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Introduction

The replacement of conventional mineral liquid acids by solid acids for green chemistry has been intensively investigated because of environmental considerations and safety concerns.¹⁻⁶ In the past years, various types of solid acid catalysts have been developed, including zeolites,⁷⁻⁹ sulfated metal oxides,10-12 and polymer based resins13,14 etc. Among these solid acid catalysts, commercially available sulfonated ion-exchange resins (IERs), represented by Amberlyst®-15 with an acidic exchange capacity as high as 4.7 mmol g^{-1} , are widely used in a wide range of acid-catalyzed liquid phase reactions. However, the IERs do not exhibit high activity because most of the acidic sites buried within the polymer beads are inaccessible in many reactions owing to their low surface areas and lack of porosity.¹⁵⁻¹⁸ Recently, Xiao and co-workers have successfully synthesized mesoporous polymer based solid acids which showed superior catalytic activities in esterification and

Designed synthesis of sulfonated polystyrene/ mesoporous silica hollow nanospheres as efficient solid acid catalysts[†]

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We report the successful synthesis of hybrid hollow nanospheres (HNs) with sulfonated polystyrene (PS– SO_3H) aligned uniformly in the mesoporous channel of a silica shell. The fabrication process involved the sulfonation of silica HNs with polystyrene highly dispersed in the mesoporous shell which was prepared by co-condensation of a mixture of tetraethoxysilane (TEOS) and alkoxysilyl-functionalized poly(methyl acrylate) (PMA) around PS nanospheres in a base medium using cetyltrimethylammonium bromide (CTAB) as structural directing agent followed by THF treatment. The surface properties of the hybrid HNs were adjusted by the amount of PMA incorporated in the silica shell during the synthesis process and also by modification with an octyl group through a grafting method. The hybrid HNs, with acid exchange capacity in the range 0.8 to 2.0 mmol g⁻¹, could efficiently catalyze the esterification reaction of lauric acid with ethanol. All hybrid HNs show much higher activity than commercial Amberlyst®-15 catalyst and the TOF of the optimized hybrid HNs is almost identical to that of concentrated sulfuric acid. The high activity of the hybrid HNs is mainly attributed to the uniform distribution of the PS–SO₃H group in the mesoporous silica shell, the penetrating mesopore, and surface hydrophobicity. It was found that the recycle stability of hybrid HNs could be enhanced greatly by octyl group modification, which may prevent the leaching of PS–SO₃H during the catalytic process.

acylation reactions due to their high surface areas, abundant mesoporosity, and high concentration of sulfonic acid groups.^{4,5} Thus, increasing the surface area and pore volume is of extreme importance for improving the catalytic performance of IERs.

Owing to their outstanding properties, such as high surface areas, large pore volumes, tunable pores sizes, and variable morphologies, mesoporous silicas have attracted much research interest and activity since their discovery.19-27 Recently, different kinds of polymer-mesoporous silicas have been synthesized due to the combined advantages from both the polymers with versatile functional groups and mesoporous silicas with high thermal stability, ordered porous structure, and high surface area.²⁸⁻³² The general strategies to incorporate polymer building blocks into mesoporous silicas involve in situ polymerization in the channels of mesoporous silicas,^{32,33} a post grafting approach,³¹ construction of mesoporous silicas in the presence of polymers,34 and so on. Usually, it is difficult to fabricate polymer-mesoporous silicas with high polymer content by these methods owing to the threat of mesostructure damage or pore blocking, and because the lack of effective interactions between polymer and silica prevent the leakage of polymers. Furthermore, most polymer-silica hybrid materials do not have a well defined morphology, therefore high accessibility of the active sites and fast diffusion of the reactants and the products cannot be guaranteed.



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Paper

Previous studies have shown that the morphology of solid catalysts greatly affects their catalytic performance because of the influence of morphology on the diffusion length of the reactants and products, the exposure degree of active sites, the crystalline phase, and so on. Recently, solid catalysts with the morphology of hollow nanospheres (HNs) have attracted much attention because the shortened diffusion lengths can not only increase the reaction rates, but also can improve selectivity by decreasing the possibility for side reactions, especially for the deep reactions of the unstable products.^{26,35-40} Recently, our group found that silica hollow nanospheres, with chiral functional groups and SO₃H/Pd incorporated in the shells of HNs, are efficient solid catalysts for asymmetric reactions and one-pot synthesis of methyl isobutyl ketone from acetone, respectively.36,38 Zeng and co-workers reported that H₄SiMo₁₂O₄₀ functionalized silica HNs exhibited excellent catalytic activity toward benzylation of toluene.40 However, the use of hollow nanospheres as catalysts is still in its infancy.

Recently, we found that dissolved polymer could be retained in the mesoporous silica shell functionalized with polymer fragments during the synthesis of silica HNs using polymer nanospheres as hard templates.⁴¹ Based on this finding, we report the fabrication of efficient solid acid catalysts, PS–SO₃H/PMA–SiO₂ HNs (PS: polystyrene; PAM: poly(methyl acrylate)) with high content of polymers (66.4 wt%) aligned uniformly in the mesoporous silica shell through sulfonation of PS/PMA–SiO₂ HNs which were synthesized by diffusion of PS core into the mesoporous silica shell functionalized with PMA fragments. The catalytic performance of hybrid solid acids was tested in the esterification of fatty acids with ethanol, therefore, the relation of polymer content and surface modification with catalytic performance was investigated.

Experimental section

Chemicals and reagents

All materials were of analytical grade and used as received without any further purification, with the exception of styrene. Styrene was washed through an inhibitor remover column and distilled under vacuum before use. Cetyltrimethylammonium bromide (CTAB) and [3-(methacryloxy)propyl]-trimethoxysilane (3-MOP, 98%) were purchased from Sigma-Aldrich Company Ltd. (USA). Tetraethoxysilane (TEOS) was obtained from Nanjing Shuguang Chemical Group (China). Methyl methacrylate (MMA, 98%), potassium persulfate (K₂S₂O₈), azobisisbutyronitrile (AIBN), tetrahydrofuran (THF), ethylether, and other reagents were purchased from Shanghai Chemical Reagent, Inc. of the Chinese Medicine Group. Poly(methacrylate)-organosilane (PMA-Si) was synthesized by free radical polymerization of [3-(methacryloxy)propyl]-trimethoxysilane (3-MOP) and methacrylate monomer (MA), initiated by AIBN, according to our previous report.41,42 The PS template spheres were prepared by emulsion polymerization in a water system according to a modified method.43

Synthetic procedures

Synthesis of PS/nPMA-SiO₂ HNs and PS/SiO₂ HNs. PS/ nPMA-SiO₂ HNs were synthesized under basic conditions using

CTAB as surfactant micellar templates, PS nanospheres as cotemplates of hollow nanospheres, and PMA-Si and TEOS as precursors. In a typical synthesis, 0.20 g of CTAB was dissolved in a mixed solvent prepared from 60 mL of deionized water and 20 mL of ethanol at 50 °C then stirred for 30 minutes. Next, the desired amount (0.1 to 0.20 g) of PS nanospheres, dispersed in 2 mL of deionized water by sonication for 30 minutes, were added to the above mixture and the mixture was stirred at 50 °C for another 30 minutes, followed by the addition of 0.7 mL of ammonium hydroxide solution (25%). TEOS, at a concentration of 0.625 g in 2 mL of ethanol, was mixed with 0.50 g of PMA-Si in 2 mL of THF. Ten minutes later, the mixture was added dropwise under constant stirring. After stirring for 2 hours at 50 °C, the mixture was transferred into a Teflon-lined autoclave and aged at 100 °C, under static conditions, for 36 hours. The solid product was recovered by filtration, washed with water and ethanol, and dried at 60 °C overnight. After surfactant extraction in ethanol-HCl (0.75 wt% of HCl), PS/nPMA-SiO₂ core shell nanospheres (CSNs) were obtained. Then, the solid product (1 g) was dispersed in 200 mL of THF and the mixture was heated at 60 °C for 12 hours. After centrifugation and washing with ethanol, $PS/nPMA-SiO_2$ HNs were obtained, where n (n =2.5, 3.3, and 5) denotes the weight ratio of PMA-Si to PS used in the synthesis process.

In a controlled experiment, PS/SiO_2 HNs were synthesized in a similar method to $PS/5PMA-SiO_2$ HNs except 0.65 g TEOS was used as the silica precursor

In a controlled experiment, SiO_2 HNs were obtained *via* calcination of the sample PS/SiO₂ HNs under air.

Modification of PS/2.5PMA–SiO₂ HNs with octyl group. PS/ 2.5PMA–C8–SiO₂ CSNs was synthesized by dispersing PS/ 2.5PMA–SiO₂ CSNs in 100 mL *n*-hexane containing 8 mmol of octyltriethoxysilane and refluxing the mixture at 70 °C for 24 hours. Then, the solid products were isolated and dried at 60 °C overnight. The following ethanol–HCl extraction and THF treatment process was almost identical to that of PS/2.5PMA– SiO₂ HNs. Finally, PS/2.5PMA–C8–SiO₂ HNs was obtained.

Sulfonation of PS/*n*PMA-SiO₂ HNs, PS/SiO₂ HNs, PS/ 2.5PMA-C8-SiO₂ HNs and SiO₂ HNs. 1 g of hybrid HNs was outgassed at 120 °C under vacuum in a two-necked round flask for 3 hours. Then, 50 mL of CH_2Cl_2 containing 10 mL of chlorosulfonic acid was added to the flask at 0 °C. The solution was stirred for 12 hours under an argon atmosphere. The suspension was washed with copious amounts of water until the filtrate was neutral. After centrifugation and washing with ethanol, the powder products were dried at 60 °C overnight. The resulting powder products were denoted accordingly as PS-SO₃H/*n*PMA-SiO₂ HNs, PS-SO₃H/SiO₂ HNs, and PS-SO₃H/ 2.5PMA-C8-SiO₂ HNs by using PS/*n*PMA-SiO₂ HNs, PS/SiO₂ HNs, and PS/2.5PMA-C8-SiO₂ HNs as precursor, respectively.

Esterification of fatty acid with ethanol

The esterification of lauric acid with ethanol was carried out in a two-necked round flask equipped with a reflux condenser and a magnetic stirrer. The catalyst was pretreated at 120 $^{\circ}$ C under vacuum for 3 hours. In a typical run, 5 mL of ethanol and

2 mmol of lauric acid were added to the flask containing 0.05 g of catalyst. The mixture was stirred at 80 °C and the aliquot was withdrawn by a syringe at regular intervals and analyzed using a precalibrated gas chromatograph (Agilent 6890) equipped with an FID detector and PEG capillary column (30 m \times 0.25 mm \times 0.25 um). Tetradecane was used as the internal standard.

To recycle the solid acid catalyst, the catalyst was filtered from the reaction system, thoroughly washed with ethanol, dried under vacuum at 60 $^{\circ}$ C overnight, and directly used in the next cycle.

Characterization

The nitrogen sorption experiments were performed at 77 K using a Micromeritrics ASAP 2020. Samples were degassed at 120 °C for 6 hours prior to the measurements. The BET surface area was calculated from the adsorption data in the relative pressure P/P_0 range from 0.04 to 0.2. Pore size distributions were determined from the adsorption branches using the Barret-Joyner-Halenda (BJH) method. Pore volume was estimated at the relative pressure P/P_0 of 0.99. Transmission electron microscopy (TEM) was performed on a HITACHI 7700 at an acceleration voltage of 100 kV. High resolution transmission electron microscopy (HR-TEM) was performed on a FEI Tecnai G2 F30 S-Twin at an acceleration voltage of 300 kV. Before measurement, the sample was dispersed in ethanol and deposited on a holey carbon film on a Cu grid. SEM was undertaken by using a FEI Quanta 200F scanning electron microscope operating at an acceleration voltage of 1-30 kV. High-resolution scanning electron microscopy (HR-SEM) was undertaken on a HITACHI S-4800 scanning electron microscope operating at an acceleration voltage of 1-20 kV. FT-IR spectra were collected with a Nicolet Nexus 470 IR spectrometer (KBr pellets were prepared) in the range 400–4000 cm^{-1} . S elemental analyses were determined by means of an Elementary Vario EL III analyzer. The MAS ¹³C NMR spectra were recorded on a Bruker DRX-400. The experimental parameters were as follows: 8 kHz spin rate, 3 s pulse delay, 4 min contact time, and 1000 scans. The acidic property of the solid materials was monitored with reference to the ³¹P NMR chemical shift of triethylphosphine oxide (TEPO) chemically adsorbed on the solid acid catalysts. ³¹P NMR spectra were performed on a Bruker Avance III 600 spectrometer operating at a frequency of 242.9 MHz using a 4 mm MAS probe. ³¹P MAS NMR spectra were recorded using high-power proton decoupling with a spinning rate of 12 kHz. One hundred scans were accumulated with a $\pi/4$ pulse width of 2.25 μ s and a 30 s recycle delay. The chemical shift spectra were referenced to an 85 wt% phosphoric acid external standard. X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG ESCALAB MK2 system, using an aluminium Ka X-ray source at 250 W and 12.5 kV. The thermogravimetric analysis (TGA) was performed using a NETZSCH STA 449F3 analyzer from 30 °C to 900 °C at a heating rate of 10 °C min⁻¹ under air atmosphere. The adsorption of water and benzene vapors was measured at 273 K on a Hiden Isochema Intelligent Gravimetric Analyzer after the sample was degassed for 6 h at 393 K. The ultrapure water and benzene used in the

vapor adsorption experiments were both treated by a freezepump-thaw technique for three cycles prior to the adsorption.

The acid exchange capacity of the catalysts was determined by acid-base titration with a standard NaOH solution. In a typical procedure, 0.05 g of solid was degassed at 120 °C for 3 hours followed by the sample being suspended in 25 mL of 2 M aqueous NaCl solution. The resulting suspension was stirred at room temperature for 24 hours until equilibrium was reached and, subsequently, titrated with standard NaOH solution.

Results and discussion

Synthesis of $\mathrm{PS}/n\mathrm{PMA}-\mathrm{SiO}_2$ HNs and $\mathrm{PS}-\mathrm{SO}_3\mathrm{H}/n\mathrm{PMA}-\mathrm{SiO}_2$ HNs

PS-SO₃H/nPMA-SiO₂ HNs were obtained by sulfonation of PS/ nPMA-SiO₂ HNs with chlorosulfonic acid (Scheme 1). Polymer nanospheres, such as polystyrene (PS), poly(methyl methacrylat) (PMMA) etc., have been widely used as hard templates for the synthesis of hollow nanospheres.43-47 After hard template removal, either by calcination or an extraction method, the hollow nanostructure was generated. In our previous report,41 it was found that the dissolved PMMA chains could be kept in the mesochannels of silica shells for the formation of hybrid silica HNs with a high concentration of PMMA based on the "dissolution and entrapment" strategy, which was proposed for the first time. Specifically, the functional group PMA poly-(methacrylate), which is incorporated into the mesoporous SiO₂ shell, can efficiently entrap the dissolved PMMA. Here, a similar strategy was employed for the synthesis of PS/nPMA-SiO₂ HNs (Scheme 1). In the first step, PS nanospheres were coated with a mixture of TEOS and PMA-Si using CTAB as the mesostructure directing agent according to a modified Stöber method.48 During the sol-gel process, the hydrolysis and polymerization of TEOS and PMA-Si formed a hybrid mesoporous shell on the PS template nanospheres and, consequently, PS/nPMA-SiO₂ core shell nanospheres (CSNs) were obtained (Fig. 1 and S1[†]). After THF treatment, PS/nPMA-SiO₂ HNs were obtained. The successful transformation from core shell to hollow nanospheres after THF treatment is shown in Fig. 1, using PS/5PMA-



Scheme 1 General procedure for the synthesis of mesoporous silica HNs with uniform distribution of PMA and sulfonated PS.



Fig. 1 TEM images of PS template nanospheres (A), PS/5PMA–SiO₂ CSNs (B) and PS/5MA–SiO₂ HNs (C).

 SiO_2 HNs as a representative. It should be mentioned that the particle size of PS/5PMA-SiO₂ HNs remains unchanged after THF treatment, thus exhibiting that the dissolved PS is mainly distributed in the mesopore of the shell. The above result clearly suggests that the dissolution of PS cores during the THF extraction process is the driving force for the formation of the hollowed structure. The loading of PS could be facilely tuned by varying the ratio of PS to silica precursor during the silica coating process.

As a control sample, PS/SiO₂ HNs, without PMA-Si incorporated in the shell, were prepared in a similar way to PS/5PMA-SiO₂ HNs. The results of thermo gravimetric analysis (TG) show that weight loss for PS/SiO₂ HNs and PS/5PMA-SiO₂ HNs before and after THF treatment was 10% and 3.65 wt%, respectively (Fig. S2†). These results indicate that the PMA-Si incorporated into the mesoporous shell can efficiently entrap the dissolved PS in the mesoporous shell. The sulfonation of PS/5PMA-SiO₂ HNs and PS/SiO₂ HNs results in the formation of hybrid solid acids.

Characterization of PS/nPMA-SiO₂ HNs

The TEM images of $PS/nPMA-SiO_2$ HNs and PS/SiO_2 HNs are shown in Fig. 2. The TEM images show that all samples are

Fig. 2 TEM images of PS/2.5PMA-SiO₂ HNs (A), PS/3.3PMA-SiO₂ HNs (B), PS/SiO₂ HNs (C) and PS/2.5PMA-C8-SiO₂ HNs (D).

monodispersed hollow nanospheres, and the particle size increases as the ratio of PMA-Si silane precursor to PS increases. The particle size increased from about 340 nm to 400 nm as the *n* increase from 2.5 to 5. Accordingly, the thickness of the hybrid silica shells also increased from 50 nm to 80 nm. This is reasonable because more silane precursors are used as the *n* increases. Based on the TEM image, PS/*n*PMA-SiO₂ HNs and PS/SiO₂ HNs all have the mesoporous channels aligning perpendicular to the cores, which would benefit the diffusion of reactants and products during the catalytic process. In comparison to PS/SiO₂ HNs, PS/nPMA-SiO₂ HNs have larger mesopores and a less condensed shell. For surface modification, PS/2.5PMA-SiO₂ HNs were grafted with octyl for the generation PS/2.5PMA-C8-SiO2 HNs. PS/2.5PMA-C8-SiO2 HNs have the same morphology as the parent PS/2.5PMA-SiO₂ HNs based on the TEM characterization, showing that the grafting process does not damage the nanostructure and morphology of the hybrid HNs (Fig. 2).

The textural properties of the obtained hybrid hollow nanospheres were investigated by nitrogen adsorptiondesorption at 77 K. Fig. 3A and B show the N2 adsorptiondesorption isotherms and corresponding pore size distribution of PS/SiO₂ HNs and PS/nPMA-SiO₂ HNs, respectively. The adsorption-desorption isotherms of the samples display type-IV isotherm patterns which is typical for mesoporous silica synthesized with CTAB as a surfactant.⁴⁰ PS/SiO₂ HNs exhibit a sharp capillary condensation step at P/P_0 less than 0.3, while PS/ *n*PMA-SiO₂ HNs show an H4-type hysteresis loop starting from the relative pressure P/P_0 at 0.45, indicating that PS/nPMA-SiO₂ HNs have larger mesopores than PS/SiO₂ HNs. This is also verified by the pore size distribution curves and consistency with the TEM results. The pore size distribution curves also show that PS/SiO₂ HNs have a more uniform distribution of mesopores than PS/nPMA-SiO₂ HNs, probably due to the interruption of the PMA polymer chain on the mesostructure formation. The textural parameters of PS/SiO2 HNs and PS/ nPMA-SiO₂ HNs are summarized in Table 1. The BET surface area of PS/SiO₂ HNs and PS/nPMA-SiO₂ HNs varies in the range



Fig. 3 N₂ adsorption–desorption isotherms (A) and the pore size distribution curves of PS/SiO₂ HNs (a), PS/5PMA–SiO₂ HNs (b), PS/ 3.3PMA–SiO₂ HNs (c), PS/2.5PMA–SiO₂ HNs (d) and PS/2.5PMA–C8–SiO₂ HNs (e).

Table 1 The textural parameters and polymer content of PS/nPMA-SiO₂ HNs and PS/SiO₂ HNs before and after sulfonation^a

Samples	$S_{ m BET} \left({ m m}^2 ~{ m g}^{-1} ight)$	D_{p}^{b} (nm)	$V_{\rm p} ({\rm cm}^3 {\rm g}^{-1})$	Polymer content ^c (wt%)	
PS/SiO ₂ HNs	297 (331)	2.2 (2.5)	0.19 (0.30)	32.5	
PS/5PMA-SiO ₂	180 (149)	5.5 (6.4)	0.26 (0.21)	64.2	
PS/3.3PMA-SiO ₂	153 (164)	4.4 (4.8)	0.21 (0.21)	66.4	
PS/2.5PMA-SiO ₂	89 (128)	5.4(4.4)	0.14(0.14)	68.2	
PS/2.5PMA-C8-SiO ₂	88 (115)	5.8 (4.2)	0.12 (0.13)	72	
Amberlyst®-15	(45)	(40)	(0.31)	_	
		,			

^{*a*} Data in parentheses are for the samples after sulfonation. ^{*b*} Pore size distribution estimated from BJH model. ^{*c*} Polymer content estimated based on TG results.

89 to 297 m² g⁻¹ and pore volume varies in the range 0.14 to 0.26 cm³ g⁻¹. In comparison to PS/2.5PMA-SiO₂ HNs, only a slight decrease in the BET surface area was observed for PS/2.5PMA-C8-SiO₂ HNs.

Based on the TG analysis, the polymer content was calculated by the weight loss in the range 200–700 °C (Table 1 and Fig. S3†). The weight loss of PS/SiO₂ HNs, in the temperature range 200–700 °C, is 32.5%. For the PS/*n*PMA–SiO₂ HNs, much higher polymer content was obtained because of the introduction of the PMA polymer. PS/5PMA–SiO₂ HNs affords a weight loss of 64.2%. From PS/5PMA–SiO₂ HNs to PS/2.5PMA–SiO₂ HNs, only about a 5.3% increase in weight loss was observed, indicating that the polymer–silica weight ratio has an upper limit in the hybrid HNs. The above results show that PS/*n*PMA–SiO₂ HNs with high PS and PMA contents, have been successfully synthesized. The weight loss of PS/2.5PMA–C8–SiO₂ HNs is about 3.8% higher than PS/2.5PMA–SiO₂ HNs based on the TG results (Fig. S4†).

Characterization of PS-SO₃H/nPMA-SiO₂ HNs

PS-SO₃H/SiO₂ HNs, PS-SO₃H/*n*PMA-SiO₂ HNs, and PS-SO₃H/ 2.5PMA-C8-SiO₂ HNs were obtained by direct sulfonation of the corresponding hybrid HNs with ClSO₃H in CH₂Cl₂ at 0 °C for 12 hours. The TEM images of sulfonated hybrid HNs are shown in Fig. 4. PS-SO₃H/SiO₂ HNs, PS-SO₃H/*n*PMA-SiO₂ HNs, and PS-SO₃H/2.5PMA-C8-SiO₂ HNs have a uniform hollow nanostructure with almost identical particle size and shell thickness to the parent hybrid HNs, thus indicating the stability of the hybrid HNs in strongly acid media. Taking PS–SO₃H/SiO₂ as an example, the SEM image (Fig. 4F) clearly shows that the sample after sulfonation has a similar nanospherical morphology to that before sulfonation. The HR-SEM images, shown in Fig. S5,† further verify that all sulfonated hybrid HNs are composed of uniform and mono-dispersed nanospheres with porous rough surfaces.

The successful sulfonation of PS in the hybrid nanospheres was verified by FT-IR, XPS, and ¹³C NMR spectroscopy (Fig. 5, S6 and S7[†]). In the FT-IR spectra (Fig. S6[†]), the appearance of a characteristic vibration of PMA at 1740 cm^{-1} arising from a C= O stretching vibration^{41,42} suggested the successful incorporation of the PMA polymer fragment into the mesoporous network of PS/nPMA-SiO₂ HNs as well as PS-SO₃H/nPMA-SiO₂ HNs. The new peaks, attributed to sulfonic acid groups at 581, 1011, and 1415 cm⁻¹, appeared in the FT-IR spectra of PS–SO₃H/SiO₂ HNs and PS-SO₃H/nPMA-SiO₂, while the intensity of C-H deformation vibration of monosubstituted phenyl groups at 700-750 cm^{-1} decreases. In the XPS spectra (Fig. 5A), the S 2p peak at 173.2 eV was observed, confirming the incorporation of sulfonic acid groups. The ¹³C NMR spectrum of PS-SO₃H/SiO₂ HNs clearly shows a signal at around 142 ppm, which could be assigned to the aromatic carbon coordinated with sulfonic acid groups. These results imply a successful sulfonation of PS with the current sulfonation method (Fig. S7[†]).



Fig. 4 TEM images of $PS-SO_3H/SiO_2$ HNs (A), $PS-SO_3H/2.5PMA-SiO_2$ HNs (B), $PS-SO_3H/3.3PMA-SiO_2$ HNs (C), $PS-SO_3H/5PMA-SiO_2$ HNs (D), $PS-SO_3H/5PMA-C8-SiO_2$ HNs (E) and SEM image of $PS-SO_3H/SiO_2$ HNs (F).

The acid strengths of Amberlyst®-15, PS-SO₃H/SiO₂ HNs and PS-SO₃H/5PMA-SiO₂ HNs were investigated using TEPO (triethylphosphine oxide) as a probe molecule in combination with the ³¹P MAS NMR technique (Fig. 5 B). The ³¹P chemical shift of



Fig. 5 XPS spectra (A) of PS–SO₃H/SiO₂ HNs (a) and PS–SO₃H/5PMA–SiO₂ HNs (b); (B) ³¹P MAS NMR spectra of Amberlyst®-15 (a),⁴⁹ PS–SO₃H/SiO₂ HNs (b) and PS–SO₃H/5PMA–SiO₂ HNs (c).



Fig. 6 TEM images of $PS-SO_3H/5PMA-SiO_2$ HNs (A) and EDS mapping analysis of Si element (B) and S element (C) according to TEM image shown in A.

TEPO, chemisorbed on the acid site, is sensitive to acid strength, and stronger acids will usually lead to larger ^{31}P chemical shifts of TEPO. The ^{31}P NMR spectrum of Amberlyst®-15 exhibits a signal at 89.4 ppm which was assigned to TEPO adsorbed on SO₃H acid sites.⁴⁹ PS–SO₃H/SiO₂ HNs and PS–SO₃H/5PMA–SiO₂ HNs exhibit a signal at 84.5 ppm and 86 ppm, respectively. The lower chemical shift indicates PS–SO₃H/SiO₂ HNs and PS–SO₃H/5PMA–SiO₂ HNs have a weaker acid strength than Amberlyst®-15. However, PS–SO₃H/5PMA–SiO₂ HNs exhibit a larger chemical shift than PS–SO₃H/SiO₂ HNs, thus indicating that the incorporation of PMA polymer could help to enhance the acid strength.

For further illustration of the distribution of sulfonic acid groups in the mesoporous shells of $PS-SO_3H/nPMA-SiO_2$ HNs, HR-TEM element mapping analysis was used as direct evidence for the location of sulfur (Fig. 6). The HR-TEM element mapping images clearly show that the Si and S element was uniformly distributed in the outer shells of the hollow nanospheres. The sulfonic acid groups, located uniformly in the outer shells, may favor the access of reactants to active sites during the catalytic process.

PS/SiO₂ HNs display a sharp diffraction peak at low diffraction angle, showing the sample has an ordered mesoporous structure. A broad diffraction peak was observed in the XRD pattern of PS/5PMA–SiO₂ HNs. This suggests that the incorporation of PMA polymer causes the deterioration of the mesostructure. PS–SO₃H/5PMA–SiO₂ HNs have a similar XRD pattern to that of PS/5PMA–SiO₂ HNs, confirming that the sulfonation process does not cause the destruction of the mesoporous structure (Fig. S8†).

The sulfonated hybrid HNs exhibit type-IV isotherm patterns similar to the parent materials (Fig. 7). It should be mentioned that an obvious H4 hysteresis loop appears in the N₂ isotherm of PS–SO₃H/SiO₂ HNs, which is probably due to the existence of defects caused during the sulfonation process. The textural parameters of the sulfonated hybrid HNs are summarized in Table 1. Only a slight decrease in BET surface area was observed after sulfonation. The BET surface area of the sulfonated hybrid varies in the range 331 to 115 m² g⁻¹, which was much higher than that of Amberlyst®-15.

In order to quantitatively analyze the number of active sites in the sulfonated hybrid HNs, the sulfur content and acid exchange capacity were obtained by element analysis and acidbase titration methods, respectively (Table 2). Increasing the amount of PMA in the hybrid HNs results in a decrease in the



Fig. 7 N₂ adsorption–desorption isotherms (A) and the corresponding pore size distribution of PS–SO₃H/SiO₂ HNs (a), PS–SO₃H/5PMA–SiO₂ HNs (b), PS–SO₃H/3.3PMA–SiO₂ HNs (c), PS–SO₃H/2.5PMA–SiO₂ HNs (d) and PS–SO₃H/2.5PMA–C8–SiO₂ HNs (e).

acid exchange capacity and sulfur content, while higher content of PS in the hybrid HNs benefits a high content of acid sites. The acid exchange capacity of the sulfonated hybrid HNs varies from 0.90 to 2.0 mmol g^{-1} while the sulfur content varies from 0.99 to 2.2 mmol g^{-1} . For the PS-SO₃H/*n*PMA-SiO₂ HNs samples, the acid exchange capacity and the sulfur content were very similar. However, for PS-SO₃H/SiO₂ HNs, the sulfur content was higher than the acid exchange capacity. The H-bond interactions may exist among sulfonic acid groups and hydroxyl groups in the mesoporous shells for PS-SO₃H/SiO₂ HNs, which may reduce the accessibility of acid sites during the titration process. For the PS-SO₃H/nPMA-SiO₂ HNs samples, the incorporation of the polymer PMA may help to weaken the interactions among sulfonic acid groups and silicon hydroxyl groups. Thus, the acid exchange capacity is similar to the sulfur content. Based on the results, we can see that the acid exchange capacity and the sulfur element content were consistent, and this consistency between H⁺ and sulfur suggests that all of the acid sites were available during the titration process.

Catalytic performance of hybrid mesoporous silica hollow nanospheres

Esterification of fatty acids with ethanol was chosen as the model reaction for the investigation of the catalytic performance of the sulfonated hybrid HNs (Table 2). The esterification of fatty acids with alcohol to produce esters represents an important pretreatment step in the production of biodiesel from high free fatty acid feed stocks. Initially, a controlled blank experiment was carried out for the esterification of lauric acid with ethanol and only 1.5% yield of laurate ethyl was obtained. For the sulfonated SiO₂ HNs samples only 4.9% yield of laurate ethyl was obtained, thus indicating that the amount of sulfonic acid groups grafted to surface silanol groups using the same method could be negligible. Under similar reaction conditions, all sulfonated hybrid HNs could efficiently catalyze the reaction, thus showing that the sulfonic acid groups are the active sites for this reaction. The catalytic performance of concentrated

Table 2 The sulfur content, acid exchange capacity and surface properties of sulfonated hybrid HNs and their catalytic performance in the esterification of lauric acid with ethanol

Sample	S content ^{<i>a</i>} (mmol g^{-1})	$H^+ \text{ content}^b$ (mmol g^{-1})	Adsorbed benzene-water molar ratio	TOF (h^{-1})	Yield (%)
H_2SO_4	_	_	_	29.3 ± 0.1	93.7 ± 1.7
Amberlyst®-15	_	4.7	_	2.4 ± 0.1	65.3 ± 0.8
PS-SO ₃ H/SiO ₂ HNs	2.29	2.0	0.08	13.6 ± 0.3	87.8 ± 0.1
PS-SO ₃ H/5PMA-SiO ₂	0.99	0.9	0.11	27.3 ± 0.2	88.9 ± 0.6
PS-SO ₃ H/3.3PMA-SiO ₂	1.43	1.5	0.12	21.1 ± 0.2	91.6 ± 0.2
PS-SO ₃ H/2.5PMA-SiO ₂	1.80	1.9	0.24	16.3 ± 0.1	91.6 ± 0.6
PS-SO ₃ H/2.5PMA-C8-SiO ₂	1.79	1.8	0.27	19.1 ± 0.1	94.7 ± 0.1
SiO ₂ HNs	—	—		—	4.9
^{<i>a</i>} Measured by element analysis	s. ^b Measured by acid	base titration method	1.		

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sulfuric acid and commercially available Amberlyst®-15 was also investigated. Among all samples, concentrated sulfuric acid affords the highest reaction rate (TOF of 29.3 \pm 0.1 h⁻¹) as expected and Amberlyst®-15 gives the lowest reaction rate with a TOF of 2.4 \pm 0.1 h⁻¹. The low activity of Amberlyst®-15 is mainly due to its low surface area. The TOF of the sulfonated hybrid HNs varies in the range 27.3 \pm 0.3 to 16.3 \pm 0.1 h⁻¹. The relatively high activity of PS-SO3H/5PMA-SiO2 HNs and PS-SO₃H/SiO₂ HNs, in comparison with Amberlyst®-15, suggests that PS-SO₃H is uniformly aligned in the mesoporous silica shell and may benefit the increase in accessibility of reactants to the sulfonic acid groups and the mesoporous shell would facilitate the fast diffusion of reactants and products during the catalytic process. Actually, most solid acid catalysts that were reported exhibit much lower activity than H₂SO₄. It should be mentioned that PS–SO₃H/5PMA–SiO₂ HNs with a TOF of 27.3 \pm $0.3 h^{-1}$ is almost as active as H₂SO₄.

Though PS-SO₃H/SiO₂ HNs have a higher BET surface area and acid exchange capacity than PS-SO₃H/nPMA-SiO₂ HNs, PS-SO₃H/nPMA-SiO₂ HNs are more active than PS-SO₃H/SiO₂. It has been reported that PMA is a hydrophobic polymer and its incorporation may modify the surface properties of the hybrid HNs.42 Therefore, water/oil adsorption experiments were performed to investigate the surface hydrophobicity. As reported,^{38,50,51} the water and benzene adsorption capacities at the low relative pressure range ($P/P_0 \leq 0.30$) were used for the calculation (Table 2). The results show that the adsorbed benzene/water molar ratio for PS-SO₃H/nPMA-SiO₂ HNs is higher than that for PS-SO₃H/SiO₂ HNs, showing that PS-SO₃H/ nPMA-SiO₂ HNs have more hydrophobic surface properties than PS-SO₃H/SiO₂ HNs. Therefore, the low activity of PS-SO₃H/ SiO₂ nanocomposites is attributed to their more hydrophilic surface properties and smaller pore size. The octyl modification could further increase the surface hydrophobicity.⁵² PS-SO₃H/ 2.5PMA-C8-SiO₂ HNs, with octyl group incorporation, show a higher activity than PS-SO₃H/2.5PMA-SiO₂ HNs (19.1 \pm 0.1 *versus* 16.3 \pm 0.1 h⁻¹) (BET surface area and pore volume were almost the same for the two samples). In combination with the catalytic results, it could be suggested that a hydrophobic surface is more favorable for obtaining higher catalytic activity. Previous studies suggest that hydrophobicity of the solid catalysts could increase catalytic activity due to the protective effect of acid sites from water attack, the increased diffusion rate of the hydrophobic reactants, and high enrichment effect for the reactants.^{5,52,53} For PS–SO₃H/*n*PMA–SiO₂ HNS, the TOF decreases monotonically with the increase in surface hydrophobicity. This is due to a decrease in the BET surface area because the textural properties also affect the catalytic activity of the solid materials, in addition to the surface properties.

The catalytic stability of the sulfonated hybrid HNs was tested using PS-SO₃H/2.5PMA-SiO₂ HNs and PS-SO₃H/ 2.5PMA-C8-SiO₂ HNs as model catalysts in the esterification of lauric acid with ethanol (Fig. 8). For the second cycle, the yield of ethyl lauric over PS-SO₃H/2.5PMA-SiO₂ HNs decreases sharply from 96.3% to 71.1%. For the next several cycles, the conversion only slightly decreases. After ten cycles, the conversion is about half that of the first cycle. The acid exchange capacity of PS-SO₃H/2.5PMA-SiO₂ HNs after 10 cycles was 1.0 mmol g⁻¹, only half of the fresh catalyst. This shows that the leaching of active sites is the main reason for the deactivation of the hybrid HNs. However, for PS-SO₃H/2.5PMA-C8-SiO₂ HNs after 10 cycles, the conversion only decreases from 96.3 to 79.6%, and the activity of the catalyst could still retain 82% of



Fig. 8 Catalytic recycle stability of $PS-SO_3H/2.5PMA-SiO_2$ HNs (a) and $PS-SO_3H/2.5PMA-C8-SiO_2$ HNs (b) in the esterification of lauric acid with ethanol.

the fresh one. The acid exchange capacity of PS-SO₃H/2.5PMA-C8-SiO₂ HNs after 10 cycles is 1.8 mmol g^{-1} , only slightly lower in comparison with the fresh one (1.9 mmol g^{-1}). The above results suggest that PS-SO₃H/2.5PMA-C8-SiO₂ HNs with octyl group modification are much more stable than PS-SO₃H/ 2.5PMA-SiO₂ HNs without octyl modification, suggesting that the octyl group could efficiently prevent the leaching of active sites during the catalytic process. We hypothesize that the hydrophobic carbon chain may tangle with the sulfonated PS polymer chain to increase its stability during the catalytic process.

Conclusions

In summary, we have demonstrated an efficient strategy for the synthesis of hybrid hollow nanospheres with a high content of sulfonic groups uniformly distributed in mesoporous silica channels. The hybrid HNs have a BET surface area from 115 to 331 m² g⁻¹, and pore size from 2.5 nm to 6.4 nm, depending on the polymer content incorporated in the silica shell. The hybrid HNs could be used as efficient solid acid catalysts for acidcatalyzed liquid reactions, such as esterification of lauric acid with ethanol. The studies show that the incorporation of PMA and surface modification by octyl groups could increase the surface hydrophobicity, which causes an increase in the catalytic activity. Under similar conditions, the hybrid HNs, with optimized surface properties and sulfonic acid content, show comparable activity to concentrated sulfuric acid. The incorporated octyl group could prevent the leaching of PS-SO₃H during the catalytic process, thus, the hybrid HNs could be recycled in a stable manner. Our results provide a new approach for the synthesis of solid acid catalysts by efficiently combining PS-SO₃H and silica and a hollow nanostructure together.

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Notes and references

- 1 A. Corma, Chem. Rev., 1995, 95, 559.
- 2 J. H. Clark, Acc. Chem. Res., 2002, 35, 791.
- 3 G. Busca, Chem. Rev., 2007, 107, 5366.
- 4 F. Liu, X. Meng, Y. Zhang, L. Ren, F. Nawaz and F. Xiao, J. Catal., 2010, 271, 52.
- 5 F. Liu, W. Kong, C. Qi, L. Zhu and F. Xiao, *ACS Catal.*, 2012, 2, 565.
- 6 R. Xing, N. Liu, Y. Liu, H. Wu, Y. Jiang, L. Chen, M. He and P. Wu, *Adv. Funct. Mater.*, 2007, **17**, 2455.
- 7 P. A. Zapata, J. Faria, M. P. Ruiz, R. E. Jentoft and D. E. Resasco, J. Am. Chem. Soc., 2012, 134, 8570.
- 8 F. Bauer, W. H. Chen, E. Biiz, A. Freyer, V. Sauerland and S. Liu, *J. Catal.*, 2007, **251**, 258.
- 9 M. Tamura, W. Chaikittisilp, T. Yokoi and T. Okubo, *Microporous Mesoporous Mater.*, 2008, **112**, 202.

- 10 C. Tagusagawa, A. Takagaki, S. Hayashi and K. Domen, *J. Am. Chem. Soc.*, 2008, **130**, 7230.
- 11 J. B. Joo, A. Vu, Q. Zhang, M. Dahl, M. Gu, F. Zaera and Y. Yin, *ChemSusChem*, 2013, **6**, 2001.
- 12 G. D. Yadav and J. J. Nair, *Microporous Mesoporous Mater.*, 1999, **33**, 1.
- 13 Y. Xu, W. Gu and D. Gin, J. Am. Chem. Soc., 2004, 126, 1616.
- 14 M. A. Harmer, W. E. Farneth and Q. Sun, *J. Am. Chem. Soc.*, 1996, **118**, 7708.
- 15 P. R. Siril, H. E. Cross and D. R. Brown, *J. Mol. Catal. A: Chem.*, 2008, **279**, 63.
- 16 M. A. Harmer and Q. Sun, Appl. Catal., A, 2001, 221, 45.
- 17 M. Hart, G. Fuller and D. R. Brown, *J. Mol. Catal. A: Chem.*, 2002, **182**, 439.
- 18 P. Barbaro and F. Liguori, Chem. Rev., 2009, 109, 515.
- 19 C. T. Kresge and W. J. Roth, Chem. Soc. Rev., 2013, 42, 3663.
- 20 S. Shylesh, P. P. Samuel, S. Sisodiya and A. P. Singh, *Catal. Surv. Asia*, 2008, **12**, 266.
- 21 F. Hoffmann, M. Cornelius, J. Morell and M. Froeba, *Angew. Chem., Int. Ed.*, 2006, **45**, 3216.
- 22 A. Sayari and S. Hamoudi, Chem. Mater., 2001, 13, 3151.
- 23 L. Zhang, Q. Yang, W. Zhang, Y. Li, J. Yang, D. Jiang, G. Zhu and C. Li, *J. Mater. Chem.*, 2005, **15**, 2562.
- 24 Y. Yang, J. Liu, X. Li, X. Liu and Q. Yang, *Chem. Mater.*, 2011, 23, 3676.
- 25 Y. Yang, X. Liu, X. Li, J. Zhao, S. Bai, J. Liu and Q. Yang, Angew. Chem., Int. Ed., 2012, **51**, 9164.
- 26 X. Li, X. Liu, Y. Ma, M. Li, J. Zhao, H. Xin, L. Zhang, Y. Yang, C. Li and Q. Yang, *Adv. Mater.*, 2012, 24, 1424.
- 27 J. Liu, Q. Yang, L. Zhang, H. Yang, J. Gao and C. Li, *Chem. Mater.*, 2008, **20**, 4268.
- 28 W. Long and C. W. Jones, ACS Catal., 2011, 1, 674.
- 29 D. Margolese, J. A. Melero, S. C. Christiansen, B. F. Chmelka and G. D. Stucky, *Chem. Mater.*, 2000, 12, 2448.
- 30 J. A. Melero, G. D. Stucky, R. van Grieken and G. Morales, J. Mater. Chem., 2002, 12, 1664.
- 31 T. Okayasu, K. Saito, H. Nishide and M. T. W. Hearn, *Green Chem.*, 2010, **12**, 1981.
- 32 A. Martin, G. Morales, F. Martinez, R. van Grieken, L. Cao and M. Kruk, *J. Mater. Chem.*, 2010, **20**, 8026.
- 33 M. Choi, F. Kleitz, D. N. Liu, H. Y. Lee, W. S. Ahn and R. Ryoo, J. Am. Chem. Soc., 2005, 127, 1924.
- 34 R. E. Mishler, II, A. V. Biradar, C. T. Duncan, E. A. Schiff and T. Asefa, *Chem. Commun.*, 2009, 6201.
- 35 H. Chen, R. Liu, M. Lo, S. Chang, L. Tsai, Y. Peng and J. Lee, J. Phys. Chem. C, 2008, 112, 7522.
- 36 J. Gao, J. Liu, S. Bai, P. Wang, H. Zhong, Q. Yang and C. Li, J. Mater. Chem., 2009, 19, 8580.
- 37 J. Y. Kim, J. C. Park, H. Kang, H. Song and K. H. Park, *Chem. Commun.*, 2010, 46, 439.
- 38 P. Wang, S. Bai, J. Zhao, P. Su, Q. Yang and C. Li, *ChemSusChem*, 2012, 5, 2390.
- 39 Z. Feng, Y. Li, D. Niu, L. Li, W. Zhao, H. Chen, L. Li, J. Gao, M. Ruan and J. Shi, *Chem. Commun.*, 2008, 2629.
- 40 J. Dou and H. C. Zeng, J. Am. Chem. Soc., 2012, 134, 16235.
- 41 L. Zhang, S. Wu, C. Li and Q. Yang, *Chem. Commun.*, 2012, 48, 4190.

- 42 J. Liu, J. Peng, S. Shen, Q. Jin, C. Li and Q. Yang, *Chem.–Eur. J.*, 2013, **19**, 2711.
- 43 M. Chen, L. Wu, S. Zhou and B. You, *Adv. Mater.*, 2006, **18**, 801.
- 44 Z. Deng, M. Chen, S. Zhou, B. You and L. Wu, *Langmuir*, 2006, 22, 6403.
- 45 Z. Zhong, Y. Yin, B. Gates and Y. Xia, *Adv. Mater.*, 2000, **12**, 206.
- 46 H. Blas, M. Save, P. Pasetto, C. Boissiere, C. Sanchez and B. Charleux, *Langmuir*, 2008, 24, 13132.
- 47 G. Qi, Y. Wang, L. Estevez, A. K. Switzer, X. Duan, X. Yang and E. P. Giannelis, *Chem. Mater.*, 2010, 22, 2693.

- 48 W. Stöber, A. Fink and E. Bohn, *J. Colloid Interface Sci.*, 1968, 26, 62.
- 49 X. Zhang, Y. Zhao, S. Xu, Y. Yang, J. Liu, Y. Wei and Q. Yang, *Nat. Commun.*, 2014, 5, 3170.
- 50 S. Inagaki and Y. Fukushima, *Microporous Mesoporous Mater.*, 1998, **21**, 667.
- 51 J. Pires, M. Pinto, J. Estella and J. C. Echeverria, J. Colloid Interface Sci., 2008, 317, 206.
- 52 J. P. Dacquin, H. E. Cross, D. R. Brown, T. Duren, J. J. Williams, A. F. Lee and K. Wilson, *Green Chem.*, 2010, 12, 1383.
- 53 K. Inumaru, T. Ishihara, Y. Kamiya, T. Okuhara and S. Yamanaka, *Angew. Chem., Int. Ed.*, 2007, **46**, 7625.