while the construction of effective microenvironment in the case of two individual fibers failed owing to the existing physical distance between hydroxyl and amine groups. The former bringing hydroxyl group in close proximity to amine group is beneficial for the nucleophilic attack of amine sites to adjacent carbonyl of acetone in identically constrained local microenvironment. Besides, PAN_{HPP}F has the same pyrrolidine catalytic sites as PAN_EF-PLA, but with hydroxyl group at the neighboring prolinamide moiety. The resulting intramolecular hydroxyl-prolinamide fiber PAN_{HPP}F afforded a slightly lower yield than that of the intermolecular hydroxyl-prolinamide fiber PAN_EF-PLA in aldol reaction (Table 3, entry 15). Kinetic profile showed that PAN_{HPP}F gave a high initial reaction rate in the first 0.5 h, similar to that of PAN_EF-PLA, and a yield of 83.6% was obtained after 5 h. Comparison of the kinetic profiles of PAN_{PLA}F and PAN_{HPP}F suggest that the introduction of intramolecular hydroxyl group onto fiber could also improve the rate of mass transport in water and a higher catalytic activity is gained accordingly.

Based on the good activity of prolinamide-functionalized fibers in aldol reaction, the effect of solvent on the catalytic efficiency was then studied. For PAN_EF-PLA (Fig. 8a and Table S4), among the solvents tested, no case showed superiority to water and a moderate yield of product was obtained in low polar solvent (n-hexane), whereas the reaction underwent in high polar solvent (methanol) was far less reactive (Table S4, entries 1-6). This trend is consistent with the catalytic results of PAN_{PLA}F under the same conditions (Fig. 8b), To reveal how the solvent with different polarities affected the aldol reaction catalyzed by fiber catalyst, the absorption experiments of PAN_EF-PLA for acetone in diverse solvents were performed. As shown in Fig. S13, the UV absorption intensity of acetone obviously weakened when water was used as solvent, suggesting that the reactants are easier to accumulate onto the fiber surface in water. Replacing water with methanol, a smaller change in the UV absorption intensity of acetone was observed, which indicates the low absorption capacity of fiber in the solvent. In addition, when the amounts of reactants were doubled (2 mmol) with the unchanged catalyst dosage and volume of solvent $(8 \text{ mL of methanol or } C_6 H_{14})$, the yields of addition product were not obviously increased even prolong the reaction time (Table S5). This result suggests that the concentration of reactants in organic solvent does not significantly affect the catalytic activity. According to above experimental results and aforementioned analysis, the low activity of fiber in organic solvent is possibly due to the poor absorption capacity of fiber for reactants and the limited mass transfer in the biphasic system. We also tested the amount of solvent (water) and found that 8 mL was the optimal amount. Reducing the amount of solvent gave rise to a decreased yield (Table S4, entry 9) which was mainly due to that the large and flurry structure of fiber requires sufficient solvent to immerse the catalyst with the aim of the adequate contact between catalyst sites and reactants. Applying smaller amount of acetone



Fig. 8. Yield of addition product under different solvent with fiber catalysts (a) PAN_EF-PLA and (b) PAN_{PLA}F; (c) Yield and selectivity of addition product over PAN_EF-PLA under different temperature; (d) Recycle experiment over PAN_EF-PLA in aldol reaction.

resulted in 57.7% yield of product (Table S4, entry 8), and the utilization of acetone solely as solvent also gave poor yield which implied the important role of water in the reaction (Table S4, entry 7). Generally, the use of water as solvent for some organic reactions cause much lower activity which is possibly associated with the limited affinity between reactants and catalyst in aqueous phase. For PAN_EF-PLA, the good hydrophilicity of fiber could finely tune the spreading of supported-catalyst in water and render it more compatible with substrates and solvent. The reactants (acetone) can easily go into the hydrophilic microenvironment of fiber consisting of hydroxyl group as well as residual cyano group and allow their accessibilities to catalytic sites. Hence, the problems related with the transport of reactants to catalytic sites can be circumvented and the rate of mass transport is enhanced accordingly in aqueous catalytic reaction. Moreover, water is demanded in catalytic cycle to hydrolyze desorption of product from fiber surface, that is, shift the reaction equilibrium toward the completion.

Furthermore, reaction temperature and catalyst dosage were screened for the aldol reaction. As expected, increasing the temperature enabled the significant improvement of yield within less time whereas the decreased product selectivity was observed, since enone product formed by the dehydration of addition product was typically preferred at higher temperature [43,59]. When the reaction was conducted at 50 °C for 5 h with PAN_EF-PLA, a quantitative conversion of aldehyde with a selectivity of 95% for addition product was achieved (Fig. 8c). This distinct product selectivity may be attributed to the fact that the hydroxyl-prolinamide pairs are weakly alkaline and much weakly acidic, which is less active to promote the dehydration. Therefore, high selectivity for addition product can be gained by selecting proper reaction time (5 h), and the tendency toward dehydration is less possible under this relatively shorter time [57]. On the other hand, the hydroxyl group of fiber surface could stabilize addition product by the formation of hydrogen bond. Similarly, only a 12% yield of enone product was generated after 1.5 h when temperature improved to 70 $^{\circ}$ C (Fig. 8c), which demonstrates that fiber catalyst is not only efficient but also highly selective for aldol reaction. Along with reducing catalyst loading from 5 mol% to 2 mol%, moderate to low yields of addition product were produced (Table S4, entries 11-12).

It is worth mentioning that fiber PAN_EF-PLA is also more efficient than previously reported acid-base bifunctional catalysts by Davis group [28,29] and Jones group [37,38,60] in aldol reaction. PAN_EF-PLA offered higher yield and selectivity in only 5 h than which silicasupported bifunctional catalysts (amine/sulfonic acid and amine/ carboxvlic acid pairs) afforded over 20 h [28,29], and even could be comparable to those observed with bifunctional catalysts of silica-supported amine/silanols [10,33,61], polystyrene-supported amine/diols [42] and cellulose nanocrystal-supported amine/carboxylic acid pairs [43]. More recently, Vylder et al. [62] reported amine-functionalized resin as stable heterogeneous catalyst for aldol reaction in water. The developed catalyst can swell sufficiently in aqueous medium which allowed the easy accessibility of the catalytic sites. However, only 20% conversion of aldehyde was observed under the optimized conditions. It can be understood that the reaction pathway of the functionalized fiber developed in this work is quite different from the acid-base bifunctional silica material decorated with isolated-organoamine and surface silanols. The more strongly-acidic silanols on silica play a direct role in the reaction mechanism that could activate acetone and enable the aldehyde to be more susceptible nucleophilic attack by enamine intermediate [57], whereas the hydroxyl group on fiber surface tunes the transport of reactant to catalytic sites for improving mass transfer in aqueous reaction.

3.3. Recycling and hot filtration test

One of the attractive advantages of fiber supported heterogeneous catalyst is their reusability and stability from the practical application



Scheme 2. Possible enamine reaction mechanism of aldol reaction between *p*-nitrobenzaldehyde and acetone catalyzed by hydrophilic prolinamide fiber.

aspect. Therefore, the recycling ability of PAN_EF-PLA was examined using *p*-nitrobenzaldehyde and acetone as reactants under optimized conditions. After the completion of reaction, fiber catalyst was separated from the reaction mixture by filtration and rinsed with ethyl acetate before their use for next cycle. As shown in Fig. 8d, PAN_EF-PLA can be reused at least seven times with the product yield still above 83%. Meanwhile, almost similar high selectivities were retained in seven consecutive cycles (Fig. 8d). The FT-IR spectra, mechanical strength test and elemental analysis of the recovered fibers (Fig. 1d, e; Table S1, entries 6-7; Table 2, entries 3-4) confirmed the preservation of fiber structure, and SEM images (Fig. 5c, d) of the fibers showed no obvious change in the morphology. All these results suggest that fiber catalyst possesses good durability and superior recycle capacity. Furthermore, in order to find out whether fiber PAN_EF-PLA act as a heterogeneous catalyst, a hot filtration test was carried out for the model reaction under optimized conditions (Table S6). After the half time of reaction, fiber catalyst was removed using tweezers and the remained reaction mixture was stirred for another 3 h. No evident increase in the yield of addition product was observed after 3 h, indicating no catalytically active debris leached from fiber surface into the solution. The result clearly demonstrates the heterogeneous nature and structure stability of fiber catalyst.

3.4. Proposed reaction mechanism

In light of literatures and our experimental results, a possible enamine-mediated reaction mechanism for prolinamide-functionalized fiber catalyzed aldol reaction was proposed, as shown in Scheme 2. At first, water-soluble acetone was enriched in the hydrophilic microenvironment of fiber surface consisting of hydroxyl group, residual cyano group and prolinamide moiety. Then basic pyrrolidine sites in PAN_EF-PLA attacked acetone to afford carbinolamine, which was subsequently dehydrated to give fiber-tethered enamine intermediate (II) exclusively [63]. Surface hydroxyl group of fiber and amide N-H of prolinamide distributed in close proximity could both form hydrogen bonds with aldehyde substrates [64]. Active enamine intermediate (II) then reacted with carbonyl group of aldehyde at a proper distance to produce the supported zwitterionic species (IV), accompanied by the formation of a new carbon-carbon bond. Finally, this species (IV) was hydrolyzed to corresponding carbinlamine, which was then decomposed to aldol product (V) and fiber catalyst for next catalytic cycle.

4. Conclusion

In summary, we successfully demonstrated a simple and effective strategy to achieve enhanced performance of heterogeneous catalytic aldol reaction over amine-functionalized polyacrylonitrile fiber with controllable surface wettability. The surface property of the fiber was tuned by introduction of auxiliary hydroxyl group and the resulting hydrophilic prolinamide-functionalized fiber PAN_EF-PLA exhibited excellent activity, selectivity and stability in aqueous aldol reaction, which outperforms the reported acid-base bifunctional catalysts. Furthermore, PAN_EF-PLA was superior to hydrophobic-modified fiber, mono-functionalized fiber and physically mixed fibers and even better than its small molecule counterpart, suggesting the advantages of present surface wettability modification. Tunable surface wettability could match both reactants to facilitate the mass transfer of reactants and their interactions with active sites. Notably, fiber catalyst can be well spread in water, simply separated from the reaction mixture, and reused at least seven times with high yield and selectivity. This investigation illustrates a simple approach to promote aldol reaction via enhancement effect of auxiliary group and shows a gallery of advanced usage of fiber-supported organocatalyst.

CRediT authorship contribution statement

Hai Zhu: Methodology, Investigation, Validation, Writing - original draft. Chenlu Zhang: Formal analysis, Validation. Ning Ma: Conceptualization, Writing - review & editing, Visualization. Minli Tao: Funding acquisition, Resources. Wenqin Zhang: Conceptualization, Writing - review & editing.

Declaration of Competing Interest

The authors report no declarations of interest.

Acknowledgment

This work was financially supported by the National Natural Science Foundation of China (No. 21777111 and No. 21572156).

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcata.2020.117842.

References

- P.I. Dalko, L. Moisan, In the golden age of organocatalysis, Angew. Chem. Int. Ed. 43 (2004) 5138–5175.
- [2] D.W. MacMillan, The advent and development of organocatalysis, Nature 455 (2008) 304–308.
- [3] S. Bertelsen, K.A. Jorgensen, Organocatalysis-after the gold rush, Chem. Soc. Rev. 38 (2009) 2178–2189.
- [4] Y. Qin, L. Zhu, S. Luo, Organocatalysis in Inert C-H Bond Functionalization, Chem. Rev. 117 (2017) 9433–9520.
- [5] S.N. Rao, D.C. Mohan, S. Adimurthy, L-proline: an efficient catalyst for transamidation of carboxamides with amines, Org. Lett. 15 (2013) 1496–1499.
- [6] A.J. Farley, C. Sandford, D.J. Dixon, Bifunctional Iminophosphorane Catalyzed Enantioselective Sulfa-Michael Addition to Unactivated alpha-Substituted Acrylate Esters, J. Am. Chem. Soc. 137 (2015) 15992–15995.
- [7] J. Lu, P.H. Toy, Organic polymer supports for synthesis and for reagent and catalyst immobilization, Chem. Rev. 109 (2009) 815–838.
- [8] C. Li, Y. Liu, Bridging Heterogeneous and Homogeneous Catalysis: Concepts, Strategies, and Applications, Wiley, 2014.
- [9] M. Ferré, R. Pleixats, M. Wong Chi Man, X. Cattoën, Recyclable organocatalysts based on hybrid silicas, Green Chem. 18 (2016) 881–922.

- [10] K. Kandel, S.M. Althaus, C. Peeraphatdit, T. Kobayashi, B.G. Trewyn, M. Pruski, I.I. Slowing, Solvent-Induced Reversal of Activities between Two Closely Related Heterogeneous Catalysts in the Aldol Reaction, ACS Catal. 3 (2013) 265–271.
- [11] F. Zhang, H. Jiang, X. Li, X. Wu, H. Li, Amine-Functionalized GO as an Active and Reusable Acid–Base Bifunctional Catalyst for One-Pot Cascade Reactions, ACS Catal. 4 (2013) 394–401.
- [12] F. Zhang, Y. Wei, X. Wu, H. Jiang, W. Wang, H. Li, Hollow zeolitic imidazolate framework nanospheres as highly efficient cooperative catalysts for [3+3] cycloaddition reactions, J. Am. Chem. Soc. 136 (2014) 13963–13966.
- [13] Q. Sun, Z. Dai, X. Liu, N. Sheng, F. Deng, X. Meng, F.S. Xiao, Highly Efficient Heterogeneous Hydroformylation over Rh-Metalated Porous Organic Polymers: Synergistic Effect of High Ligand Concentration and Flexible Framework, J. Am. Chem. Soc. 137 (2015) 5204–5209.
- [14] J.D. Bass, A. Solovyov, A.J. Pascall, A. Katz, Acid-base bifunctional and dielectric outer-sphere effects in heterogeneous catalysis: a comparative investigation of model primary amine catalysts, J. Am. Chem. Soc. 128 (2006) 3737–3747.
- [15] C.M. Parlett, K. Wilson, A.F. Lee, Hierarchical porous materials: catalytic applications, Chem. Soc. Rev. 42 (2013) 3876–3893.
- [16] K.-C. Kao, T.-S. Lin, C.-Y. Mou, Enhanced Activity and Stability of Lysozyme by Immobilization in the Matching Nanochannels of Mesoporous Silica Nanoparticles, J. Phy. Chem. C 118 (2014) 6734–6743.
- [17] Q. Sun, Y. Tang, B. Aguila, S. Wang, F.S. Xiao, P.K. Thallapally, A.M. Al-Enizi, A. Nafady, S. Ma, Reaction Environment Modification in Covalent Organic Frameworks for Catalytic Performance Enhancement, Angew. Chem. Int. Ed. 58 (2019) 8670–8675.
- [18] Y. Song, J. Zhou, J.-B. Fan, W. Zhai, J. Meng, S. Wang, Hydrophilic/Oleophilic Magnetic Janus Particles for the Rapid and Efficient Oil-Water Separation, Adv. Funct. Mater. 28 (2018) 1802493.
- [19] S. Eom, D.W. Kang, M. Kang, J.H. Choe, H. Kim, D.W. Kim, C.S. Hong, Fine-tuning of wettability in a single metal-organic framework via postcoordination modification and its reduced graphene oxide aerogel for oil-water separation, Chem. Sci. 10 (2019) 2663–2669.
- [20] M. Liu, S. Shi, L. Zhao, M. Wang, G. Zhu, J. Gao, J. Xu, Wettability Control of Co-SiO₂@Ti-Si Core-Shell Catalyst to Enhance the Oxidation Activity with the In Situ Generated Hydroperoxide, ACS Appl. Mater. Interfaces 11 (2019) 14702–14712.
- [21] L. Fu, S. Li, Z. Han, H. Liu, H. yang, Tuning the wettability of mesoporous silica for enhancing the catalysis efficiency of aqueous reactions, Chem. Commun. 50 (2014) 10045–10048.
- [22] F. Xue, Y. Zhang, F. Zhang, X. Ren, H. Yang, Tuning the Interfacial Activity of Mesoporous Silicas for Biphasic Interface Catalysis Reactions, ACS Appl. Mater. Interfaces 9 (2017) 8403–8412.
- [23] T. Li, J. Wang, F. Wang, L. Zhang, Y. Jiang, H. Arandiyan, H. Li, The Effect of Surface Wettability and Coalescence Dynamics in Catalytic Performance and Catalyst Preparation: A Review, ChemCatChem 11 (2019) 1576–1586.
- [24] Y. Wu, J. Feng, H. Gao, X. Feng, L. Jiang, Superwettability-Based Interfacial Chemical Reactions, Adv. Mater. 31 (2019) 1800718.
- [25] I. Mbaraka, B. Shanks, Design of multifunctionalized mesoporous silicas for esterification of fatty acid, J. Catal. 229 (2005) 365–373.
- [26] L. Wang, J. Sun, X. Meng, W. Zhang, J. Zhang, S. Pan, Z. Shen, F.S. Xiao, A significant enhancement of catalytic activities in oxidation with H₂O₂ over the TS-1 zeolite by adjusting the catalyst wettability, Chem Commun. 50 (2014) 2012–2014.
- [27] S. Huh, H.T. Chen, J.W. Wiench, M. Pruski, V.S. Lin, Cooperative catalysis by general acid and base bifunctionalized mesoporous silica nanospheres, Angew. Chem. Int. Ed. 44 (2005) 1826–1830.
- [28] R.K. Zeidan, S.J. Hwang, M.E. Davis, Multifunctional heterogeneous catalysts: SBA-15-containing primary amines and sulfonic acids, Angew. Chem. Int. Ed. 45 (2006) 6332–6335.
 [29] R. Zeidan, M. Davis, The effect of acid–base pairing on catalysis: An efficient
- [29] R. Zehan, M. Davis, The effect of actd=base pairing on catalysis: An efficient acid=base functionalized catalyst for aldol condensation, J. Catal. 247 (2007) 379–382.
- [30] Y. Kubota, H. Yamaguchi, T. Yamada, S. Inagaki, Y. Sugi, T. Tatsumi, Further Investigations on the Promoting Effect of Mesoporous Silica on Base-Catalyzed Aldol Reaction, Top. Catal. 53 (2010) 492–499.
- [31] B. Liu, H. Liu, C. Wang, L. Liu, S. Wu, J. Guan, Q. Kan, Exploration of acid-base geometric influence on cooperative activation for aldol reaction, App. Catal. A: Gen. 443–444 (2012) 1–7.
- [32] N.A. Brunelli, C.W. Jones, Tuning acid–base cooperativity to create next generation silica-supported organocatalysts, J. Catal. 308 (2013) 60–72.
- [33] J. Lauwaert, E. De Canck, D. Esquivel, J.W. Thybaut, P. Van Der Voort, G.B. Marin, Silanol-Assisted Aldol Condensation on Aminated Silica: Understanding the Arrangement of Functional Groups, ChemCatChem 6 (2014) 255–264.
- [34] K.C. Kim, E.G. Moschetta, C.W. Jones, S.S. Jang, Molecular Dynamics Simulations of Aldol Condensation Catalyzed by Alkylamine-Functionalized Crystalline Silica Surfaces, J. Am. Chem. Soc. 138 (2016) 7664–7672.
- [35] J.-F. Zhang, Z.-M. Wang, Y.-J. Lyu, H. Xie, T. Qi, Z.-B. Si, L.-J. Liu, H.-Q. Yang, C.-W. Hu, Synergistic Catalytic Mechanism of Acidic Silanol and Basic Alkylamine Bifunctional Groups Over SBA-15 Zeolite toward Aldol Condensation, J. Phy. Chem. C 123 (2019) 4903–4913.
- [36] V.E. Collier, N.C. Ellebracht, G.I. Lindy, E.G. Moschetta, C.W. Jones, Kinetic and Mechanistic Examination of Acid–Base Bifunctional Aminosilica Catalysts in Aldol and Nitroaldol Condensations, ACS Catal. 6 (2015) 460–468.
- [37] N.A. Brunelli, S.A. Didas, K. Venkatasubbaiah, C.W. Jones, Tuning cooperativity by controlling the linker length of silica-supported amines in catalysis and CO₂ capture, J. Am. Chem. Soc. 134 (2012) 13950–13953.

- [38] N.A. Brunelli, K. Venkatasubbaiah, C.W. Jones, Cooperative Catalysis with Acid–Base Bifunctional Mesoporous Silica: Impact of Grafting and Co-condensation Synthesis Methods on Material Structure and Catalytic Properties, Chem. Mater. 24 (2012) 2433–2442.
- [39] K. Kandel, S.M. Althaus, C. Peeraphatdit, T. Kobayashi, B.G. Trewyn, M. Pruski, I.I. Slowing, Substrate inhibition in the heterogeneous catalyzed aldol condensation: A mechanistic study of supported organocatalysts, J. Catal. 291 (2012) 63–68.
- [40] J. Lauwaert, E. De Canck, D. Esquivel, P. Van Der Voort, J.W. Thybaut, G.B. Marin, Effects of amine structure and base strength on acid-base cooperative aldol condensation, Catal. Today 246 (2015) 35–45.
- [41] D. Singappuli-Arachchige, T. Kobayashi, Z. Wang, S.J. Burkhow, E.A. Smith, M. Pruski, I.I. Slowing, Interfacial Control of Catalytic Activity in the Aldol Condensation: Combining the Effects of Hydrophobic Environments and Water, ACS Catal. 9 (2019) 5574–5582.
- [42] C.B. Hoyt, L.-C. Lee, A.E. Cohen, M. Weck, C.W. Jones, Bifunctional Polymer Architectures for Cooperative Catalysis: Tunable Acid-Base Polymers for Aldol Condensation, ChemCatChem 9 (2017) 137–143.
- [43] N.C. Ellebracht, C.W. Jones, Optimized Cellulose Nanocrystal Organocatalysts Outperform Silica-Supported Analogues: Cooperativity, Selectivity, and Bifunctionality in Acid–Base Aldol Condensation Reactions, ACS Catal. 9 (2019) 3266–3277.
- [44] T. Mayer-Gall, J.-W. Lee, K. Opwis, B. List, J.S. Gutmann, Textile Catalysts-An unconventional approach towards heterogeneous catalysis, ChemCatChem 8 (2016) 1428–1436.
- [45] Y. Fan, H.J. Liu, Y. Zhang, Y. Chen, Adsorption of anionic MO or cationic MB from MO/MB mixture using polyacrylonitrile fiber hydrothermally treated with hyperbranched polyethylenimine, J. Hazard. Mater. 283 (2015) 321–328.
- [46] R. Zhao, X. Li, B. Sun, Y. Li, Y. Li, R. Yang, C. Wang, Branched polyethylenimine grafted electrospun polyacrylonitrile fiber membrane: a novel and effective adsorbent for Cr(VI) remediation in wastewater, J. Mater. Chem. A 5 (2017) 1133–1144.
- [47] G. Xu, L. Wang, Y. Xie, M. Tao, W. Zhang, Highly selective and efficient adsorption of Hg⁽²⁺⁾ by a recyclable aminophosphonic acid functionalized polyacrylonitrile fiber, J. Hazard. Mater. 344 (2018) 679–688.
- [48] W. Chen, X. Zhang, Y. Zhang, M. Mamadiev, Facile and efficient synthesis of polyacrylonitrile-based functional fibers and its sorption properties of perfluorooctane sulfonate and perfluorooctanoate, J. Mol. Liq. 241 (2017) 1013–1022.
- [49] J.W. Lee, T. Mayer-Gall, K. Opwis, C.E. Song, J.S. Gutmann, B. List, Organotextile catalysis, Science 341 (2013) 1225–1229.
- [50] G. Li, J. Xiao, W. Zhang, Knoevenagel condensation catalyzed by a tertiary-amine functionalized polyacrylonitrile fiber, Green Chem. 13 (2011) 1828–1836.
- [51] J. Cao, G. Xu, P. Li, M. Tao, W. Zhang, Polyacrylonitrile Fiber Supported N-Heterocyclic Carbene Ag(1) As Efficient Catalysts for Three-Component Coupling and Intramolecular 1,3-Dipolar Cycloaddition Reactions under Flow Conditions, ACS Sustain. Chem. Eng. 5 (2017) 3438–3447.
 [52] H. Zhu, G. Xu, H. Du, C. Zhang, N. Ma, W. Zhang, Prolinamide functionalized
- [52] H. Zhu, G. Xu, H. Du, C. Zhang, N. Ma, W. Zhang, Prolinamide functionalized polyacrylonitrile fiber with tunable linker length and surface microenvironment as efficient catalyst for Knoevenagel condensation and related multicomponent tandem reactions, J. Catal. 374 (2019) 217–229.
- [53] X.-L. Shi, Y. Chen, P. Duan, W. Zhang, Q. Hu, Conversion of CO₂ into Organic Carbonates over a Fiber-Supported Ionic Liquid Catalyst in Impellers of the Agitation System, ACS Sustain. Chem. Eng. 6 (2018) 7119–7127.
- [54] X.-L. Shi, B. Sun, Q. Hu, Y. Chen, P. Duan, Fiber-supported Fe(III) complex catalyst in spinning basket reactor for cleaner ring-opening of epoxides with alcohols, Green Chem. 21 (2019) 3573–3582.
- [55] S.M. Badawy, A.M. Dessouki, Cross-Linked Polyacrylonitrile Prepared by Radiation-Induced Polymerization Technique, J. Phys. Chem. B 107 (2003) 11273–11279.
- [56] R.X. Liu, B.W. Zhang, H.X. Tang, Synthesis and characterization of poly(acrylaminophosphonic-carboxyl-hydrazide) chelating fibre, React. Funct. Polym. 39 (1999) 71–81.
- [57] Y. Xie, K.K. Sharma, A. Anan, G. Wang, A.V. Biradar, T. Asefa, Efficient solid-base catalysts for aldol reaction by optimizing the density and type of organoamine groups on nanoporous silica, J. Catal. 265 (2009) 131–140.
- [58] A. De Vylder, J. Lauwaert, D. Esquivel, D. Poelman, J. De Clercq, P. Van Der Voort, J.W. Thybaut, The role of water in the reusability of aminated silica catalysts for aldol reactions, J. Catal. 361 (2018) 51–61.
- [59] N.C. Nelson, U. Chaudhary, K. Kandel, I.I. Slowing, Heterogeneous Multicatalytic System for Single-Pot Oxidation and C–C Coupling Reaction Sequences, Top. Catal. 57 (2014) 1000–1006.
- [60] E.G. Moschetta, N.A. Brunelli, C.W. Jones, Reaction-dependent heteroatom modification of acid–base catalytic cooperativity in aminosilica materials, Appl. Catal. A: Gen. 504 (2015) 429–439.
- [61] A. De Vylder, J. Lauwaert, D. Esquivel, D. Poelman, J. De Clercq, P. Van Der Voort, J.W. Thybaut, The role of water in the reusability of aminated silica catalysts for aldol reactions, J. Catal. 361 (2018) 51–61.
- [62] A. De Vylder, J. Lauwaert, J. De Clercq, P. Van Der Voort, C.W. Jones, J.W. Thybaut, Aminated poly(ethylene glycol) methacrylate resins as stable heterogeneous catalysts for the aldol reaction in water, J. Catal. 381 (2020) 540–546.
- [63] Z. An, J. He, Y. Dai, C. Yu, B. Li, J. He, Enhanced heterogeneous asymmetric catalysis via the acid–base cooperation between achiral silanols of mesoporous supports and immobilized chiral amines, J. Catal. 317 (2014) 105–113.
- [64] Z. Tang, F. Jiang, X. Cui, L.Z. Gong, A.Q. Mi, Y.Z. Jiang, Y.D. Wu, Enantioselective direct aldol reactions catalyzed by *L*-prolinamide derivatives, Proc. Natl. Acad. Sci. U S A. 101 (2004) 5755–5760.