Green Chemistry

PAPER

Piperazine-functionalized ordered mesoporous polymer as highly active and reusable organocatalyst for water-medium organic synthesis

Fang Zhang,*[a] Xushi Yang,[a] Lei Jiang,[b] Chao Liang,[a] Ruixing Zhu[a] and Hexing Li*[a]

A piperazine-functionalized mesoporous polymer (PP-MPs) was synthesized through a one-step surfactant-directed phenol–formaldehyde–piperazinecarbaldehyde oligomer self-assembly approach. This novel PP-MP catalyst exhibited highly catalytic reactivity and selectivity for water-medium Knoevenagel reaction, water-medium [3 + 3] cycloaddition reaction and intermolecular cross-conjugated addition reaction. The excellent performance could be attributed to its high dispersion of piperazine active sites and ordered mesoporous structure, which effectively diminished the steric hindrance and diffusion limitation. Moreover, its pure organic framework could enhance surface hydrophobicity, which promoted organic reactant molecule adsorption, especially in water. Meanwhile, piperazine functional groups embedded in the polymeric framework could inhibit the leaching of active species and thus resulted in the excellent durability without significant loss of activity for recovery and recycling at least four times.

Introduction

The development of more green and safer chemical transformations for effective synthesis of fine chemicals is an important goal in our society.[1] The use of water as a sole medium of organic reactions would greatly contribute to the development of environmentally friendly processes.[2] Most of this research has been focused on homogeneous catalytic processes. Although highly active and selective, homogeneous catalysts are difficult for handling and separation, leading to significant economical and ecological disadvantages.[3] Recently, the use of heterogeneous catalysts in water-medium organic transformations has become a promising strategy to overcome the inherent problems associated with homogeneous catalytic systems.[4] To date, various catalytic active species attached to either inorganic or organic materials, such as silica,[5] layered clays,[6] carbon,[7] polymers[8] and metal–organic frameworks (MOFs),[9] have been successfully fabricated by using covalent and non-covalent immobilization approaches. Although these catalytic systems are effective, the critical issues associated with using expensive and toxic metal-based active species are believed to be challenging obstacles in the future.[10] Therefore, new and general paradigms for preparing metal-free

heterogeneous catalysts for aqueous organic synthesis are urgently needed.

In the last decade, organocatalysts have gained tremendous importance from the synthetic community because they are less expensive, non-toxic, readily available, and environmentally friendly.[11] Accordingly, considerable efforts have been made in developing water-compatible organocatalysts for performing organic transformations in water.[12] Although homogeneous organocatalysts have high reactivity and selectivity, most of them suffer from high catalyst loadings (typically 10–20%) and tedious separation from the products, which raises significant concerns regarding their practical applications and feasibility on a large scale preparation.[13] To circumvent this difficulty, the development of recoverable and reusable organocatalysts appears as one of the most advantageous strategies.[14] Most attempts to gain the advantage of water-compatible heterogeneous organocatalysts have so far been directed toward the anchoring of efficient soluble organic active sites on insoluble polymer matrixes.[15] However, such polymer-supported organocatalysts often suffered from tedious synthetic routes, less and inhomogeneously distributed active sites, poor stability, and low efficiency in mass transport, especially in water.[16]

Recently, a novel phenol-formaldehyde polymer with an ordered mesoporous structure and high surface area, offers the potential to serve as an alternative solid support for catalyst immobilization and improves the catalyst activity.[17] In our group, we have synthesized mesoporous polymer-supported organometallic catalysts, which displayed comparable activity

[a]The Education Ministry Key Laboratory of Resource Chemistry and Shanghai Key Laboratory of Rare Earth Functional Materials, Shanghai Normal University, Shanghai 200234, China. E-mail: zhangfang@shnu.edu.cn, HeXing-Li@shnu.edu.cn
[b]Shanghai Haide Pharmaceutical Co. Ltd., Shanghai 201203, China

and selectivity to homogenous organometallic complexes in a wide of water-medium organic reactions.[18] Encouraged by these successful efforts and aiming to develop a stable and highly active solid organocatalyst, we reported for the first time the bottom-up construction of a robust ordered mesoporous polymer-supported piperazine organocatalyst (PP-MP) by using a one-step surfactant-directed phenol–formaldehyde–piperazinecarbaldehyde oligomer self-assembly approach. The obtained PP-MP catalysts possessed a highly ordered mesostructure, large surface area and uniform pore size. In the water-medium Knoevenagel reaction, [3 + 3] cycloaddition reaction and intermolecular cross-conjugated addition reaction, the PP-MP catalyst exhibited almost the same catalytic reactivity and selectivity as a homogeneous piperazine catalyst, which was possibly attributable to the highly dispersed organoamine group in the mesoporous polymer framework and the intrinsic hydrophobic microenvironment around the active sites. Moreover, this heterogeneous organocatalyst can be recycled and reused several times without loss of catalytic efficiency.

Experimental

Synthesis of piperazine-derived oligomers (PP-ROs)

The piperazine-derived polymer precursor was obtained through base-catalyzed polymerization with phenol, formaldehyde and 1-piperazinecarbaldehyde. In a typical synthesis, 61 mg 1-piperazinecarbaldehyde and 4.2 g 37 wt% formaldehyde aqueous solution were mixed at 40 °C and then the mixture was refluxed at 70 °C for 0.5 h. Following that, the solution pH value was adjusted to 10.0 by adding a suitable amount of 20 wt% NaOH. Then, 2.4 g phenol was introduced in the above solution and stirred for another 2.0 h. Finally, the solution pH value was adjusted to 7.0 by using 2.0 M HCl and then water was removed by rotary evaporation to give the phenol–formaldehyde–piperazinecarbaldehyde oligomer. The final oligomers could be defined as PP-ROs-1, PP-ROs-2 and PP-ROs-3, corresponding to 1-piperazinecarbaldehyde–formaldehyde molar ratios of 2.0, 4.0, and 6.0% in the initial mixture, respectively.

Synthesis of piperazine-functionalized mesoporous polymer

The PP-MP was prepared by a one-step surfactant-directed evaporation-induced self-assembly (EISA) approach using PP-ROs precursor and triblock copolymer F127 (Scheme 1). In a typical synthetic procedure, 1.0 g F127 was added into 25 ml ethanol solution containing 1.2 g PP-ROs and stirred for 1.0 h to form a clear solution. The mixture was transferred into dishes and exposed in air at 30 °C for 12 h to evaporate ethanol and further thermo-polymerize at 120 °C for 96 h. The as-made materials were calcined in a tubular furnace at 350 °C for 6.0 h in argon atmosphere to remove the F127 template. The final products were denoted as PP-MPs-1, PP-MPs-2 and PP-MPs-3, which involved the three corresponding PP-RO precursors as functional building blocks.
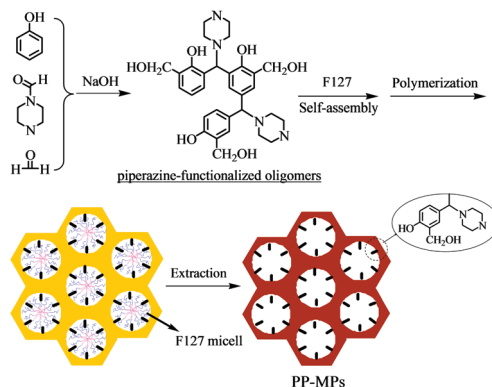
Scheme 1 Illustration of the preparation of the PP-MPs catalyst.

Characterization

Small-angle X-ray diffraction (XRD) patterns were conducted on a Rigaku D/maxr B diffractometer with Cu Kα radiation (40 kV, 20 mA). N_2 sorption isotherms were measured at 77 K on a Quantachrome NOVA 4000e analyzer. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas. Transmission electron microscopy (TEM) experiments were performed on a JEM2011 microscope operated at 200 kV. The sample for TEM measurement was suspended in ethanol and supported onto a holey carbon film on a Cu grid. ^{13}C Solid nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DRX-400 NMR spectrometer under the condition of magic angle spinning (MAS), and the spectra were collected at room temperature at a frequency of 100.6 MHz. The surface electronic states were analyzed by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 5000C ESCA). All of the binding energy values are calibrated by using $C_{1S} = 284.6$ eV as a reference. The nitrogen content was determined by elemental analysis using an Element Vario EL III analyzer. Water and toluene vapour absorption measurements were carried out on an intelligent gravimetric analyser (Hiden Isochema IGA-002) by introducing a dosed amount of high-purity vapor directly into the sample chamber and recording the weight change after a stable equilibrium pressure was reached.

Activity test

All these reactions were carried out in a 10 ml round-bottomed flask. The reaction conditions and the product analysis methods are described in reaction I and II. The reproducibility was checked by repeating experiments at least three times and was found to be within acceptable limits (± 5%).

Reaction I. In a typical run of water-medium Knoevenagel condensation reaction, 0.20 mmol ethyl cyanoacetate, 0.24 mmol benzaldehyde, 0.15 mmol *n*-decane as internal standard, 5.0 ml distilled water and a catalyst containing 0.020 mmol piperazidine were mixed and allowed to stir at 40 °C for 3.0 h. After extracting with ethyl acetate, the products were analyzed on a gas chromatograph (GC, Agilent 1790) equipped with a JWDB-5, 95% dimethyl 1-(5%)-diphenylpolysiloxane column and a FID detector.

Table 1 Structural parameters and catalytic performances of PP-MPs catalysts with different piperazidine content in water-medium Knoevenagel condensation reaction[a]

Catalyst	N loading (wt%)	S_{BET} (m^2 g^{-1})	D_p (nm)	V_p (cm^3 g^{-1})	Conv. (%)	Select. (%)	Yield (%)
PP-MPs-1	0.090	155	3.2	0.23	83	99	82
PP-MPs-2	0.330	132	3.1	0.21	93	99	92
PP-MPs-3	1.100	100	2.9	0.18	87	99	86

[a] Reaction conditions: a catalyst containing 0.020 mmol piperazidine, 0.20 mmol ethyl cyanoacetate, 0.24 mmol benzaldehyde, 5.0 ml distilled water, t = 3.0 h, T = 40 °C.

Reaction II. In each run of intermolecular cross-conjugated addition reactions, 0.50 mmol α-methyl-β-nitrostyrene, 1.0 mmol 1,3-diphenyl-2-propenone, 0.50 mmol DMAP and 3.0 ml DMSO, and a catalyst containing 0.050 mmol piperazidine were mixed. After reaction under vigorous stirring for 16 h, the catalyst was removed by centrifugation and washed with CH$_2$Cl$_2$ 3 times. The organic layer was diluted with 10 ml CH$_2$Cl$_2$, followed by washing with water and brine subsequently. After being dried in anhydrous sodium sulfate, the solvent was distilled under reduced pressure. Then, the solid product was dissolved in 10 ml THF, followed by quantitatively analyzing to determine conversion, selectivity and yield to target product. The product analysis was performed on a HPLC-MS (Agilent 6410B) by using the external standard. The conversion was calculated based on α-methyl-β-nitrostyrene since the ketone compounds are in excess. Selectivity was calculated from the relative peak area ratio of the product and byproduct, which was calibrated by using experimental data reported by Shi *et al.*[19] There were four enantiomers of the target product. The HPLC-MS could not distinguish the *R,R* and *S,S* enantiomers or *R,S* and *S,R* enantiomers, but the *R,R* and *S,S* enantiomers could be easily distinguished from the *R, S* and *S,R* enantiomers. The diastereomeric ratio (d.r.) refers to the molar ratio between *syn*-isomers (*R,R* + *S,S*) and *trans*-enantiomers (*R,S* + *S,R*), which could be calculated based on the respective peak areas.

Reaction III. In a typical run of water-medium [3 + 3] cycloaddition reactions, a catalyst containing 0.050 mmol piperazidine, 0.50 mmol 1,3-cyclohexanedione and 0.50 mmol α,β-unsaturated aldehydes, 5.0 ml H$_2$O were mixed and allowed to stir at 20 °C for 12 h. The products were extracted with methanol, followed by analysis by a high-performance liquid chromatograph (Agilent 6410 Series Triple Quad) equipped with Agilent C18 20 cm × Ø 5 mm column.

Determination of catalyst leaching and durability

In order to determine the catalyst durability, the heterogeneous catalyst was centrifuged after each run of the reactions and the clear supernatant liquid was decanted slowly. The residual solid catalyst was washed thoroughly with distilled water and ethyl acetate, followed by drying at 80 °C for 8.0 h under vacuum conditions. Then, the catalyst was re-used with a fresh charge of solvent and reactants for subsequent recycle runs under the same reaction conditions.

Results and discussion

Elemental analysis revealed that the nitrogen content in a series of PP-MPs samples was in the range from 0.090 to 1.1 wt% (Table 1), indicating the existence of an organoamine species. The chemical composition of the representative PP-MPs-2 was further investigated by solid NMR spectroscopy. As shown in Fig. 1, the ^{13}C CP-MAS NMR spectra of non-functionalized mesoporous polymer displayed two peaks around 149 and 128 ppm, which belonged to –OH substituted carbon in phenol and other aromatic carbons. A shoulder peak around 119 ppm could be assigned to the non-substituted aromatic *ortho* carbons. Meanwhile, the broad overlapping signals at 36 and 69 ppm could be attributed to methylene linkages between phenolic rings and benzyl hydroxyl groups, respectively.[20] The peaks around 175 and 75 ppm marked with asterisks were considered as rotational sidebands, which had been confirmed by changing rotational speed. In comparison with MPs, the PP-MPs-2 sample displayed one additional peak around 48 ppm, which could be assigned to the methylene carbon in the piperazine units,[21] demonstrating the successful incorporation of piperazine functional groups in the mesoporous polymeric framework. According to IR and NMR data, the introduction of piperazine species in the mesoporous polymer framework could be achieved through a base-catalyzed condensation reaction between 1-piperazinecarbaldehyde, formaldehyde and phenol and thus the obtained soluble oligomers were further interacted with surfactant to give the functionalized mesoporous polymer since the oligomers have a large number of hydroxy groups.[17] Meanwhile, the XPS
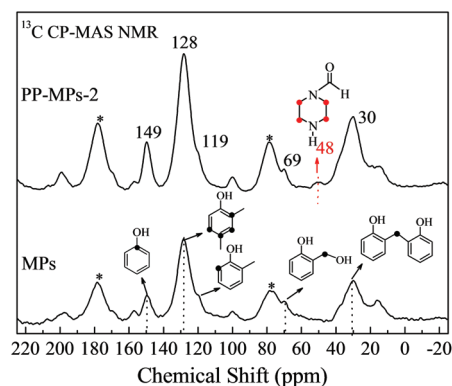

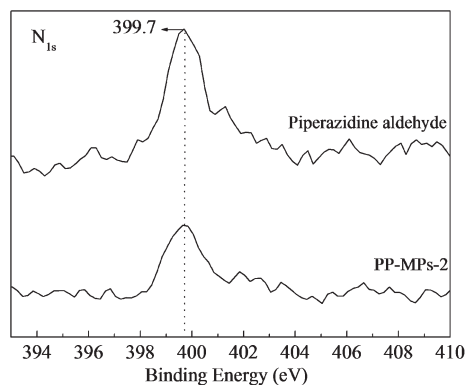**Fig. 1** ^{13}C CP MAS NMR spectra of PP-MPs-2 and MPs samples.

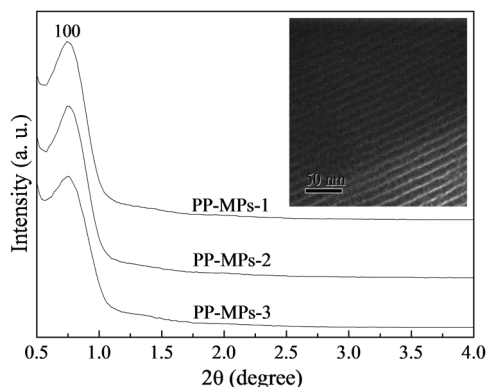Fig. 2 XPS spectra of piperazidine aldehyde and PP-MPs-2 samples.

Fig. 3 XRD patterns of PP-MPs samples with varying piperazine content and TEM image (inset) of representative PP-MPs-2 sample.

Fig. 4 N$_2$ sorption isotherms of PP-MPs samples with varying piperazine content.

analysis (Fig. 2) demonstrated that nitrogen species in the PP-MPs-2 were present in a negative trivalent state, corresponding to a binding energy of 399.7 eV in N$_{1s}$ level.[22] As expected, the binding energy value of the PP-MPs-2 sample was much the same as that of piperazine, suggesting the chemical structure of piperazine could be well retained after supramolecular self-assembly and thermal co-polymerization processes.

Fig. 3 showed small-angle XRD patterns for PP-MPs with varying piperazine content. All the PP-MPs samples exhibited a well resolved peak at $2\theta = 0.75°$ characteristic of the (100) diffraction, suggesting the formation of an ordered two-dimensional $p6mm$ hexagonal mesoporous structure.[23] The XRD peak intensity decreased with the increase of piperazine content due to the decrease in ordering degree of the mesoporous structure, which revealed that more piperazine units in the precursor potentially disturbed the effective assembly between triblock co-polymer and the hydrophilic phenolic –OH groups. TEM image (inset) of the representative PP-MPs-2 sample further confirmed it exhibited a two-dimensional hexagonal arrangement of one-dimensional channels with uniform size.[24] Ordered mesoporous morphology can be observed in large domains, without distinct defects. The pore structure of these samples was further characterized using nitrogen
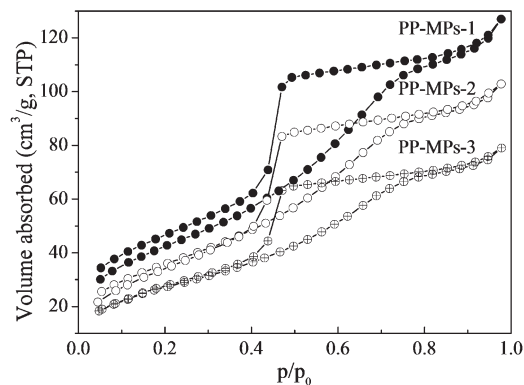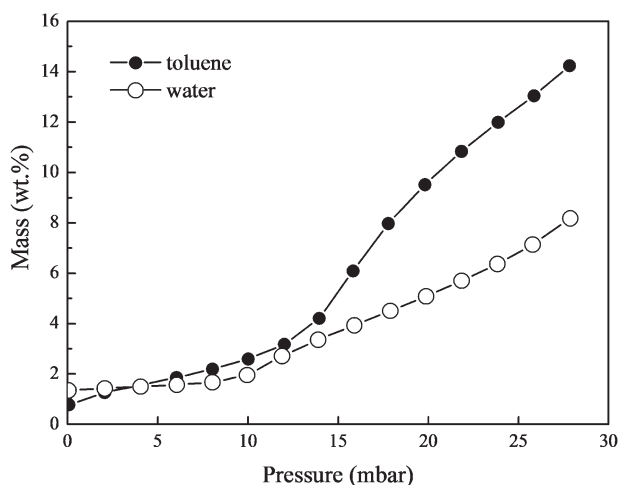
sorption experiments. All the PP-MPs materials displayed typical type IV N$_2$ adsorption–desorption isotherms with a H$_1$-type hysteresis loop characteristic of mesoporous structure (Fig. 4). The BET surface areas, average pore size, and pore volume of these functionalized mesoporous polymers were summarized in Table 1. An increase of piperazine content resulted in the decrease of S_{BET}, D_p and V_p due to the decreased ordered degree of the mesoporous structure. This phenomenon was potentially due to the reduced hydrophilic –OH groups in the PP-ROs with more piperazine units, which was unfavorable for –OH groups to interact with EO block to form the final ordered mesostructures during the solvent evaporation-induced self-assembly process. Based on these results, it can be safely concluded that the current approach for the introduction of piperazine functional groups into the mesoporous polymer framework could effectively avoid the degradation of the original mesoporosity and mesoscopic ordering.

Water-medium Knoevenagel condensation reaction was used to evaluate the catalytic performance of the piperazine-functionalized mesoporous polymer. As summarized in Table 1, a series of PP-MPs displayed highly catalytic reactivity, indicating that the piperazine functional group was indeed a catalytically active site. Firstly, we investigated the effect of nitrogen content on the catalytic activity in the condensation of benzaldehyde with ethyl cyanoacetate. The results showed that the yield of ethyl α-cyanocinnamate increased from 82 to 92% with the increase of nitrogen content from to 0.090 to 0.33 wt%. However, the yield drastically dropped to 87% when nitrogen content increased to 1.1 wt%. The inferior catalytic reactivity of PP-MPs-1 could be attributed to the lower active site density, which reduced the requisite substance contact. Meanwhile, the decreased ordered degree of pore structure of PP-MPs-3 disfavored the transport limitation and/or the interaction between organic piperazine species and the reactants, which resulted in the reduced catalytic efficiency. Furthermore, we examined the difference in catalytic activity between PP-MPs-2 and homogeneous catalyst (Table 2). Notably, we found that PP-MPs-2 exhibited similar catalytic reactivity to that of piperazine, confirming its almost unchanged chemical microenvironment. Meanwhile, the pure organic framework of
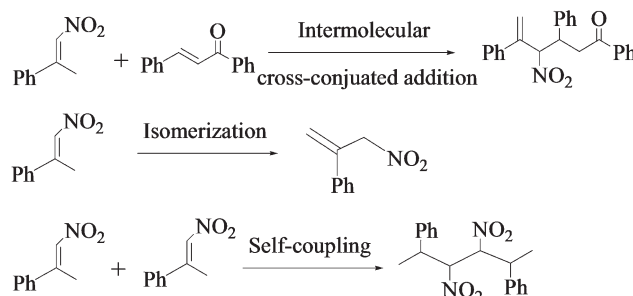
Table 2 Catalytic performances of PP-MPs-2 and piperazidine catalysts in water-medium Knoevenagel condensation reaction[a]

Catalyst	R	Conv. (%)	Select. (%)	Yield (%)
PP-MPs-2	H	93	99	92
Piperazidine		97	99	96
PP-MPs-2	OCH$_3$	78	99	77
Piperazidine		82	99	81
PP-MPs-2	NO$_2$	99	99	98
Piperazidine		100	99	99

[a] Reaction conditions are given in Table 1.

Fig. 5 Toluene and water vapor absorption tests of PP-MPs-2 catalyst.

Scheme 2 Reaction equations between α-methyl-β-nitrostyrene and 1,3-diphenyl-2-propenone.

Table 3 Catalytic performances of PP-MPs and piperazidine catalysts in the intermolecular cross-conjugated addition reaction[a]

Catalyst	T (°C)	t (h)	Conv. (%)	Select. (%)	Yield (%)	d.r. (syn : anti)
PP-MPs-2	30	16	86	88	76	1 : 1.2
PP-MPs-2	40	16	95	87	83	1 : 1.2
PP-MPs-2	50	16	98	87	85	1 : 1.2
PP-MPs-2	40	8	53	89	47	1 : 1.2
PP-MPs-2	40	24	99	86	85	1 : 1.2
Piperazidine	40	16	97	89	86	1 : 1.2

[a] Reaction conditions: a catalyst containing 0.050 mmol piperazidine, 0.50 mmol α-methyl-β-nitrostyrene, 1.0 mmol 1,3-diphenyl-2-propenone, 0.50 mmol DMAP, 3.0 ml DMSO.

PP-MPs-2 catalyst guaranteed the surface hydrophobicity, leading to the deceased mass transport limitation in water. To gain precise insight into the hydrophobic effect, both toluene and water vapor absorption tests were employed to test the hydrophobicity of PP-MP-2 catalyst (Fig. 5). All the isotherms were of type V, indicative of weak absorbent–absorbate interaction.[25] However, the adsorption capacity of PP-MP-2 for toluene (13 wt%) was much higher than that of water (5.7 wt%). This result demonstrated that its mesopore surface was hydrophobic, leading to selective adsorption for organic reactants. Next, we tested a series of electron donors and the withdrawing capability of substituents in the benzene ring of derivatives under the same reaction conditions. As expected, a benzaldehyde derivative with an electron withdrawing substituent (–NO$_2$) in its benzene ring was conducive to Knoevenagel reaction and 99% yield of the condensation product was obtained. On the contrary, the existence of an electron donor substituent (–OCH$_3$) led to a lower 77% yield.

With the aim of examining the possibility of the wide use of PP-MPs-2 catalyst, intermolecular cross-conjugated addition reaction between α-methyl-β-nitrostyrene and 1,3-diphenyl-
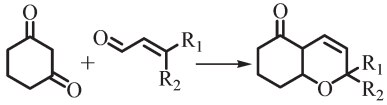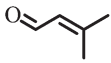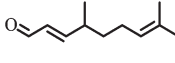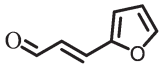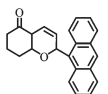
2-propenone was chosen as a probe to test its catalytic efficiency. Besides the target product, two byproducts were also detected by HPLC-MS. One resulted from the isomerization of α-methyl-β-nitrostyrene and the other was due to the self-coupling reaction of α-methyl-β-nitrostyrene (see the reaction equations in Scheme 2). As shown in Table 3, the conversion increased with the increase of either the reaction temperature or the reaction time but the selectivity and d.r. value remained almost identical. The optimum reaction conditions were determined as 40 °C and 16 h, corresponding to the yield of 83% to the target product, which was almost the same as that obtained in the presence of homogeneous piperazine organocatalyst. Moreover, we also extended this system to water-medium [3 + 3] cycloaddition reaction for constructing pyranyl heterocycle, which is one of the most common structural sub-units in natural products and biologically active compounds.[26] The results were summarized in Table 4. PP-MPs-2 catalyst could efficiently catalyze all the α,β-unsaturated aldehydes to react with 1,3-cyclohexanedione and obtained their corresponding pyranyl-containing compounds. Meanwhile, we also found that it displayed almost the same catalytic performance with homogeneous piperazine catalyst. Interestingly, even for 3-(anthracen-10-yl)acrylaldehyde with relatively large molecular size, PP-MPs-2 also exhibited comparable catalytic reactivity with that of piperazine. The high activity and selectivity of PP-MPs-2 catalyst could be attributed to the similar Lewis base strength and chemical microenvironment of piperazine active sites to free piperazine. Meanwhile, the large surface

Table 4 Catalytic performances of PP-MPs-2 and piperazidine catalysts in water-medium [3 + 3] cycloaddition reaction between 1,3-cyclohexanedione and various α,β-unsaturated aldehydes[a]

Catalyst	Aldehyde	Product	Conv. (%)	Select. (%)	Yield (%)
PP-MPs-2			84.3	99	83.3
Piperazidine			88.5	99	88.4
PP-MPs-2			80.5	99	80.4
Piperazidine			82.8	99	82.7
PP-MPs-2			78.0	99	77.9
Piperazidine			79.6	99	79.5
PP-MPs-2			60.2	99	60.1
Piperazidine			65.3	99	65.2

[a] Reaction conditions: a catalyst containing 0.050 mmol piperazidine, 0.50 mmol 1,3-cyclohexanedione, 0.50 mmol aldehyde, 5.0 ml distilled water, t = 12 h, T = 20 °C.

area and the ordered mesoporous channels of mesoporous polymer support facilitated the diffusion and adsorption of reactant molecules.

To ensure the reactivity originated from the immobilized piperazine rather than from dissolved piperazine either from the absorbed piperazine or from catalyst leaching, the following procedure, proposed by Sheldon *et al.*, was carried out.[27] After reaction for 1.5 h at which time the conversion exceeded 45% in water-medium Knoevenagel reaction between benzaldehyde and ethyl cyanoacetate, the mixture was filtered to remove the solid catalyst and the mother liquor was allowed to react for another 3.0 h under the same reaction conditions. No significant activity was observed, demonstrating that the active species were not the dissolved piperazine leached from PP-MPs-2 catalyst. Therefore, it was reasonable to suggest that the present catalysis was heterogeneous in nature.

An important merit of heterogeneous catalysts is that they should be conveniently recycled and reused. Firstly, we examined the durability of PP-MPs-2 catalyst for the water-medium Knoevenagel reaction between benzaldehyde and ethyl cyanoacetate. As shown in Fig. 6a, no significant decrease could be found in either the activity or the selectivity after being used repetitively for six times. Then we further determined the lifetime of PP-MPs-2 catalyst for intermolecular cross-conjugated addition reaction between α-methyl-β-nitrostyrene and 1,3-diphenyl-2-propenone. As shown in Fig. 6b, PP-MPs-2 catalyst could be used repetitively for more than four times without significant deactivation. Elemental analysis revealed that after being used, the nitrogen content in the recycled PP-MP-2 catalyst remained almost the same (0.32 wt%), indicating that the mesoporous polymer framework could effectively inhibit the
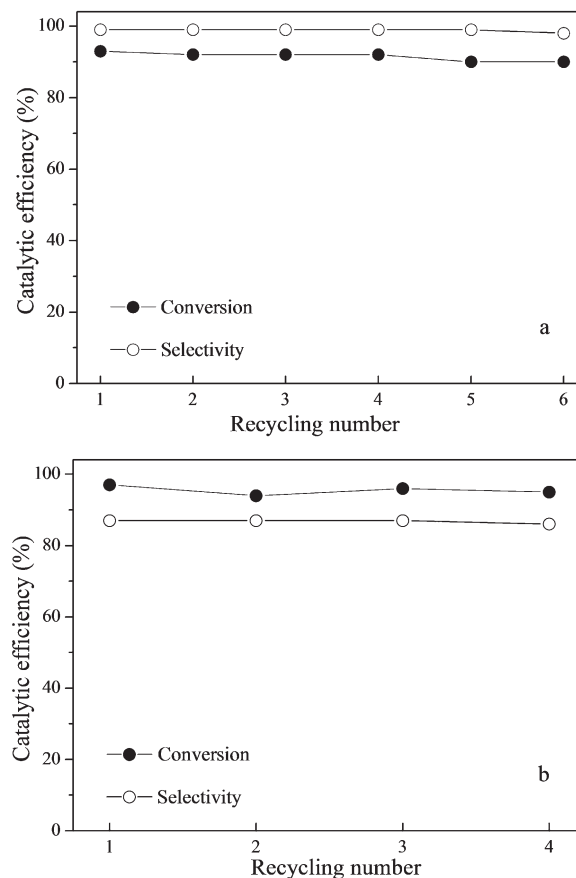

Fig. 6 Recycling test of PP-MPs-2 catalyst in water-medium Knoevenagel reaction (a, reaction I) and intermolecular cross-conjugated addition reaction (b, reaction II). Reaction conditions are given in the experimental section.
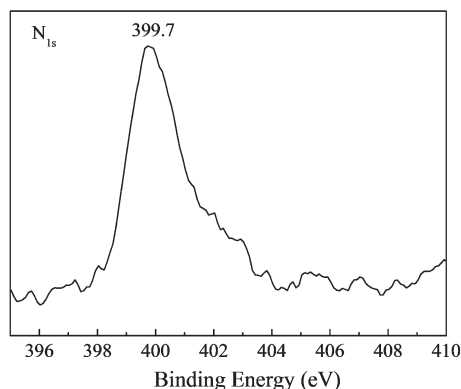
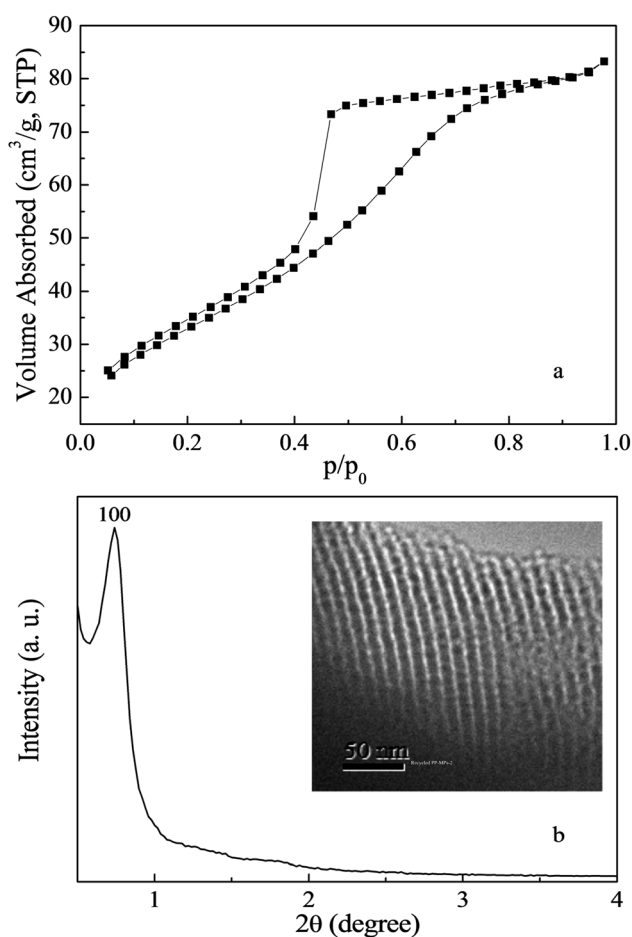**Fig. 7** XPS spectrum of PP-MPs-2 catalyst after being reused six times in water-medium Knoevenagel reaction.

Fig. 8 N$_2$ sorption isotherm (a), XRD pattern (b) and TEM image (inset) of PP-MPs-2 catalyst after being reused six times in water-medium Knoevenagel reaction.

leaching of active sites. Furthermore, XPS data displayed the similar nitrogen binding energy value (Fig. 7), suggesting the unchanged chemical microenvironment. In addition, N$_2$ sorption isotherm (Fig. 8a) and low-angle XRD pattern (Fig. 8b) as well as TEM image (inset) confirmed that the ordered

mesoporous structure of the urea-MP-2 was well preserved after being reused, resulting in its excellent stability.

Conclusions

In summary, we demonstrated the synthesis of piperazine-functionalized mesoporous polymers through a one-step solvent evaporation-induced self-assembly approach. These heterogeneous organocatalysts showed high reactivity, selectivity and stability in the water-medium Knoevenagel reaction, water-medium [3 + 3] cycloaddition reaction and intermolecular cross-conjugated addition reaction, presumably as a result of the ordered mesoporous structure and favorable hydrophobic micro-environment. This facile self-assembly route is of great potential in the controlled synthesis of high active mesoporous polymer-supported organocatalysts for various chemical transformations.

Acknowledgements

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