

Cite this: *RSC Adv.*, 2014, 4, 55028

Hierarchical PS/PANI nanostructure supported Cu(II) complexes: facile synthesis and study of catalytic applications in aerobic oxidation†

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Hierarchical heterogeneous copper catalysts were prepared by immobilization of a homogeneous copper(II) complex on the surface of polystyrene/polyaniline (PS/PANI) microspheres with oriented PANI nanofibers. EDX element maps and XPS spectra indicated that Cu²⁺ ions strongly coordinated with PANI imine. PS/PANI@Cu(OSO₂CF₃)₂ exhibited excellent catalytic activity for selective aerobic oxidation of alcohols and highly efficient aerobic epoxidation of alkenes under mild conditions. The supported copper(II) catalyst maintained high levels of conversion and selectivity in these reactions after six cycles and showed good stability.

Received 10th July 2014
Accepted 7th October 2014

DOI: 10.1039/c4ra06944g

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1. Introduction

Selective oxidations are among the most important organic transformations in industry. During these processes, stoichiometric use of inorganic oxidants and large amounts of solvent are generally employed.^{1,2} However, many of the commonly used oxidants are expensive and/or toxic, for example chromium compounds^{3,4} and permanganates.^{5,6} Catalytic oxidations have attracted much attention recently because these processes are more atom-efficient and less harmful to the environment. The implementation of a catalytic oxidation process requires stoichiometric amounts of oxidizing reagents, many of which are also dangerous or toxic.^{7–9} As environmental concerns increase, there has been an increase in the use of molecule oxygen as the oxidant, which has the advantage of being inexpensive, abundant, safe, and environmentally friendly.^{10–13}

It has been reported that noble metal nanoparticles,^{14–18} Ru^{19,20} and Pd^{21–24} can be used as catalyst to promote aerobic oxidation of alcohols, alkanes, glucose and aryl carbonyl derivatives. However, the use of noble metallic nanoparticles in aerobic oxidation leads to high cost and limits its application for use in industry. Recently, inexpensive transitional metals including Co,^{25,26} Fe,^{27,28} V^{29,30} and Cu^{31,32} have been developed to promote the oxidation reactions in the presence of molecule oxygen. Among these transition metals, copper is one of the most abundant elements in nature and relatively inexpensive

and non-toxic. A copper-based catalyst for aerobic oxidation reaction is worth developing due to the excellent catalytic activity of copper and its ready availability.

So far, several copper catalysts such as CuBr₂(2,2'-bipyridine)/*t*-BuOK³³, CuBr·Me₂S,³⁴ Cu(II)-diimine complexes,³⁵ Cu(OAc)₂·H₂O/pytl-β-cyclodextrin,³⁶ [Cu(μ-Cl)Cl(phen)]₂³⁷ and Cu(C₈F₁₇(CH₂)₂-CO₂)₂(R_f-tacn)³⁸ have been reported to show excellent catalytic activity in aerobic oxidation of hydrocarbons, alkenes and alcohols. However, homogeneous copper(II) catalysts are difficult to separate and recover from the reaction system. Thus, studies of heterogeneous copper catalysts have gained growing attention, due to the ease of separation and recyclability. So far, there are only a few heterogeneous copper catalysts that were studied for the selective aerobic oxidation transformations.^{39,40} A variety of conventional supports such as silica,^{41–44} graphene oxide⁴⁵ and functional polymer^{46–48} have been utilized as the support for copper salts. Amongst the available supports, polyaniline would be an ideal support for immobilizing copper complex because of its low cost, easy synthesis, good thermal and chemical stability in most organic solvents. Furthermore, facile control of morphology and a large number of imino groups along polyaniline backbone would control copper loading, which would determine the activity and reproducibility of the resulting catalysts.

Herein, we have developed a novel system for aerobic oxidation of alcohols and olefins employing hierarchical polystyrene/polyaniline microspheres supported copper(II) salts. The catalytic activity of three heterogeneous copper(II) catalysts were evaluated by the selective aerobic oxidation of alcohols and olefins. Great yields and recyclability were demonstrated utilizing one of the as-synthesized heterogeneous copper catalysts, PS/PANI@Cu(OSO₂CF₃)₂, under the optimized reaction condition.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c4ra06944g

2. Experimental

2.1 Materials

Styrene, aniline, iron(III)nitrate nonahydrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$], ethanol, cupric chloride [CuCl_2] and cupric nitrate [$\text{Cu}(\text{NO}_3)_2$] were obtained from Beijing Chemical Reagent Co., Beijing, China., potassium persulfate [$\text{K}_2\text{S}_2\text{O}_8$, KPS], Copper(II) trifluoromethanesulfonate [$\text{Cu}(\text{OSO}_2\text{CF}_3)_2$], 2,2,6,6-tetramethyl-1-piperidinyloxy [TEMPO] were purchased from Alfa Aesar. All the reagents above were used without any further purification except the two monomers. Styrene was washed with 1 mol L^{-1} aqueous NaOH three times to remove the inhibitor, then washed with water until neutral. Aniline was purified according to literature procedure.⁴⁹

2.2 Synthesis of polystyrene (PS) microspheres

A soap-free emulsion polymerization was used to prepare the PS seed nanoparticles according to literature.⁵⁰ Deionized water (140 mL) and styrene (10 g) were added into a 250 mL four-necked round-bottom flask with a mechanical stirrer, a N_2 inlet and a reflux condenser. The oxygen in solution was removed by N_2 bubbling for 10 min under stirring (300 rpm) before heated up to 70°C in an oil bath. KPS aqueous solution (10 mL, 0.023 g mL^{-1}) was injected into the solution to start the polymerization. After the polymerization lasted for 24 h, the PS microspheres were collected by centrifugation, followed by washing with water and ethanol three times and dried under vacuum.

2.3 Synthesis of sea urchin-like PS/PANI microspheres

The PS/PANI microspheres with sea urchin-like morphology were prepared by the method illustrated in previous literature⁵¹ with $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as the oxidant and PS microspheres as the template. First, PS microspheres template (0.3 g) were added in deionized water (20 mL) to form emulsion, followed by addition of aniline (3 mmol) under vigorous stirring at room temperature. The solution was stirred for 12 h to allow the swelling of aniline into the PS templates. Immediately the oxidant $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (18 mmol) was added, the aniline was polymerized at the interface of PS template and the solution to form the shell and fibers. The solution became dark green after 12 h, the PS/PANI microspheres were centrifuged, washed with water until the supernatant colorless, and dried under vacuum.

2.4 Preparation of PS/PANI microspheres supported Cu(II) homogenous catalysts

The PS/PANI microspheres-supported Cu(II) catalysts were synthesized by mixing the sea urchin-like PS/PANI microspheres (300 mg) and homogenous Cu(II) compounds (300 mg) in acetonitrile (15 mL) with stirring at room temperature for 48 h. Afterwards, the solid was filtered, washed with acetonitrile, and dried under vacuum to obtain a black powder.

2.5 Typical catalytic procedure for alcohol oxidation

Alcohol (1 mmol) and supported Cu(II) catalyst (1 mol%) were added to acetonitrile (5 mL) with TEMPO (0.5 equiv.) and

Na_2CO_3 (1 equiv.). The reaction mixture was stirred at 75°C under 1 atm of O_2 . After the reaction, the PS/PANI supported Cu(II) catalysts were filtered from the solution by centrifugation.

2.6 Typical catalytic procedure for olefin epoxidation

Olefin (1 mmol) and PS/PANI@Cu(OSO_2CF_3)₂ catalyst (0.2 mol%) were added to acetonitrile (5 mL) with trimethylacetaldehyde (2 equiv.). The reaction mixture was stirred at room temperature under 1 atm of O_2 . After the reaction, the PS/PANI@Cu(OSO_2CF_3)₂ catalyst were filtered from the solution by centrifugation.

2.7 Catalyst recycling

The recyclability of the heterogenous catalyst were tested by using the recovered catalyst according to the reaction conditions described above. The catalyst was filtered from the reaction solution after the catalytic reaction ended, washed with acetonitrile, dried and reused for the next run.

2.8 Characterization

Scanning electron microscope (SEM) images were taken by ZEISS SUPRA 55 instrument at an acceleration voltage of 10 kV. High resolution transmission electron microscope (HRTEM) images and the EDX element maps were obtained by FEI Tecnai F20 electron microscope with an acceleration voltage of 200 kV. Fourier-transformed infrared spectra (FT-IR) were recorded by a NICOLET 6700 infrared spectrophotometer. X-Ray photoelectron spectroscopy (XPS) spectra were tested by a Kratos AXIS Ultra DLD photo-electron spectroscope. C 1s line at 284.8 eV from adventitious carbon was used as the reference for binding energy. Thermal gravimetric analysis (TGA) were operated on a Netzsch model STA F409 instrument in nitrogen atmosphere with the heating rate of 10 K min^{-1} .

3. Results and discussion

3.1 Synthesis of PS/PANI microspheres supported copper(II) homogenous catalysts

The preparation of PS/PANI@Cu(II) heterogenous catalysts was achieved by mixing homogenous copper(II) salts and PS/PANI support in acetonitrile. The as-synthesized catalysts were characterized with SEM, EDX, TEM, XPS and FTIR spectra. The sea urchin like PS/PANI microsphere supports of PS/PANI@Cu(II) catalysts were prepared by a chemical oxidation polymerization using PS spheres as template utilizing soap-free emulsion polymerization method. The scanning electron microscopy (SEM) images of PS/PANI composite microspheres are shown in Fig. 1a. The PS/PANI hybrid microspheres, with a uniform size of 700 nm, exhibit unique hierarchical sea urchin-like architecture assembled from ultrathin PANI nanofibers on the surface of PS microspheres. Immobilizing the three copper(II) homogeneous catalysts on the surface of the PS/PANI microspheres had no effect on the morphology (Scheme 1).

The elemental maps showed additional evidence of the existence and distribution of Cu^{2+} and other elements in

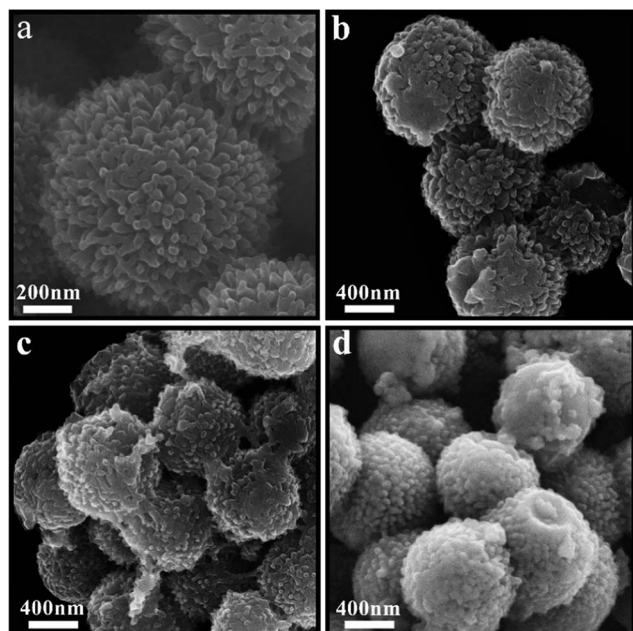


Fig. 1 SEM images of PS/PANI microspheres (a), PS/PANI@CuCl₂ catalyst (b), PS/PANI@Cu(NO₃)₂ catalyst (c) and PS/PANI@Cu(OSO₂CF₃)₂ catalyst (d).

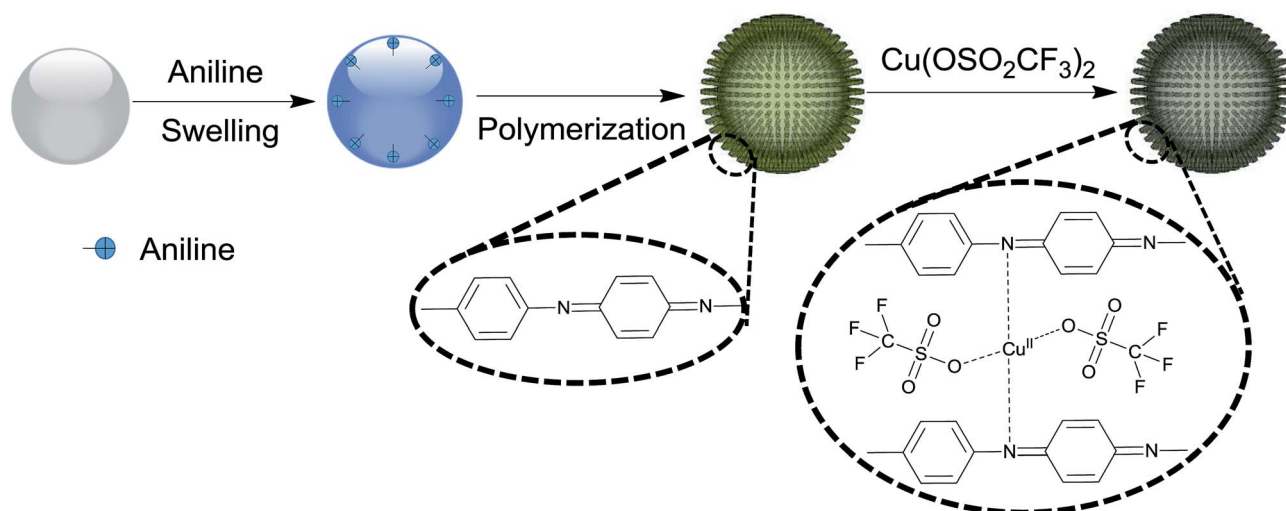
corresponding anions (Fig. 2 and S3[†]). PS/PANI@CuCl₂ anchored the most amount of copper(II) species among three supported catalysts may be affected by steric hindrance of anion. In comparison to counterions NO₃[−] and CF₃SO₃[−], the smallest anion, Cl[−], has the smallest ionic radii and has very little bulk with PANI-imine bound Cu²⁺. The small radii of Cl[−] results the exceptionally high copper loadings in PS/PANI@CuCl₂ catalyst. The amount of Cu(II) was determined by ICP results, the contents of Cu in PS/PANI@CuCl₂, PS/PANI@Cu(NO₃)₂ and PS/PANI@Cu(OSO₂CF₃)₂ were 5.25 wt%, 1.79 wt% and 1.54 wt%, respectively. The thermal stability of the heterogeneous catalysts

were examined by thermal gravimetric analysis (TGA). The PS/PANI supported copper catalysts showed relatively good thermal stability with the significant weight loss at ~400 °C. The increase of the amount of homogeneous copper species loading on the supports led to the decrease of the weight loss of the supported catalysts according to the TGA results (Fig. S5[†]).

Two intense peaks at 934.9 eV and 954.7 eV were attributable to Cu²⁺ 2p_{3/2} and Cu²⁺ 2p_{1/2}, respectively. Shake-up satellite peaks were also observed at 942.3–944.8 eV, which belongs to the Cu²⁺ species.⁵² The Cu 2p XPS spectra also exhibits two additional peaks centered at 932.4 and 952.2 eV, which were attributable to the coordination between Cu²⁺ species and amino groups.⁵³

The peak-fitted N 1s core-line spectrums of three PS/PANI@Cu(II) composites were shown in Fig. 3. There are three different N species present in the spectra except that of PS/PANI@Cu(NO₃)₂. The peaks attributed to neutral nitrogen in imine (=N−) groups and amine (−NH−) groups along the chain of PANI were at 398.4 and 399.7 eV, respectively. The binding energy of the positively charged nitrogen (N⁺) atoms is at 400.8 eV. The existence of positively charged amine is the result of the attachment of the Cu²⁺ ions to the PS/PANI particles surface. The binding energies of the N species in PS/PANI@Cu(OSO₂CF₃)₂ are shifted to higher regions as the result of the electronegativity of the anions in copper(II) complex. Therefore, the electron withdrawing triflate was the strongest among three different copper catalysts. The spectrum of PS/PANI@Cu(NO₃)₂ exhibited a fourth peak at 406.7 eV which is due to the existence of the N in NO₃[−] group.⁵⁴

Characteristic bands at 1570 cm^{−1} and 1494 cm^{−1} of FTIR spectra (Fig. 4) were assigned to be the stretching deformation of the C=C in quinoid and benzenoid rings, respectively. The absorption bands at 1300 cm^{−1} and 1141 cm^{−1} were attributed to the stretching of C−N of the secondary amines and the bending of C−H.⁵⁵ All four peaks above were observed in PANI supports and three heterogeneous copper catalysts. The area ratios of quinoid rings to benzenoid rings in three supported



Scheme 1 Schematic illustration of the synthesis process of the PS/PANI@Cu(II) catalysts.

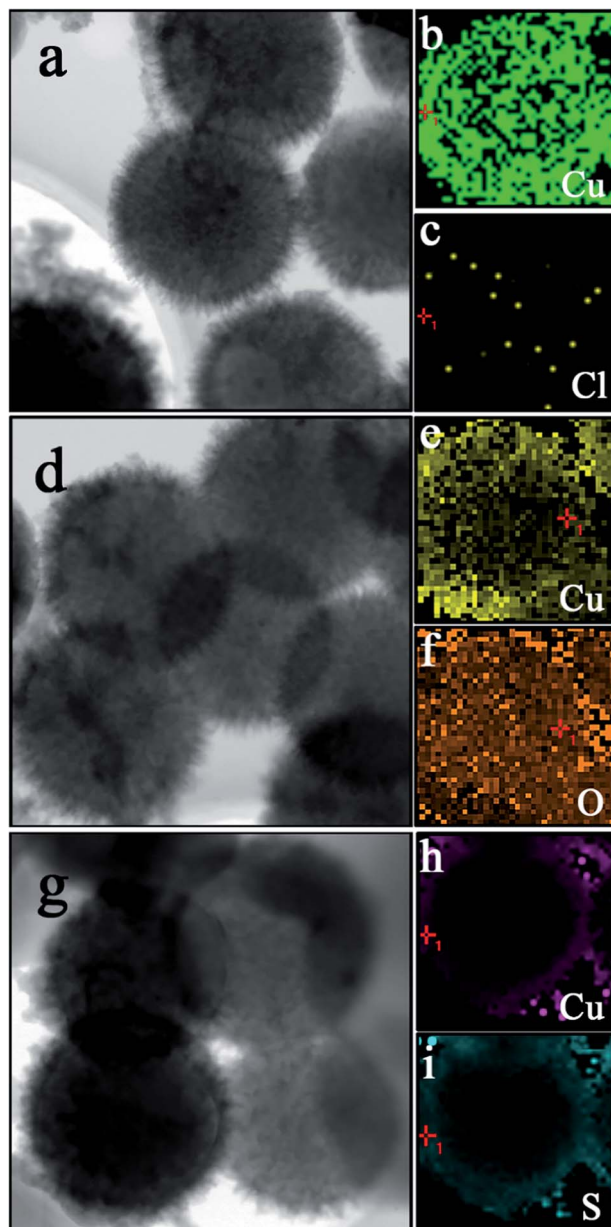


Fig. 2 PS/PANI@CuCl₂: (a) TEM image, (b) EDX elemental maps of Cu, (c) EDX elemental maps of Cl; PS/PANI@Cu(NO₃)₂: (d) TEM image, (e) EDX elemental maps of Cu, (f) EDX elemental maps of O and PS/PANI@Cu(OSO₂CF₃)₂: (g) TEM image, (h) EDX elemental maps of Cu, (i) EDX elemental maps of S.

catalysts were all about 0.6 which showed good agreement with the results calculated by XPS spectra. Due to the difference on the anion of copper salts, the characteristic peaks vary significantly. For PS/PANI@CuCl₂, the characteristic peak at 1600 cm⁻¹ is caused by the vibration of chloride anion. For PS/PANI@Cu(NO₃)₂, the peak at 1380 cm⁻¹ was attributed to asymmetric stretching of NO₃. For PS/PANI@Cu(OSO₂CF₃)₂, peaks at 1248 and 1033 cm⁻¹ are assigned to asymmetric and symmetric vibrations of SO₃, respectively, which are the indicative of the coordination behavior of the triflate ligand.^{56,57}

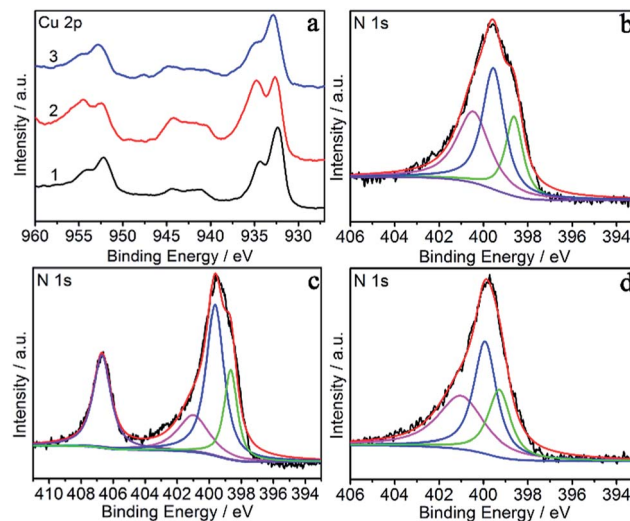


Fig. 3 Cu 2p XPS spectra of three supported catalysts ((1) PS/PANI@CuCl₂, (2) PS/PANI@Cu(NO₃)₂ and (3) PS/PANI@Cu(OSO₂CF₃)₂) (a) and N 1s XPS spectra of PS/PANI@CuCl₂ (b), PS/PANI@Cu(NO₃)₂ (c) and PS/PANI@Cu(OSO₂CF₃)₂ (d).

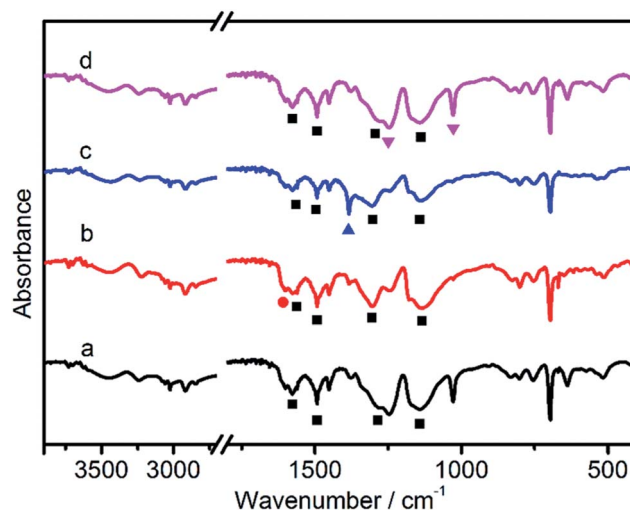
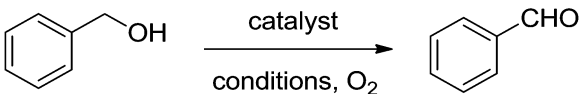


Fig. 4 FTIR spectra of PS/PANI (a), PS/PANI@CuCl₂ (b), PS/PANI@Cu(NO₃)₂ (c) and PS/PANI@Cu(OSO₂CF₃)₂ (d).

3.2 Catalytic aerobic oxidation of alcohol

The aerobic oxidation activity of the as-synthesized supported copper(II) catalysts was evaluated employing alcohol substrates employing TEMPO as the radical initiator.⁵⁸ Benzaldehyde cannot be produced through aerobic oxidation of benzyl alcohol in the absence of catalyst or in the presence of PS/PANI support (Table 1, entries 1 and 2). Decent yield was achieved using PS/PANI@CuCl₂, which suggested the crucial role of copper catalyst (Table 1, entry 3). The amounts of PS/PANI@CuCl₂, PS/PANI@Cu(NO₃)₂ and PS/PANI@Cu(OSO₂CF₃)₂ added in this reaction were 12.1 mg, 35.4 mg and 41.1 mg based on the same Cu loading. The evaluation of all three supported copper catalysts suggested that PS/PANI@Cu(OSO₂CF₃)₂ was the best

Table 1 The optimization of aerobic oxidation of benzyl alcohol^a

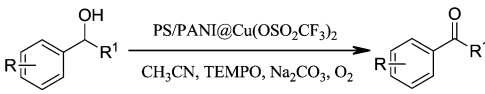
				
Entry	Catalyst	Solvent	Yield ^b	Selectivity ^b
1	—	CH ₃ CN	0%	—
2	PS/PANI	CH ₃ CN	0%	—
3	PS/PANI@CuCl ₂	CH ₃ CN	53%	99%
4	PS/PANI@Cu(NO ₃) ₂	CH ₃ CN	45%	99%
5	PS/PANI@Cu(OSO ₂ CF ₃) ₂	CH ₃ CN	99%	99%
6	PS/PANI@Cu(OSO ₂ CF ₃) ₂	ClCH ₂ CH ₂ Cl	85%	99%
7	PS/PANI@Cu(OSO ₂ CF ₃) ₂	PhCH ₃	72%	99%
8	PS/PANI@Cu(OSO ₂ CF ₃) ₂	EtOH	22%	99%

^a Reaction conditions: alcohol (1 mmol), 1 mol% catalyst based on copper, 5 mL solvent, TEMPO (0.5 mmol), Na₂CO₃ (1 mmol) 75 °C for 24 h, 1 atm O₂. ^b Determined by GC-MS using nitrobenzene as the internal standard.

catalyst (Table 1, entries 3–5). The superb catalytic performance of PS/PANI@Cu(OSO₂CF₃)₂ is attributed to the coordination ability of the anions to the Cu²⁺. The interactions between the copper(II) center and the chloride and nitrate ions are stronger than triflate because triflate anion is known to be weakly coordinated to various metal ions.⁵⁹ Therefore, the alcoholate intermediate can coordinate with the Cu²⁺ in copper triflate complex much easier than the other supported copper salts. Further solvent screens showed that CH₃CN is the most suitable solvent for the benzyl alcohol oxidation (Table 1, entry 6), because of its polarity and ability to stabilize the Cu(I) species formed during the catalytic cycle.⁵⁹ Chlorinated solvents, such as 1,2-dichloroethane, gave slightly compromised yields (Table 1, entry 7). Low polarity solvents, such as toluene, gave only low yield at the standard reaction condition (Table 1, entry 8). Furthermore, alcoholic solvents, such as ethanol, were not suitable due to coordination and competing oxidation reactions.

With the optimal reaction condition on hand, several alcohol substrates were chosen to study the aerobic oxidation catalytic performance of PS/PANI@Cu(OSO₂CF₃)₂ under the optimal reaction condition. Benzyl alcohol was transformed to the corresponding benzaldehyde in 99% yield after 24 h (Table 2, entry 1). For aerobic oxidation of benzyl alcohol, the turnover frequency (TOF) was calculated to be 4.125 h⁻¹ using PS/PANI@Cu(OSO₂CF₃)₂ as catalyst. In the meanwhile, M. F. Semmelhack reported homogeneous TEMPO/CuCl system with TOF of 4.7 h⁻¹ for aerobic oxidation of benzyl alcohol.⁶⁰ Roger A. Sheldon reported PIPO/CuCl catalyzed aerobic oxidation of benzyl alcohol with a TOF of 2.3 h⁻¹ in dimethylformamide (DMF) solvent.⁶¹ MCM-41-ether-TEMPO/CuCl synthesized by D. Brunel gave an average TOF of 0.5 h⁻¹ in aerobic oxidation of benzyl alcohol reaction.⁶² The TOF of benzyl alcohol catalyzed by Cu–Mn oxide/C oxidation was calculated to be 5.8 h⁻¹ at 80–100 °C in CH₂Cl₂.⁶³ The efficiency of our heterogeneous catalytic




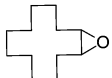




Table 2 Benzylic alcohol aerobic oxidation using PS/PANI@Cu(OSO₂CF₃)₂ catalyst^a

				
Entry	Substrate	Product	Conversion ^b	Selectivity ^b
1			99%	99%
2			95%	99%
3			99%	99%
4			92%	99%
5			65%	99%
6			33%	99%
7			57%	99%
8			92%	99%
9			5%	99%

^a Reaction conditions: alcohol (1 mmol), 1 mol% PS/PANI@Cu(OSO₂CF₃)₂ catalyst, 5 mL acetonitrile, TEMPO (0.5 mmol), Na₂CO₃ (1 mmol), 75 °C for 24 h, 1 atm O₂. ^b Determined by GC-MS.

system is comparable to other efficient aerobic oxidation system. *p*-Methyl benzyl alcohol also reacted smoothly under the same reaction conditions (Table 2, entry 2). Electron-rich benzylic alcohols, such as *p*-methoxy benzylic alcohol and *m*-methoxy benzylic alcohol were suitable reactive under the optimal reaction conditions, which gave 99% and 92% yield, respectively (entries 3 and 4). Electron-withdrawing functional groups were tolerated utilizing PS/PANI@Cu(OSO₂CF₃)₂ catalyst, however, compromised yields were observed for *p*-F and *o*-F benzylic alcohols due to lower reactivity (entries 5 and 6). Hetero-aromatic alcohol, 2-thiophenemethanol, reacted well in the presence of the as-synthesized catalyst (entry 7). In order to test the transformation from secondary alcohols to ketone, 1-phenylethanol was catalyzed to acetophenone as the model reaction. Cinnamyl alcohol was also evaluated as the allylic alcohol and cinnamaldehyde was formed as the only product in 92% yield (Table 3, entry 8). Unfortunately, our catalytic system is not compatible with secondary alcohols, such as 1-phenylethanol, and low conversions were observed. Prolonged reaction time

Table 3 Epoxidation of olefins using PS/PANI@Cu(OSO₂CF₃)₂ catalyst with oxygen^a

$ \begin{array}{c} \text{R}_1 \quad \text{R}_3 \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{R}_2 \quad \text{R}_4 \end{array} \xrightarrow[\text{CHO, O}_2, \text{CH}_3\text{CN}]{\text{PS/PANI@Cu(OSO}_2\text{CF}_3)_2} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{R}_1 \text{---} \text{C} \text{---} \text{C} \text{---} \text{R}_3 \\ \diagdown \quad \diagup \\ \text{R}_2 \quad \text{R}_4 \end{array} $					
Entry	Substrate	Product	Time (h)	Conversion ^b (%)	Selectivity ^b (%)
1			18	>99	>99
2			30	65	>99
3			48	50	>99
4			9	>99	>99

^a Reaction conditions: olefin (1 mmol), 0.2 mol% PS/PANI@Cu(OSO₂CF₃)₂ catalyst, 5 mL acetonitrile, trimethylacetaldehyde (2 mmol), room temperature, 1 atm O₂. ^b Determined by GC-MS.

and increased reaction temperature did not improve the yields of the desired acetophenone product (Table 2, entry 9).

Hot filtration test was conducted to confirm the heterogeneous nature of the aerobic oxidation catalysis with PS/PANI@Cu(OSO₂CF₃)₂. The PS/PANI@Cu(OSO₂CF₃)₂ catalyst was centrifuged and isolated at 9 h and the mixture was stirred for another 15 h at 75 °C. The increase in conversion was stopped after the filtration step, and the yield of aldehyde remained 65% (Fig. 5). This result indicated Cu(OSO₂CF₃)₂ was strongly bound to the surface of the PS/PANI support and only very trace amounts of Cu²⁺ species exist in solution.

3.3 Catalytic aerobic epoxidation of olefins

The catalytic activity was further extended to the epoxidation of a variety of olefins in the presence of molecule oxygen. The

aerobic epoxidation of cyclic alkenes were evaluated by PS/PANI@Cu(OSO₂CF₃)₂ in acetonitrile at room temperature. The results of the catalytic epoxidation are listed in Table 3. Bulkier cycloalkenes such as cyclooctene, cyclododecene and norbornene were transformed to corresponding epoxides with excellent selectivity. The aerobic oxidation of cyclooctene reacted smoothly exhibiting remarkable conversion over 99% of cyclooctene oxide as the sole product. Cyclododecene resulted in moderate yields of cyclododecene oxide (conversion 65%, selectivity 99%). Poor yield of *exo*-epoxynorbornane was obtained even after a reaction time of 48 h. The tri-substituted alkene such as α-pinene resulted in α-pinene oxide with high selectivity and conversion of over 99% (Table 3, entry 4). For aerobic olefin epoxidation reaction, PS/PANI@Cu(OSO₂CF₃)₂ catalyzed cyclooctene epoxidation and α-pinene with TOF of 27.5 h⁻¹ and 55 h⁻¹, respectively. This result is significantly higher than literature reported TOF for epoxidation reaction. Shun-Ichi Murahashi synthesized copper-crown ether catalyzed olefins epoxidation using oxygen as oxidant with TOF of 5.82 h⁻¹.⁶⁴ Shun-Ichi Murahashi reported Cu(OH)₂ catalyzed olefin epoxidation with TOF of 5.88 h⁻¹.⁶⁵

The recyclability of aerobic oxidation of benzyl alcohol and cyclooctene were studied at 75 °C and room temperature, respectively, utilizing the PS/PANI@Cu(OSO₂CF₃)₂ catalyst in acetonitrile. Six recycling tests of PS/PANI@Cu(OSO₂CF₃)₂ catalyst were carried out and the selectivity of the product was retained at 99%. Conversion of benzyl alcohol and cyclooctene maintained 90% and 94%, respectively, with slight loss compared with the first run. Yields of benzaldehyde decreased a little more than that of cyclooctene oxide during the each successive reaction because of the higher reaction temperature (Fig. 6). The high conversion and selectivity after six cycles indicated the high stability of supported copper heterogeneous catalyst and low leakage of copper ion. FTIR spectrum showed

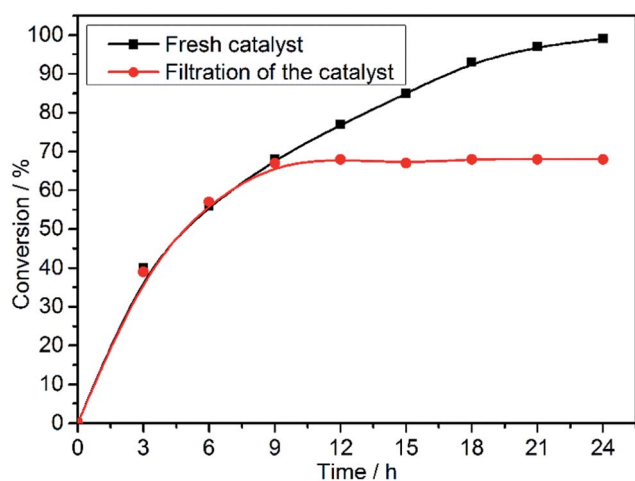


Fig. 5 Leaching test for benzyl alcohol oxidation catalyzed by PS/PANI@Cu(OSO₂CF₃)₂.

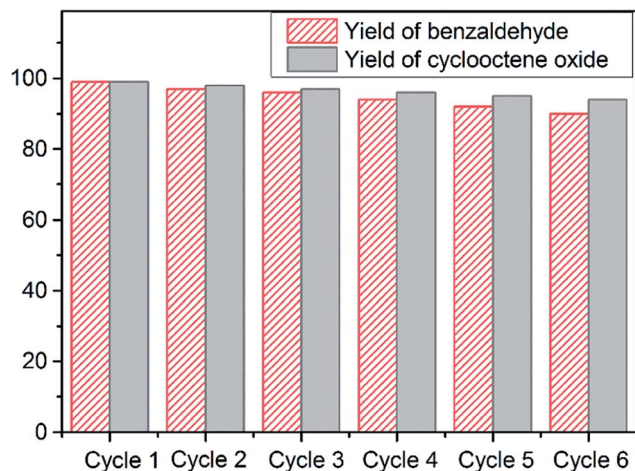


Fig. 6 Recycling tests of PS/PANI@Cu(OSO₂CF₃)₂ for benzyl alcohol (red) and cyclooctene (gray) oxidation.

no obvious difference between fresh PS/PANI@Cu(OSO₂CF₃)₂ and the one after six uses (Fig. S4†).

4. Conclusions

In summary, three novel supported copper(II) catalysts have been prepared by anchoring homogeneous copper(II) salts onto the hierarchical PS/PANI microspheres. Selective aerobic oxidation of the alcohols were studied utilizing supported copper(II) catalysts in different solvents. PS/PANI@Cu(OSO₂CF₃)₂ catalysts showed the best catalytic activity towards the aerobic oxidation of the alcohols and a wide variety of alcohol substrates were tolerated. The great activity of as-synthesized PS/PANI@Cu(OSO₂CF₃)₂ was further extend to catalyze the aerobic epoxidation reaction. The catalytic activity of heterogeneous catalysts was maintained without significant loss of yield after six recycles, which indicated the high stability of the as-synthesized PS/PANI@Cu(OSO₂CF₃)₂ catalyst during the reaction. These results indicate the advantages and great immobilization ability of the PANI support.

Acknowledgements

We thank the National High Technology Research and the Development Program of China (863 Program) (no. 2013AA031702) and Beijing Natural Science Foundation (Grant no. 2144052) for financial support.

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