



Polystyrene-supported CuI–imidazole complex catalyst for aza-Michael reaction of imidazoles with α,β -unsaturated compounds

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ABSTRACT

The polystyrene-supported CuI–imidazole complex catalyst was prepared and characterized by IR spectroscopy, elemental analysis, SEM/TEM and TG/DSC. The complex catalyst was globular with the size of 400–500 nm and showed a good thermal stability at high temperature. The immobilized Cu metal in the complex catalyst was about 0.85 mmol/g. By using the catalyst, aza-Michael reaction of imidazoles to α,β -unsaturated compounds was performed with good yields in 4–8 h. The catalyst showed an excellent recycling efficiency over five cycles without distinct leaching of metal from the polymer support.

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1. Introduction

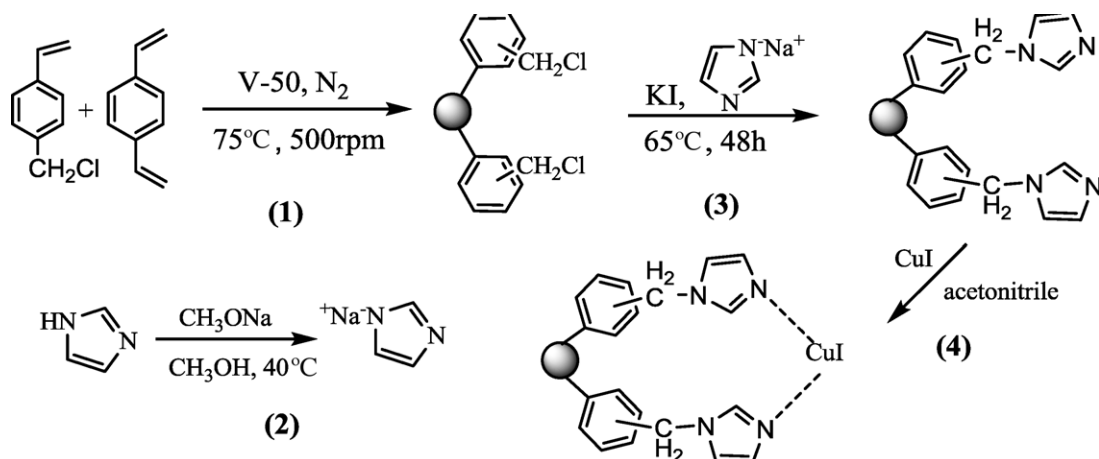
Aza-Michael reaction (AMR, i.e. conjugated addition of nitrogen nucleophiles to α,β -unsaturated compounds) is an important C–N bond forming reaction and usually used for the synthesis of β -amino carbonyl functionality which serves as an essential intermediate in the synthesis of β -amino ketones, β -amino acids, β -lactam antibiotics, and chiral auxiliaries [1–3]. These compounds were previously synthesized via the Mannich reaction and featured by rigorous reaction conditions, low reaction yield and tedious reaction pretreatment [4], which promoted to develop other more effective and green synthesis methods. As noticed in the early 1960s, AMR is a less by-products and atomic economical reaction. The AMR of imidazoles to α,β -unsaturated compounds for the synthesis of *N*-substituted imidazoles has been a current area of investigation, in view of their pharmacological importance. To get a simple, green and efficient synthesis procedure, many alternative strategies have been developed in recent twenty years. In particular, various catalysts have been investigated such as: K_2CO_3 /DMF [5], $Bi(NO_3)_3$ [6], guanidine [7], $[Ti_4H_{11}(PO_4)_9] \cdot nH_2O$ [8], alkaline protease and hydrolase [9–11]. Unfortunately, most of these procedures require long reaction times (several days), highly dangerous

chemicals, or produce products in moderate yield. Furthermore, most of the catalysts could not be recycled.

Recently, some alternative strategies with good yield have been reported. Martín-Aranda reported [12] microwave-assisted synthesis of *N*-substituted imidazoles using basic clay catalysts. Later a number of studies about microwave-promoted Michael reactions were reported [13–17]. Many studies showed that microwave and sonochemical [18] could effectively promote AMR reactions to get aim-products in very short time with good yields. There are, however, limitations associated with such synthesis methods, in particular poor reproducibility of reactions and hard controlling the reaction precisely [19], which are disadvantageous to industrialize. Xia reported [20] a highly efficient KF/Al_2O_3 catalyst for hetero-Michael addition of α,β -ethylenic compounds in room temperature, but these reactions required long reaction time and the efficient of catalyst decreased rapidly after several recycles. More recently, a series of ionic liquid catalyst system [23] has been reported for the reaction of *N*-heterocycles with α,β -unsaturated compounds at room temperature (rt), which usually was carried out at short time, however, the preparation and treatment process of the catalyst was expensive and inconvenient. Recent years, *N*-arylation of imidazoles reactions catalyzed by $PS[DMVBIM][Pro]-CuI$ [24], $Cu(acac)_2$ in $[bmim][BF_4]$ [25], $PANI-CuI$ [26] were reported. The results of these studies showed that the copper catalysts were very efficient and reusable for such reactions. In addition, Mirkhani had successfully bonded $[Mn(salophen)Cl]$ to imidazole modified polystyrene to use as biomimetic alkene

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Scheme 1. Preparation of the PS-imCuI catalyst.

epoxidation and alkane hydroxylation catalyst with sodium periodate [27]. Here, polystyrene-bound imidazole was not only a support for immobilization of Mn(III) salen but also a heterogeneous axial base. Udayakumar reported [28] polystyrene-supported palladium-imidazole complex catalyst for hydrogenation of substituted benzylideneanilines. These results prompted us to investigate the catalytic activity of polystyrene-supported CuI-imidazole (PS-imCuI) complex in *N*-arylation reactions.

Polystyrene (PS) is one of the most widely used support polymers in various catalyzed organic synthesis due to its easy preparative protocol from inexpensive starting material, high environmental stability and easy functionalised properties. In this study, highly chloromethylated polystyrene beads (VBC-DVB) were functionalised with imidazole, then CuI was anchored on the functionalised beads to get the heterogeneous catalyst. FT-IR, SEM and TG/DSC were employed to characterize the structure and property of the catalyst. The catalytic performance of the synthesized catalyst was investigated for ARM of imidazoles to α,β -unsaturated compounds.

2. Experimental

2.1. Chemical reagents, method and equipments

Vinylbenzyl chloride (VBC, 95%, mixture of isomers, Merger Chemical Technology Shanghai Company), and divinylbenzene (DVB, mixture of isomers, J&K chem. Co. Ltd., Shanghai, China) were freed from inhibitors by reduced pressure distillation. 2,2'-Azobis(2-amidinopropane) dihydrochloride (V-50), imidazoles, sodium methoxide, dichloromethane, acrylonitrile, methyl acrylate and other corresponding chemicals were commercially available and used without further purification.

IR spectra were recorded using a Nicolet IS10 FTIR spectrometer. C, H and N contents were determined by dry combustion in an autoanalyzer and analyses using Vario MICRO EL (Elementar Analysensysteme, Hanau, Germany). Cu content was determined using Jarrel-Ash J-A1100 plasma-spectrometer. TG studies were carried out using a METTLER TOLEDO SDTA851e instrument under nitrogen atmosphere. DSC studies were carried out using a METTLER TOLEDO DSC823e instrument under nitrogen atmosphere. HPLC studies were recorded using a Waters ODS-BP column and UV detector, and determination wave-length was 254 nm. The ^1H NMR spectra were recorded with a FT-NMR 300 (300 MHz, bruker) spectrometer, and $\text{CCl}_3\text{D-d}_6$ was used as solvent. SEM was recorded on a Leica S440i. TEM was recorded on a JEM-2100. ACME silica gel (100 200 mesh) was used for column chromatography. Thin-layer

chromatography (TLC) was performed on Merck precoated silica gel 60-F254 plates.

2.2. Preparation of PS-CH₂Cl

The PS-CH₂Cl was synthesized via surfactant-free emulsion polymerization according to the previous reports [29,30] and the synthetic process was shown in Scheme 1. First, the glass reactor, a 500 mL round-bottom (RB) flask, charged with 250 mL distilled water was heated to 75 °C, the reaction temperature. Then stirring at 450–550 rpm 13 mL comonomer mixture (volume ratio: VBC:DVB = 98:2) was added. Following the mixture of V-50 (0.21 g, 2.95×10^{-3} mol/L) dissolved in deionized water (10 mL) was added. The polymerization was continued under N₂ for 6 h. The cooled emulsion was dried by rotary evaporation followed by freeze-drying to give a free-flowing fine white powder.

2.3. Preparation of PS-CH₂-imidazole

Functionalisation of PS-CH₂Cl with imidazole referenced to the previous reports [31–34] and the synthetic process was shown in Scheme 1(2) and (3). Imidazole (6.8 g, 0.1 mol) and KI (0.1 g) were dissolved in 5 mL toluene, and the mixture was heated to 40 °C in the presence of N₂. Then sodium methylate (5.4 g, 0.104 mol) in methanol (10 mL) was added dropwise with constantly stirring for about 0.5 h to form imidazole sodium salt. The PS-CH₂Cl particles (1.8 g, 0.01 mol -CH₂Cl) in acetonitrile (15 mL) were added to the formed imidazole sodium salt solution. The reaction was continued at 65 °C for 48 h. The functionalised beads were washed by ethanol and dried under vacuum at 40 °C.

2.4. Preparation of PS-imCuI complex catalyst

The synthetic process of PS-imCuI complex was shown in Scheme 1(4) [34]. The mixture of PS-CH₂-imidazole (2 g), cuprous iodide (500 mg) and acetonitrile (30 mL) was stirred at room temperature under nitrogen atmosphere for 48 h. The resultant complex catalyst was filtered off and washed with acetonitrile followed by acetone for several times. The residue was dried for 24 h in air to afford the aquamarine complex catalyst.

2.5. General procedure for aza-Michael reaction of imidazoles with α,β -unsaturated compounds

In an oven dried 10 mL RB flask, imidazoles (1 mmol), α,β -unsaturated compound (1.1 mmol), PS-imCuI and solvent (2 mL)

were taken and stirred at appropriate temperature for appropriate time. After the completion of the reaction as monitored by TLC (dichloromethane: petroleum ether = 1:1, V/V), the catalyst was filtered off and washed with water, ethanol and acetone successively, and then dried under room temperature several hours. The filtrate was diluted with 15 mL ethyl acetate and washed with 5 mL saturated aqueous NaCl solution. The organic layer was dried over anhydrous Na_2SO_4 and concentrated to get the crude product. The crude product was column chromatographed using mixture of dichloromethane and petroleum ether as eluent. The products were identified by NMR and compared with those reported in the literature [9–11,22].

3. Results and discussion

3.1. Characterization of the catalyst

3.1.1. Infrared spectral studies

The IR spectra of PS- CH_2Cl and PS- CH_2 -imidazole were recorded and a comparative study was shown in Fig. 1. For PS- CH_2Cl (Fig. 1a), the characteristic peaks of polystyrene exhibited the C-H stretching vibration of aromatic ring at 3016 cm^{-1} , and C-H asymmetric and symmetric stretching vibrations of methylene at 2920 cm^{-1} and 2855 cm^{-1} [35], respectively. The peaks at 1609 cm^{-1} and 1507 cm^{-1} were due to the C-C skeleton vibration of aromatic ring of polystyrene. Moreover, a typical peak at 1265 cm^{-1} was attributed to stretching vibrations of the functional group - CH_2Cl , and another peak at 672 cm^{-1} was due to stretching vibrations of C-Cl. The two typical peaks were practically omitted or were seen as a weak band after introduction of imidazole on the polystyrene and a peak assigned to the C=N stretching vibration of imidazole ring at 1563 cm^{-1} [36,37] appeared at the same time (Fig. 1b), which was indicated the successful attachment of imidazole on

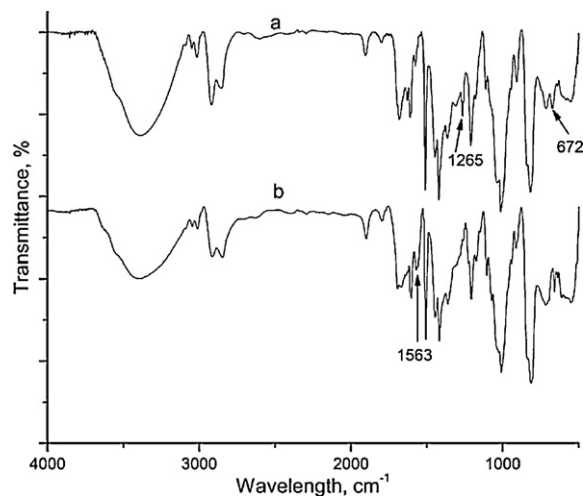


Fig. 1. IR-spectra of PS- CH_2Cl (a) and PS- CH_2 -imidazole (b).

the polystyrene support by covalent bond. In addition, no obvious band changes were observed when CuI was anchored on to PS- CH_2 -imidazole beads.

3.1.2. Elemental analysis

Elemental analysis for PS- CH_2Cl , PS- CH_2 -imidazole and PS-imCuI complex catalyst were carried out and the data were tabulated in Table 1. It can be estimated that the Cl content in PS- CH_2Cl was about 21.47% which meant that the polystyrene beads could be highly functionalised with imidazole. The content of nitrogen in PS- CH_2 -imidazole was 11.17%, which meant some chloromethyl groups inside the polystyrene were not displaced

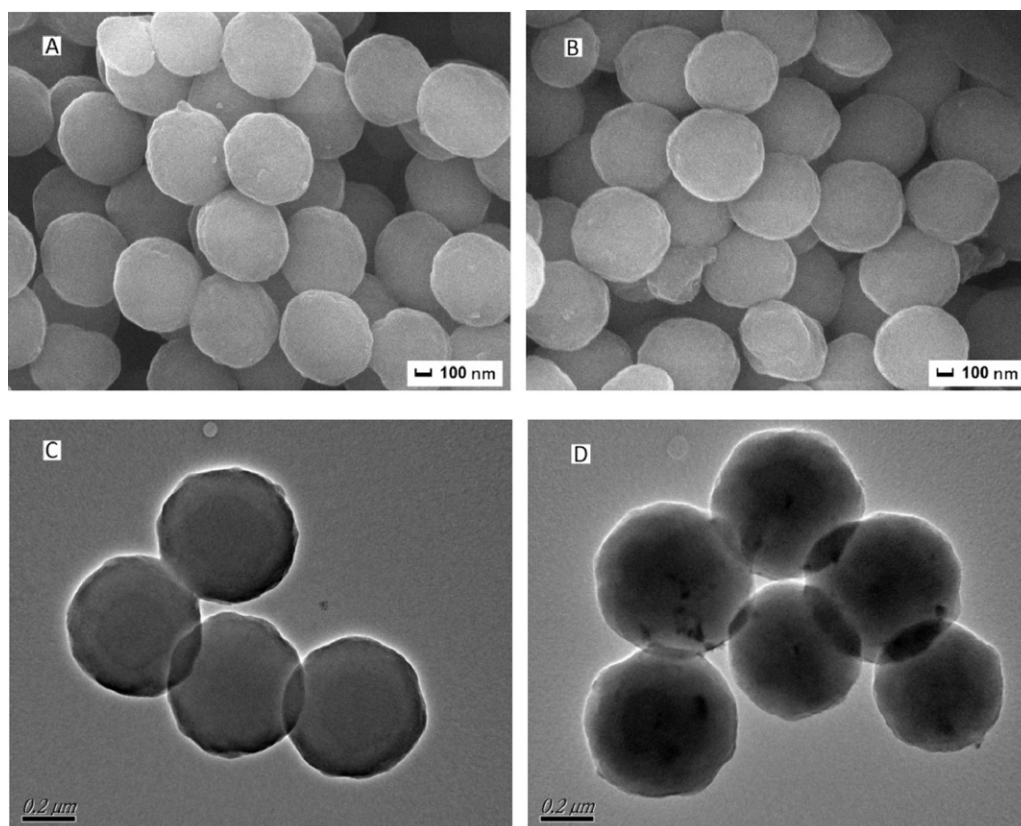


Fig. 2. SEM of PS- CH_2Cl (A) and PS-imCuI catalyst (B), TEM of PS- CH_2Cl (C) and PS-imCuI catalyst (D).

Table 1
Elemental analysis of polymer support and polymer bound catalyst.

	%C	%H	%N	%Cu
PS-CH ₂ Cl	72.32	6.21	–	–
PS-CH ₂ -imidazole	73.76	6.90	11.17	–
PS-imCuI	–	–	–	5.41%, 4.8% ^a , 4.76% ^b

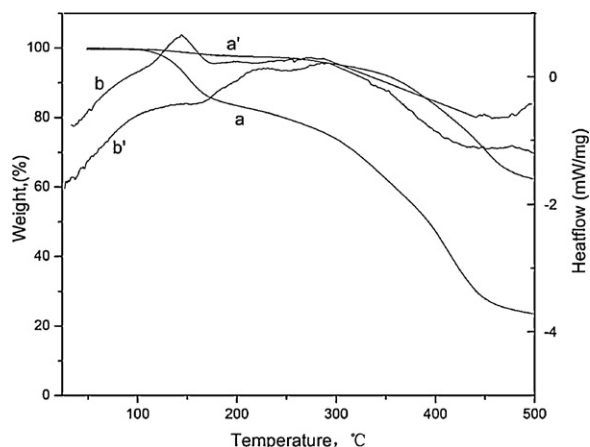
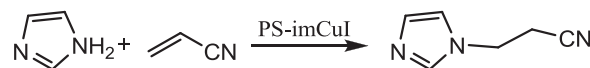
^a After second cycle.^b After fourth cycle.

by imidazole. Since the content of nitrogen was still very high, the PS-CH₂-imidazole could immobilize a lot of CuI. The amount of metal was determined by stripping the bound metal from the support and analyzed using inductively coupled plasma atomic emission spectrometry. The content of Cu metal in PS-imCuI complex catalyst were 5.41% (about 0.85 mmol/g), 4.8% and 4.76% at beginning, after second and fourth cycle, respectively.

3.1.3. SEM/TEM and TG/DSC studies

SEM of PS-CH₂Cl (A) and PS-imCuI catalyst (B), and TEM of PS-CH₂Cl (C) and PS-imCuI catalyst (D) were shown in Fig. 2. It was seen both PS-CH₂Cl and PS-imCuI catalyst showed uniform globular morphologies with the size of 400–500 nm. After the introduction of CuI-imidazole complex, the size and the shape had no obvious change.

TG/DSC analysis was carried out to investigate the thermal stability of PS-CH₂Cl and PS-imCuI catalyst in N₂ atmosphere with heating rate of 10 °C/min up to 500 °C. As shown in Fig. 3, weight loss of PS-imCuI catalyst and PS-CH₂Cl began at about 110 °C (Fig. 3a' and a). In the range of 110–300 °C, no obvious weight loss was observed from PS-imCuI catalyst. Comparatively, obvious weight loss was observed from PS-CH₂Cl. Correspondingly for the DSC curve of PS-CH₂Cl (Fig. 3b), a small exothermic peak appeared around 142 °C, however, it did not appear in the DSC curve of PS-imCuI catalyst (Fig. 3b'). The weight loss and the exothermic peak in the DSC curve of PS-CH₂Cl were possibly ascribed to the water inside the porous PS-CH₂Cl particles. When the CuI-imidazole complex was immobilized onto the PS-CH₂Cl surface in organic solvent, the water droved and the holes were jammed. When the temperature further increased up to higher than 300 °C, weight loss obviously displayed in TG curves of not only PS-CH₂Cl but PS-imCuI catalyst. A possible reason is that their structures were destroyed or the chloromethyl groups and the CuI-imidazole separated from the surface of PS. Finally, it was observed that the residue weight of PS-imCuI and PS-CH₂Cl was about 65% and 25% at 475 °C, respectively. These results indicated that the immobilization of CuI-imidazole onto the PS-CH₂Cl

**Fig. 3.** TG-DSC patterns of PS-CH₂Cl (a, b) and PS-imCuI catalyst (a', b').**Scheme 2.** Model reaction of N-substituted imidazoles using PS-imCuI complex catalyst.

surface could improve the thermal stability of PS-CH₂Cl, and the PS-imCuI catalyst was thermo-stable at high temperature.

3.2. Aza-Michael reactions of imidazoles with α,β -unsaturated compounds

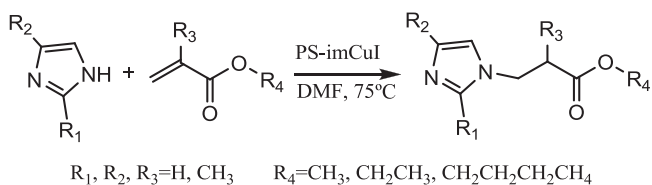
3.2.1. Catalyst activity of PS-imCuI in model reaction and optimized reaction conditions

To evaluate the catalyst activity of PS-imCuI in AMR of imidazoles with α,β -unsaturated compounds, the reaction between imidazole and acrylonitrile was chosen as a model reaction (Scheme 2). The influences of solvent, temperature, catalyst dosage and reaction time on the AMR process were investigated in detail and the results were summarized in Table 2. Six kinds of solvent on the reaction were studied at constant reaction temperature, catalyst dosage and duration (Table 2, entries 1–6). Best yield was obtained by using DMF as solvent (Table 2, entry 4). In addition, it can be seen that reaction temperature had a great effect on the reaction (Table 2, entries 4, 7–9). A higher reaction temperature resulted in a better yields, and the tendency became slow when the temperature over 70 °C. The influence of catalyst dosage (molar ratio, relative to imidazole) on the reaction was carried out at constant substrate concentration at a temperature of 75 °C using DMF as a solvent. It is noteworthy that no product formation was detected without PS-imCuI complex catalyst (Table 2, entry 10), which meant that the reaction hardly carried out without catalyst in DMF. When homogeneous CuI (8.5 mol%) was used instead of PS-imCuI catalyst, very low amount of product formation was observed (Table 2, entry 12b). Here most probably imidazole group in the complex catalyst is playing a macro ligand which facilitates the reaction as reported by using other nitrogen containing ligands [38–40]. With the increase of the catalyst dosage, the yields increase quickly. But the increase slow down when the catalyst usage over 0.1 g (Cu, 8.5 mol%). At constant substrate concentration, reaction temperature of 75 °C, PS-imCuI (Cu, 8.5 mol%), DMF as solvent, the influence of reaction duration time on the model reaction was studied (Table 2, entries 12, 14–16) at last. The reaction carried out 92%

Table 2
Optimization of catalytic conditions for the AMR using imidazole and acrylonitrile.^a

Entry	PS-imCuI (g)	Solvent	Temperature (°C)	Time (h)	Yield (%) ^b
1	0.05	MeOH	60	8	58
2	0.05	CH ₃ CN	60	8	63
3	0.05	DMSO	60	8	52
4	0.05	DMF	60	8	71
5	0.05	Acetone	60	8	47
6	0.05	THF	60	8	58
7	0.05	DMF	50	8	60
8	0.05	DMF	70	8	88
9	0.05	DMF	85	8	91
10	0	DMF	75	4	0
11	0.05	DMF	75	4	66
12	0.1	DMF	75	4	92, 5 ^c
13	0.15	DMF	75	4	93
14	0.1	DMF	75	6	93
15	0.1	DMF	75	8	93
16	0.1	DMF	75	10	94

^a Reaction conditions: imidazole (1 mmol), acrylonitrile (1.1 mmol), solvent (2 mL).^b Determined by HPLC based on imidazole, corresponding pure product as internal standard substance.^c CuI (8.5 mol%) used as catalyst.



Scheme 3. Production of N-substituted imidazoles using PS-imCuI complex catalyst.

after 4 h (monitored by TLC), and as prolonging the duration to 10 h the yield increased to 94%, which suggested that completion of the reaction monitored by TLC was acceptable, and more reaction time was not necessary.

From above studies, it was noted that PS-imCuI is efficient to catalyze the AMR of imidazole and acrylonitrile, and the better reaction conditions is DMF as solvent, 8.5 mol% (Cu) PS-imCuI catalyst and reaction temperature 75 °C, which was also chosen to study the latter reactions. The activity of the PS-imCuI catalyst in the AMR of imidazole and acrylonitrile with other reported catalysts system was further compared, as shown in Table 3. From the table, it can be seen that the activity of PS-imCuI catalyst is more or less similar to the other reported systems, and the reaction is conducted at shorter reaction time (4 h) in the present system.

3.2.2. Catalytic activity of PS-imCuI catalyst in different substrate reaction

In order to further investigate the application of PS-imCuI catalyst for AMR of different substrate, various activated alkenes such as acrylonitrile, methyl acrylate, methyl methacrylate, ethyl acrylate, and butyl methacrylate were reacted with imidazole, 2-methyl imidazole, 4-nitro imidazole, and benzimidazole (Scheme 3). The results were displayed in Table 4.

The results showed that PS-imCuI catalyst is efficient for these AMR of imidazoles with α,β -unsaturated compounds. It can be seen that the yields were different for the reactions of imidazole with different activated alkenes at same reaction conditions (Table 4, entries 1–5). The yield of reaction of imidazole with acrylonitrile was best, followed by with ethyl acrylate and butyl methacrylate, and then with methyl acrylate, and the yield of reaction of imidazole with methyl methacrylate was worst. The possible reasons [41,42] are that the electronegativity of cyano group is bigger than that of ester group in DMF so that the reaction of imidazole with acrylonitrile is easier than with acrylate. The inductive effect of long-chain alkoxy is bigger than that of short-chain alkoxy so that the reaction of imidazole with ethyl acrylate is faster than with methyl acrylate, and with butyl methacrylate is faster than with methyl methacrylate [43]. Steric hindrance afford the reaction of imidazole with methyl methacrylate slightly less yield than that with methyl acrylate. Similar experiment phenomena were also appeared in the reaction of various alkenes with 2-methyl imidazole and 4-nitro imidazole (Table 4, entries 6–8 and 9–10). It was seemed that the imidazole with electron donating methyl was also less active than simple imidazole (Table 4, entries 6 and 1), which could be due to the steric hindrance of the 2-methyl imidazole.

Table 3
Comparison of activity of different catalyst system for the aza-Michael addition reaction of imidazole and acrylonitrile.

Entry	Catalyst	Reaction conditions	Yield (%)	Reference
1	[Ti ₄ H ₁₁ (PO ₄) ₉]-nH ₂ O	[Ti ₄ H ₁₁ (PO ₄) ₉]-nH ₂ O: 2 mol%, 50 °C, solvent-free, 5 h	83	[8]
2	KF/Al ₂ O ₃	KF/Al ₂ O ₃ : 10 mol%, rt, CH ₃ CN, 20 h	96	[20]
3	[bmim]OH	[bmim]OH: 30 mol%, rt, 6 h	90	[21]
4	[Bmim]Im	[Bmim]Im: 2 mol%, rt, 1 h	89	[23]
5	Cu(acac) ₂ in [bmim][BF ₄]	Cu: 2 mol%, 60 °C, 8 h	95	[25]
6	PANI-CuI	Cu: 2.5 mol%, 60 °C, MeOH, 8 h	95	[26]
7	PS-imCuI	Cu: 8.5 mol%, 75 °C, DMF, 4 h	92	This study

The nitro-imidazole derivatives are pharmacological significance as immunosuppressants, aldehyde dehydrogenase inhibitors and radiotherapy synergists. It can be seen that the reaction of 4-nitro-imidazole and 2-methyl-5-nitro-imidazole with acrylonitrile or methyl acrylate could afford good or medium yield (Table 4, entries 9, 10 and 11) with this PS-supported CuI-imidazole complex catalyst, which had not been reported by other supported CuI catalysts [24,26]. In addition, extending the duration benzimidazole could react with acrylonitrile and afford good yield (Table 4, entry 12).

Spectroscopic data of the products: 3-(1'-imidazole)-propionitrile (Table 4, entry 1) ¹H NMR (CDCl₃) δ : 7.57 (s, 1H), 7.11 (d, 1H), 7.03 (d, 1H), 4.27 (t, 2H), 2.83 (t, 2H). Methyl 3-(1'-imidazole)-propionate (Table 4, entry 2) ¹H NMR (CDCl₃) δ : 7.57 (s, 1H), 6.95 (s, 1H), 6.87 (s, 1H), 4.20 (t, 2H), 3.62 (s, 3H), 2.72 (t, 2H). Ethyl 3-(1'-imidazole)-propionate (Table 4, entry 3) ¹H NMR (CDCl₃) δ : 7.55 (s, 1H), 7.10 (d, 1H), 6.96 (d, 1H), 4.27 (t, 2H), 4.15 (m, 2H), 2.77 (t, 2H), 1.24 (t, 3H). Methyl 2-methyl-3-(1'-imidazole)-propionate (Table 4, entry 4) ¹H NMR (CDCl₃) δ : 7.56 (s, 1H), 7.12 (s, 1H), 6.89 (s, 1H), 4.00–4.25 (m, 2H), 3.68 (s, 1H), 2.47 (m, 1H), 1.20 (d, 3H). *n*-Butyl 2-methyl-3-(1'-imidazole)-propionate (Table 4, entry 5) ¹H NMR (CDCl₃) δ : 7.56 (s, 1H), 7.09 (d, 1H), 6.98 (d, 1H), 6.09 (m, 1H), 5.54 (t, 1H), 4.14 (t, 2H), 1.94 (s, 3H), 1.65 (m, 2H), 1.40 (m, 2H), 0.94 (t, 3H). 3-[1'-(2-methyl imidazole)]-propionitrile (Table 4, entry 6) ¹H NMR (CDCl₃) δ : 7.01 (s, 1H), 6.96 (s, 1H), 4.19 (t, 2H), 2.78 (t, 2H), 2.44 (s, 3H). Methyl 2-methyl-3-[1'-(2-methyl imidazole)]-propionate (Table 4, entry 7) ¹H NMR (CDCl₃) δ : 6.83 (s, 1H), 6.78 (s, 1H), 3.88–4.2 (m, 2H), 3.69 (s, 3H), 2.88 (m, 1H), 1.22 (d, 3H). Ethyl 3-[1'-(2-methyl imidazole)]-propionate (Table 4, entry 8) ¹H NMR (CDCl₃) δ : 6.87 (s, 1H), 6.83 (s, 1H), 4.13 (m, 4H), 2.7 (t, 2H), 2.37 (s, 3H), 1.22 (t, 3H). 3-[1'-(4-nitro imidazole)]-propionitrile (Table 4, entry 9) ¹H NMR (CDCl₃) δ : 7.96 (d, 1H), 7.61 (d, 1H), 4.40 (t, 2H), 2.98 (t, 2H). Methyl 3-[1'-(4-nitro imidazole)]-propionate (Table 4, entry 10) ¹H NMR (CDCl₃) δ : 7.78 (s, 1H), 7.51 (s, 1H), 4.33 (t, 2H), 3.68 (s, 3H), 2.89 (t, 2H). 3-[1'-(2-methyl-5-nitro imidazole)]-propionitrile (Table 4, entry 11) IR (neat): 1729, ¹H NMR (CDCl₃) δ : 7.79 (s, 1H), 4.29 (t, 2H), 2.89 (t, 2H), 2.55 (s, 3H). 3-(1'-benzimidazole)-propionitrile (Table 4, entry 12) ¹H NMR (CDCl₃) δ : 8.01 (s, 1H), 7.83 (d, 2H), 7.35 (m, 2H), 4.50 (t, 2H), 2.90 (t, 2H).

3.3. Recycling experiments

For any supported catalyst, it is important to know its ease of separation and possible reuse. PS-imCuI catalyst can be easily separated by common filtration. The reusability of PS-imCuI catalyst was evaluated in the AMR of imidazole with acrylonitrile at a constant catalyst dosage of 8.5 mol%, substrate of 1 mmol imidazole and 1.1 mmol acrylonitrile in 2 mL DMF at 75 °C with constant stirring. As shown in Table 4 (entry 1), the reused PS-imCuI catalyst still showed high activity for the yield of 3-(1'-imidazole) propionitrile after reusing for 5 times. It was noticed that there was a little metal leaching from the catalyst in the first runs, and the color of the catalyst became shallow after the first run. No metal leaching was found at the later cycles. The possible reason was that there were some CuI that was not immobilized well on the PS, which had not

Table 4
Aza-Michael reaction of imidazoles with α,β -unsaturated compounds using PS-imCul catalyst.^a

Entry	Imidazoles	Alkenes	Product	Time (h)	Yield (%) ^b
1				4	92, 91 ^c , 89 ^d
2				4	90
3				4	91
4				4	88
5				4	91
6				6	90
7				6	85
8				6	89
9				8	88 ^e
10				8	75 ^e
11				10	77 ^f
12				8	87 ^e

^a Reaction conditions: imidazoles (1 mmol), alkenes (1.1 mmol), DMF (2 mL), 75 °C.^b Determined by HPLC based on imidazole, pure product as internal standard substance.^c Second cycle.^d Fifth cycle.^e Reaction temperature 85 °C.^f Reaction temperature 100 °C.

been washed off when the catalyst was prepared. In addition, some insoluble solid particles were found after fifth runs, which might be CuI–imidazole complex that peeled off from PS-imCul catalyst. Metal estimation was carried out at the end of second cycle and at the end of fourth cycle of the reaction (Table, entry 3). Percentage of metal in the catalyst was no obvious change in both the cases. From this it is evident that there is no distinct leaching of metal

from the catalyst. All these results indicated that PS-imCul catalyst was efficient and reusable.

4. Conclusion

In conclusion, the PS-imCul catalyst was prepared and applied in the C–N formation reaction. The catalyst showed a better

thermal stability than that of PS-CH₂Cl resin. Using the synthesized catalyst, aza-Michael reactions of imidazoles with a variety of α,β -unsaturated compounds were developed with good yields in 4–8 h. The PS-imCuI catalyst could be recovered by simple filtration, and the yield had no significant decrease after reusing for 5 times. These preliminary results indicate that the PS-imCuI catalyst was an excellent recyclable catalyst for the AMR of imidazoles with α,β -unsaturated compounds and showed potential application in industry. Further studies and additional applications are currently underway.

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