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Recyclable polyetheretherketone fiber-supported N-heterocyclic carbene catalysts for nucleophilic acylation of fluorobenzenes†

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We report for the first time a novel support of polyetheretherketone fiber for the synthesis of recyclable N-heterocyclic carbene (NHC) catalysts. The fiber catalysts were verified in nucleophilic acylation of fluorobenzenes with superior catalytic activities, and successfully recycled by a tiny pair of tweezers over 21 cycles with minimal loss of performance.

Recently, organocatalysis related to green chemistry has been stimulating much interest and has also been advanced significantly.[1–6] Among them, N-heterocyclic carbenes (NHCs) are known as organocatalysts due to their lone pair of carbene electrons with nucleophilic behavior in an extensive scope of synthetic transformations.[7–10] However, most of the small-molecule NHCs are difficult to handle on account of their high reactivity and sensitivity.[11,12] To overcome this limitation, the precursors such as imidazolium or thiazolium salts are often employed to generate NHCs by *in situ* deprotonation with a strong base.[13–16] Although the practice has found success in this regard, the recovery of azolium salts still astricts the reuse of NHCs. Some studies used poly(NHC) precursors to bypass this restriction;[17–20] however, tedious polymerization processes were often required, thereby hampering their scalable applications. Moreover, a promising method for NHC recycling is to incorporate the azolium salt into a material, and after catalytic applications NHCs are regenerated to their original forms on the support so as to be easily recycled.[21–23] In this respect, several supports including polymers or silica,[24–26] montmorillonite[27,28] and some porous materials[29,30] have been reported for this objective. Nevertheless, some of them suffer from lower catalytic efficiency and inferior reusability, probably owing to poor stability or degradation of the catalytic materials under a strongly alkaline environment. Therefore, exploiting more stable and efficient support materials for the heterogenization of NHCs needs to be further investigated.

In our previous work, we have developed a series of polyacrylonitrile (PAN) fiber-supported catalysts for different sorts of reactions and displayed many superiorities, especially for their prominent recyclability and convenient operations.[31–35] However, the PAN fiber involves plenty of cyano groups on its polymer chains, and the strong alkaline medium would intensely disrupt the mechanical properties of the fiber, further restricting its application in supported-NHC catalysis. Given many superiorities such as acid-proof and alkali resistant, high strength and toughness, polyetheretherketone (PEEK) fiber[36,37] as a new rising star among synthons provides an appealing option to many other fibers as the support for heterogeneous catalysis. In addition, nucleophilic aromatic substitution is an important method in synthetic aromatic chemistry;[38] however, the nucleophilic aromatic substitutions of halogen atoms by carbanions are infrequent due to the halonitroarenes often reacting with carbanions.[39,40] Based on the above considerations and in continuation of our interest in novel fiber catalysts, we here designed a new type of PEEK fiber-supported NHC catalyst to evaluate their behaviour in nucleophilic acylation of fluorobenzenes (Scheme 1).

The commercially available PEEK fiber was selected as a raw material for preparing fiber-supported NHC precursor by a post-functionalization process. And, as shown in Scheme 1, the counterplan for the synthesis and regulation of the fiber catalyst was performed firstly by chloromethylation to build functional groups which would act as the active sites for

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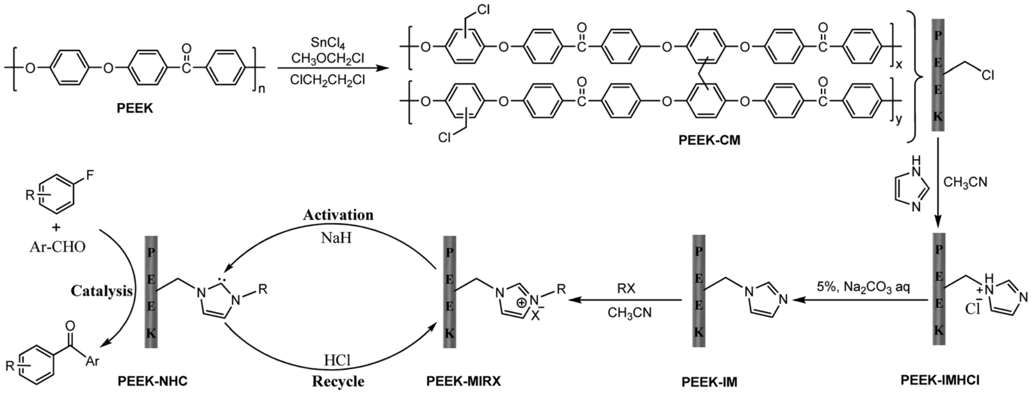
† Electronic supplementary information (ESI) available: Experimental details and optimization results, characterizations of photographs, elemental analysis, FTIR spectroscopy and mechanical properties of fiber materials in different stages, and the physical data, ^{1}H and ^{13}C NMR data and copies of spectra of the synthesized compounds. See DOI: 10.1039/d0cc04394j



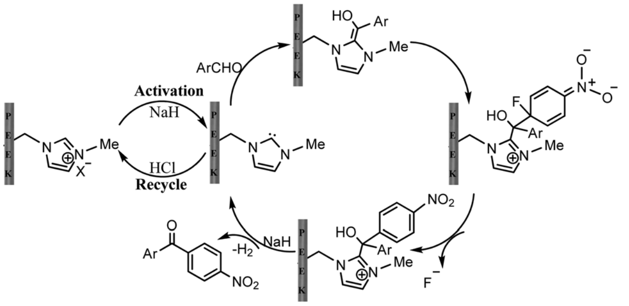
Scheme 1 Preparation of PEEK fiber-supported NHC catalysts and the mediated nucleophilic acylation of fluorobenzenes.

subsequent immobilization, and then conducted through imidazole grafting, neutralization and finally formation of onium salts to complete the precatalyst preparation process. The degree of functionality in each step was evaluated by weight gain (weight gain [%] = $[(W_2 - W_1)/W_1] \times 100$, where W_1 and W_2 are the weights of the fiber sample before and after functionalization, respectively).

In step 1, in order to retain enough mechanical properties of PEEK fiber for the succedent grafting, a weight gain of 27.6% chloromethyl functionalized PEEK (PEEK-CM) was obtained after optimization. Next, PEEK-CM was reacted with imidazole to immobilize imidazole groups, and the formed PEEK-supported imidazole hydrochloride (PEEK-IMHCl) exhibited a weight gain of 18.5%, and the content of imidazole hydrochloride was 2.29 mmol g^{-1} calculated by mass change, which is consistent with the elemental analysis value (Table S2, ESI†). Then, PEEK-IMHCl was neutralized in Na$_2$CO$_3$ aqueous solution to remove hydrogen chloride and the acquired imidazole functionalized PEEK (PEEK-IM) exhibited a weight gain of −9.38%, and the content of imidazole was 2.83 mmol g^{-1}. Finally, PEEK-IM was reacted with methyl iodide and ethyl bromide to afford two kinds of fiber-supported imidazoliums (PEEK-IMRX), and owing to different reactivity of the halides, the imidazolium contents of PEEK-supported methyl imidazolonium iodide salts (PEEK-IMMI) and PEEK-supported ethyl imidazolonium bromide salts (PEEK-IMEB) were 1.37 mmol g^{-1} and 0.79 mmol g^{-1} calculated by mass change, respectively. However, the molar ratios of imidazoliums are not quite consistent with the elemental analysis data, since the imidazole groups in the fiber could not get a 100% conversion to imidazoliums.

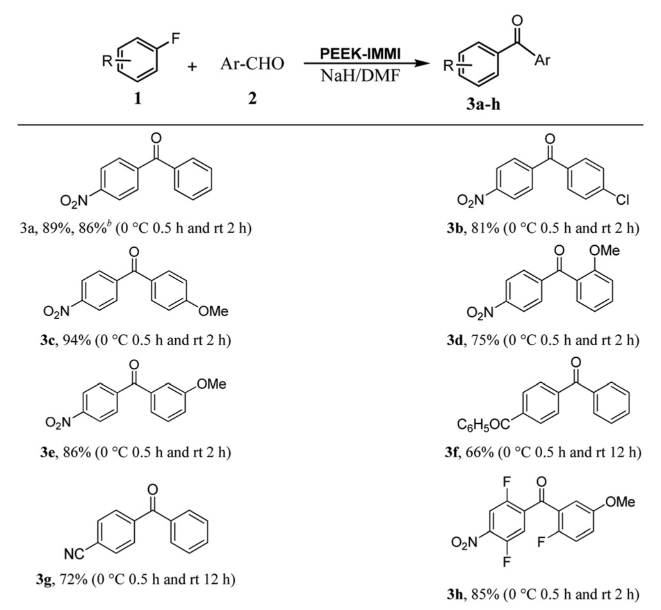
With the PEEK-IMRX in hand, their activities for nucleophilic acylation of fluorobenzenes were compared. Initial efforts were focused on the optimization of the reaction conditions for the model reaction (nucleophilic acylation of 4-fluoronitrobenzene by benzaldehyde), and the catalyst types, solvents, base (to generate NHCs *in situ*), catalyst loading, reaction temperature and time were all tested (Table S1, ESI†). On the whole, without any catalyst or initial PEEK, PEEK-CM as well as the PEEK-IMHCl and PEEK-IM containing the imidazole groups were all invalid to the nucleophilic acylation, which indicated that the catalytic activities came from imidazoliums (NHCs precursor) after the base activation, and not derived from the fiber backbone. Moreover, the catalytic abilities of PEEK-IMMI and PEEK-IMEB were better than the small molecule catalyst 1,3-dimethylimidazolium iodide (DMII), the enhanced efficiency of PEEK-IMRX perhaps due to a synergistic effect between the active sites and the PEEK backbone, which could stabilize the intermediate (Scheme 2) and prevent the dimerization or structural change in NHCs. In addition, PEEK-IMMI possessed a higher catalytic activity than PEEK-IMEB, probably because of its smaller steric hindrance for easier contact to the substrates. Furthermore, the performance of organic base or bulk inorganic base was lower than NaH. Afterwards, under the optimized conditions (PEEK-IMMI as the precatalyst, NaH as the base, with the solvent of DMF at room temperature), we then examined the substrate scope to generalize the versatility of this methodology, and the nucleophilic acylation results are summarized in Table 1.

It was interesting to observe that the PEEK fiber-supported NHC systems have a good group tolerance; different substituted fluorobenzenes (Table 1, **3a**, **3f** and **3g**) and aromatic aldehydes (Table 1, **3a–e**), as well as the multisubstituted substrates (Table 1, **3h**) for the synthesis of a highly functionalized benzophenone in total synthesis of an anticancer natural product termicalcicolanone A,[41] were all reacted efficaciously to obtain the corresponding nucleophilic acylation products with isolated yields of 66% to 94%. However, lower activities of the substrates when electron-poor or sterically hindered aldehydes were used, and a higher reactivity of fluorobenzene were observed when it had a



Scheme 2 Possible mechanism of PEEK-IMMI mediated nucleophilic acylation of 4-fluoronitrobenzene by aldehyde.

Table 1 PEEK-IMMI mediated nucleophilic acylation of fluorobenzenes[a]



3a, 89%, 86%[b] (0 °C 0.5 h and rt 2 h)

3b, 81% (0 °C 0.5 h and rt 2 h)

3c, 94% (0 °C 0.5 h and rt 2 h)

3d, 75% (0 °C 0.5 h and rt 2 h)

3e, 86% (0 °C 0.5 h and rt 2 h)

3f, 66% (0 °C 0.5 h and rt 12 h)

3g, 72% (0 °C 0.5 h and rt 12 h)

3h, 85% (0 °C 0.5 h and rt 2 h)

[a] Reaction conditions unless otherwise specified: NaH (1.5 mmol) and PEEK-IMMI (10 mol%, based on aldehyde), fluorobenzene (1 mmol) and aldehyde (1 mmol) in DMF (10 mL) under N_2. [b] Gram-scale test.

stronger electron-withdrawing group. To be more precise, the PEEK fiber-supported NHC catalyst-mediated procedure possessed a selective applicability for nucleophilic acylation of fluorobenzenes. On the basis of the above, an NHC-mediated umpolung and base-promoted mechanism was proposed (Scheme 2). Beyond that, a Gram-scale test for the methodology was also conducted, and this nucleophilic acylation proceeded smoothly without any extension of the reaction time to obtain a similar product yield of 86% (Table 1, **3a**[b]).

Thereafter, the recyclability and stability of PEEK-IMMI were also inspected. After accomplishing the reaction, a solution of 4.0 M HCl in dioxane was added, and the resulting mixture was stirred for an additional 1 h to bring the NHC catalyst to its precursor. The returned PEEK-IMMI was easily recovered with a tiny pair of tweezers, and was used directly for the next cycle after simple washing and drying. It could be found that the activity of PEEK fiber-supported NHC catalysts was almost consistent for 21 cycles (Fig. 1, from 89% to 81%, no test for more runs). As a control, the small molecule of DMII could not be recycled from the nucleophilic acylation using an analogous protocol. Furthermore, a certain stability of PEEK-IMMI was also inspected because during the research the fiber catalyst stored without special protection (just drying before use) remained equally active after at least up to three months.

To verify the reliability of this method, various technologies were used to characterize the fibers resulted from different stages. The photographs (Fig. S1, ESI†), elemental analysis (Table S2, ESI†), FTIR spectroscopy (Fig. S2, ESI†) and mechanical properties (Table S3, ESI†) of the original PEEK fiber, PEEK-CM, PEEK-IMHCl, PEEK-IM, PEEK-IMMI, and the recovered precatalysts PEEK-IMMX-1 and PEEK-IMMX-21 from the 1st and 21st runs in model nucleophilic acylation all confirmed the dependability of the preparation method for synthesizing the PEEK fiber-supported NHC precursors and the stability of the fiber catalyst after many cycles. In addition, the SEM images of the fresh PEEK-IMMI and the recovered fiber precatalysts PEEK-IMMX-1 and PEEK-IMMX-21 are shown in Fig. 2, apart from them becoming increasingly coarser and more flecks emerging in the surface of the recycled precatalysts (probably because of the vigorous strong base or acid conditions, and some nucleophilic acylation substrates or products were grafted or adsorbed onto the fiber), there was no remarkable change in the morphology or size of the fiber precatalyst with repeated use. In addition, the fiber-supported NHC precatalysts were also determined by solid-state ^{13}C NMR spectra; the peak around 37.81 ppm could be assigned to the methyl attached to an imidazole group, and the carbon peak of methylene which linked the imidazole group and benzene ring of the PEEK polymer chain is centered at 49.47 ppm, these above two carbon signals indirectly demonstrated that the imidazolium

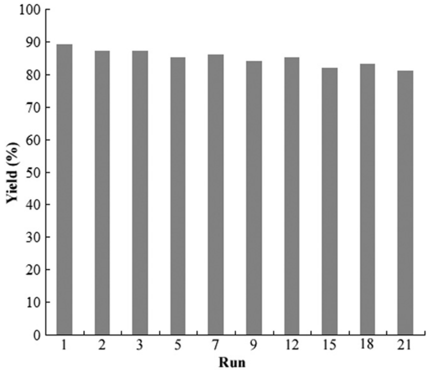


Fig. 1 Recyclability of the fiber-supported NHC catalysts for nucleophilic acylation.

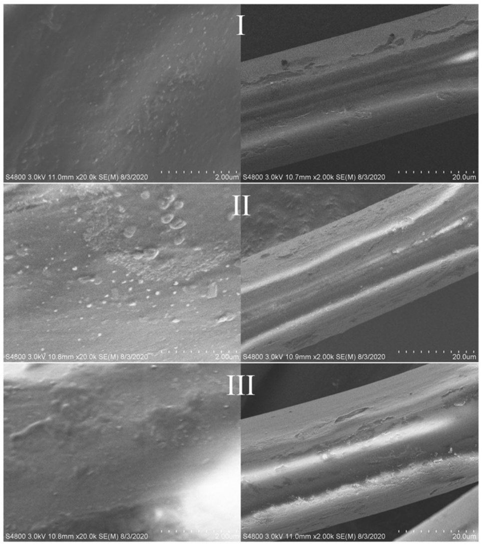


Fig. 2 SEM images of (I) PEEK-IMMI, (II) PEEK-IMMX-1 and (III) PEEK-IMMX-21. (Scale bars = 2 μm and 20 μm.).

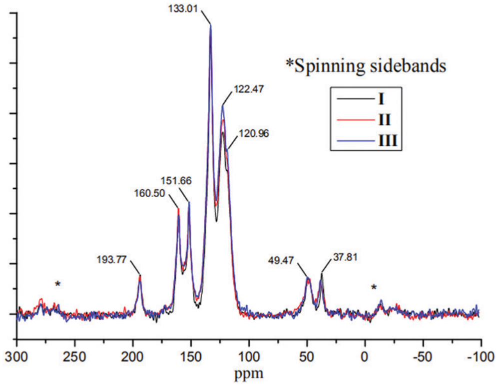


Fig. 3 ^{13}C NMR spectra of (I) PEEK-IMMI, (II) PEEK-IMMX-1 and (III) PEEK-IMMX-21.

was immobilizes on the PEEK fiber, and the almost unchanged characteristic peaks of PEEK-IMMI, PEEK-IMMX-1 and PEEK-IMMX-21 further proved the reliability of the fiber catalyst before and after catalytic applications (Fig. 3).

In summary and to the best of our knowledge, we presented here the first example of the application of commercially available PEEK fiber as a novel material for recyclable supported-NHC catalysts. The fiber-supported NHCs were generated *in situ* and used to facilitate the nucleophilic acylation of fluorobenzenes with good product yields, and regenerated conveniently for reuse up to 21 runs. Moreover, various technologies for the characterization of the fiber materials from different stages further validated the reliability of this method. These results revealed that the PEEK fiber was sufficiently stable to endure the vigorous strong base or acid conditions for NHC-mediated umpolung reactions, and also indicated that the enhanced catalytic activities of NHCs upon incorporation with the fiber backbone which further contributed to its superior recyclability. Complementary studies on the PEKK-supported NHCs with different structures for nucleophilic acylation and further applications of fiber-supported NHC catalysts in umpolung reactions are now in progress.

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Conflicts of interest

There are no conflicts to declare.

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