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Efficient and stable PS-SO₃H/SiO₂ hollow nanospheres with tunable surface properties for acid catalyzed reactions

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Graphical abstract



Silica hollow nanospheres with sulfonated polystyrene and octyl groups dispersed in nanopores act as efficient solid catalysts for esterification and transesterification reactions.

Highlights

- PS-SO₃H/SiO₂ hybrids hollow nanospheres with high content of octyl group in the shell were synthesized by one-pot co-condensation method using chlorosilanes as precursor.
- The surface hydrophilicity/hydrophobicity of PS-SO₃H/SiO₂ hybrids hollow nanospheres could be facilely adjusted.
- The solid acid modified with perfluorinated octyl shows even higher activity than liquid sulfuric acid in the transesterification reaction.
- The octyl group incorporated in the silica shell could also prevent the leaching of PS-SO₃H during the catalytic process.

Abstract

Facile synthesis of hybrid solid acids with finely engineered surface properties was successfully realized via sulfonation of polystyrene (PS) dispersed in nanopores of silica hollow nanosphere modified with different organic group. It was found that octyl or perfluorinated octyl could efficiently increase the surface hydrophobicity of the hybrid solid acids. Benefited from the facile adjustability of the surface properties, the catalytic performance of the solid acids could be readily improved in both the esterification of lauric acid with ethanol and the transterification between tripalmitin and methanol. The solid acid modified with perfluorinated octyl shows even higher activity than liquid sulfuric acid in the transseterification reaction. The octyl group incorporated in the silica shell could also prevent the leaching of PS-SO₃H during the catalytic process.

Keywords: solid acid; octyl; hydrophobicity; esterification; transesterification.

1. Introduction

The development of sustainable and green energy is of quite importance due to energy crisis and environment pollution. Similar to solar-, hydro-, and wind-energy, biofuel including bioethanol and biodiesel have received considerable attentions as sustainable energy sources.[1-7] Compared with traditional fossil energy, biodiesel has low sulfur and aromatic content, high flash point, high cetane number, good lubricity. [1, 8, 9] Compared with base catalysts, acid catalysts can simultaneously catalyze the esterification and transesterification reactions to achieve biodiesel production without soap formation.[8] However, liquid acids meet many problems in industrial application, such as waste water production, equipment corrosion and so on.[10-14] Therefore, the usage of solid acids for transesterification reactions is highly desirable.[5, 12-14]

Polystyrene sulfonic acid resins (PS-SO₃H) represent one of the most efficient organic solid acids and have widely been used in industry.[15-17] However, this kind of solid acid generally has poor thermal stability and very low surface area. For solving the above problems, mesoporous polystyrene sulfonic acid [5, 18] and polystyrene sulfonic acid/inorganic oxide composites have been synthesized.[19, 20] There are two major factors that influence the catalytic performance of solid acids could greatly affect the diffusion rates of reactants and products during the catalytic process.[8, 21-26] Secondly, the surface wettability (i.e. the hydrophobicity and hydrophilicity) may have big influence on the adsorption and desorption of the reactants and products and also the surface transfers between catalysts and molecules.[27-30] The high performance solid acid catalysts should have suitable surface wettability for fast adsorption of reactants on the active sites and also the fast

desorption of products from the active sites. [31] For achieving the above goal, the surface wettability, nanostructure and the morphology of the solid acid catalysts should be carefully engineered. Recently, we have reported the synthesis of PS-SO₃H/MS hybrids hollow nanospheres with poly(methyl acrylate) (PMA) modified shell for acid catalyzed reactions.[33] The hollow nanostructure with shell thickness of ~ 50 nm could facilitate the fast diffusion of reactants and products due to its shortened diffusion pathway. Also, it was found that further modification of silica shell with octyl group via grafting method could increase both the activity and stability of the solid acid catalysts. However, the amount of octyl group incorporated in the silica hollow nanospheres is limited and also the sharp decrease in BET surface area was obseved using grafting method. Our recent studies suggest that higher content of organic functional groups could be incorporated into mesoporous silicas via one-pot co-condensation method using chlorosilanes.[34] Thus, it is possible for the synthesis of PS-SO₃H/SiO₂ hybrids hollow nanospheres with high content of octyl group in the shell by one-pot co-condensation method using chlorosilanes as precursor to further investigate the influence of octyl groups on the activity and stability of the hybrid solid acids.

Herein, we report the synthesis of sufonated polystyrene functionalized hollow nanospheres with high acid concentration and finely engineered surface properties. PS-SO₃H/SiO₂ hollow nano-spheres were facilely fabricated via one-pot condensation of tetraethoxysilane (TEOS) with chlorosilanes (Cl₃SiC₈H₄F₁₃ or Cl₃SiC₈H₁₇), using polystyrene (PS) nanospheres and cetyltrimethylammonium bromide (CTAB) micellar as template followed by the structure transformation from core-shell to hollow and sulfonation. Benefited from the facile adjustability of the surface properties, the catalytic activity of the solid acids was readily improved. In the esterification between

lauric acid with ethanol and the transterification between tripalmitin and methanol, the solid acids show much higher activity than Amberlyst-15 and liquid acid, H₂SO₄.

2. Experimental section

2.1. Chemicals and reagents

All materials were of analytical grade. Cetyl-trimethylammonium bromide (CTAB, 99%) was purchased from Sigma-Aldrich Company Ltd. (USA). Tetraethoxysilane (TEOS, 99.9%) was obtained from Nanjing Shuguang Chemical Group (China), and 1H. 1H. 2H. 2H-perfluorooctyltrichlorosilane (C₈H₄F₁₃SiCl₃, 97%) and n-octyltrichlorosilane (C₈H₁₇SiCl₃, 98%) were obtained from Alfa Aesar (UK). Other reagents such as anhydrous ethanol (99.5%) and tetrahydrofuran (THF, 99%). were purchased from Shanghai Chemical Reagent, Inc. of the Chinese Medicine Group. Styrene (99%) was washed through an inhibitor remover column for removing the inhibitor and then distilled under vacuum before use. The other materials were used as received without any further purification. PS nanospheres with particle size of about 240 nm were prepared according to previous report. [32]

2.2. Characterization

FT-IR spectra were collected with a Nicolet Nexus 470 IR spectrometer (KBr pellets were prepared) in the range of 400-4000 cm⁻¹. N₂ sorption isotherms were carried out on a Micromeritics ASAP2020 volumetric adsorption analyzer. Before the sorption measurements, samples were out-gassed at 120 °C for 6 h. The BET surface area was calculated from the adsorption data at a relative pressure P/P₀ in the range of 0.04-0.2. Pore size distributions were determined from the adsorption branch using nonlocal density functional theory (NLDFT) method. Pore volume was estimated at a relative pressure P/P₀ 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 (HRTEM) was performed on a FEI TecnaiG2 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 electro-microscope operating at an acceleration voltage of 1–30 kV.

Solid-state NMR spectra were obtained with a Bruker DRX 400 spectrometer equipped with a magic-angle spin probe using a 4-mm ZrO₂ rotor.¹³C signals were referenced to tetramethylsilane (TMS). The experimental parameters are as follows: 8 kHz spin rate, 3 s pulse delay, 4 min contact time, and1000 scans.

Water contact angle measurements were performed on KRÜSS DSA100, and the sample films were prepared via pressing the material powder at a pressure of 8 MPa on tablet press.

The acid exchange capacity of solid acids was determined by acid-base titration with NaOH solution. In a typical experiment, solid samples (40~50 mg) was degassed at 120 °C for 3 h and suspended in NaCl solution (2M, 25 mL). After stirring at room temperature for 24 h to reach the equilibrium, the resulting suspension was titrated with a standard NaOH solution (8.38 $\times 10^{-3}$ M).[32,33,35,36]

2.3. Synthesis of PS@SiO₂ core-shell nanospheres (CSNs) with different surface properties

PS@SiO₂ CSNs with different surface properties were prepared by coating PS nanospheres with TEOS and chlorosilane under basic conditions using CTAB as surfactant. In a typical synthesis, the solution containing 0.20 g of CTAB, 60 mL of

deionized water and 20 mL of ethanol was stirred at 50 °C for 30 minutes, followed by the addition of PS nanospheres (0.20 g) dispersed in 2 mL of deionized water. The above mixture was stirred at 50 °C for another 0.5 h, followed by the addition of ammonium hydroxide solution (0.7 mL, 25%). Then, TEOS (0.6175 or 0.585 or 0.585g) in 2 mL ethanol was added into above mixture under vigorous stirring. After 5 min, chlorosilanes (36 or 72 or 116 μ L) was added slowly. After stirring at 50 °C for 2 h, the mixture was transferred into a Teflon-lined autoclave and aged at 100 °C under static conditions for 36 h. The solid product was recovered by filtration, washed with water and ethanol, and dried at 60 °C overnight. The surfactant was extracted by dispersing the solid product (1g) in ethanol-HCl (200 mL, 0.75 wt % of HCl) and the mixture was refluxed at 70 °C for 8 h. The samples were denoted as PS@C8-SiO2-x (x=0.05 or 0.10) CSNs and PS@C8F-SiO2-0.10 CSNs respectively prepared with n-octyltrichlorosilane and 1H,1H,2H,2H-perfluorooctyltrichlorosilane as chlorosilane precursors, where x is the mol ratio of chlorosilane/(chlorosilane + TEOS).

In a controlled experiment, PS@SiO₂ CSNs were synthesized in a similar method to PS@C₈-SiO₂-x CSNs except only TEOS (0.65 g) was used as the silica precursor.

2.4. Synthesis of PS/SiO₂ hollow nanospheres (HNs) with different surface properties

PS/SiO₂ HNs was prepared by dispersing PS@SiO₂ CSNs (1 g) in 200 mL of THF and the mixture was heated at 60 °C for 4 h. After centrifugation and washing with ethanol, PS/SiO₂ HNs were obtained. The samples were denoted as PS/C₈-SiO₂-x (x=0.05 or 0.10) HNs, PS/C₈F-SiO₂-0.10 HNs and PS/SiO₂ HNs using PS@C₈-SiO₂-x (x=0.05 or 0.10) CSNs, PS@C₈F-SiO₂-0.10 CSNs and PS@SiO₂ CSNs as precursors, respectively.

2.5. Synthesis of PS-SO₃H/SiO₂ hollow nanospheres (HNs) with different surface

properties

PS/SiO₂ HNs (1g) was outgassed at 120 °C under vacuum in a two-necked round flask for 3 h. Then, 50 mL of CH₂Cl₂ containing 10 mL of chlorosulfonic acid was added to the flask at 0 °C. The mixture was stirred for 12 h 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 as PS-SO₃H/C₈-SiO₂-x (x=0.05 or 0.10) HNs, PS-SO₃H/C₈F-SiO₂-0.10 HNs and PS-SO₃H/SiO₂ HNs using PS/C₈-SiO₂-x (x=0.05 or 0.10) HNs, PS/C₈F-SiO₂-0.10 HNs and PS/SiO₂ HNs as precursors, respectively.

2.6. General procedure for acid-catalyzed reactions

The catalysts were pretreated at 120 °C under vacuum for 3 h before acid-catalyzed reactions.

Esterification of lauric acid with ethanol was carried out in a two-necked round flask equipped with a reflux condenser and a magnetic stirrer. In a typical experiment, 10 mmol of ethanol and 2 mmol of lauric acid were added to the flask charged with PS-SO₃H/SiO₂ catalysts (0.04 mmol of H⁺). The mixture was stirred at 80 °C for 6 h. The products were collected by a syringe at regular intervals and analyzed using a precalibrated gas chromatograph (Agilent 7890) equipped with a flame ion detector (FID) and PEG capillary column (30 m × 0.25 mm × 0.25 mm). Tetradecane was used as an internal standard.

Transesterification of tripalmitin and methanol was carried out in a two-necked round flask equipped with a reflux condenser and a magnetic stirrer. In a typical experiment, 0.72 mmol of tripalmitin and 2 mL of methanol were added to the flask charged with PS-SO₃H/SiO₂ catalysts (0.04 mmol of H⁺). The mixture was stirred at

80 °C for 21 h. The products were analyzed by Agilent 7890 gas chromatography with a flame ionization detector (FID) and HP-INNOWax capillary column (30 m \times 0.25 mm \times 0.25 mm). Dodecane was used as an internal standard.

3. Results and discussion

The general procedure for the synthesis of PS-SO₃H/SiO₂ HNS was outlined in Fig. 1A. In the first step, PS@SiO₂ CSNs with different surface properties were synthesized via sol-gel coating of PS by one-pot condensation of TEOS and chlorosilanes (Cl₃SiC₈H₄F₁₃ or Cl₃SiC₈H₁₇) using CTAB as template. TEM images clearly reveal the core shell nanostructure with dark core (PS) and gray shell layer (SiO₂) (Fig. 1B). The surface properties of the PS@SiO₂ CSNs could be facilely adjusted by the type and amount of chlorosilane precursor. After THF treatment, PS core was dissolved and diffused into the mesopore of the silica shell for the formation of hollow nanospheres as evidenced by the TEM image in Fig. 1C. Then, sulfonation of PS/SiO₂ HNs results in the formation of PS-SO₃H/SiO₂ HNs with different surface properties. The TEM images clearly verify that all PS-SO₃H/SiO₂ HNs functionalized with different type and different amount of organic groups are composed of hollow nanospheres (Fig. 2). SEM image shows the sample is composed of mono-dispersed nanospheres with porous rough surfaces and uniform partcile size distribution in the range of 370 to 350 nm, taking PS-SO₃H/C₈-SiO₂-0.10 HNs as an example. Based on the TEM image, the average shell thick of PS-SO₃H/SiO₂ HNs is around 60 to 70 nm.

It should be mentioned that the location of the sulfonic acid site is very important for catalysis. The HRTEM element mapping was used to reveal the location of sulfonic acid sites, taking PS-SO₃H/C₈-SiO₂-0.10 HNs as an example (Fig. 2C). The result clearly shows that Si and S are mainly distributed in the shell of hollow nanospheres. This further confirms that PS diffuses into the mesopore of silica shell

during THF treatment of core-shell structured nanospheres.

The N_2 adsorption-desorption isotherms of PS-SO₃H/SiO₂ HNs, PS-SO₃H/C₈-SiO₂-x (x=0.05, 0.10) HNs, and PS-SO₃H/C₈F-SiO₂-0.10 HNs are showed in Fig. 3. Clearly, PS-SO₃H/SiO₂ HNs display typical type-IV isotherms with a steep capillary condensation in the relative pressure range between $0.20 < P/P_0 < 0.40$, showing that this sample has mesoporous structure in the shell. The hysteresis loop at 0.45 < P/P₀ < 0.95 is probably from the hollow interior of hollow nanospheres. Compared with PS-SO₃H/SiO₂ HNs, the capillary condensation step is less defined for PS-SO₃H/C₈-SiO₂-x (x=0.05, 0.10) HNs, and PS-SO₃H/C₈F-SiO₂-0.10 HNs, suggesting that the incorporation of octyl and perfluorinated octyl group deteriorate the mesostructural order in the shell [37]. PS-SO₃H/SiO₂ HNs show higher BET surface area and larger pore volume and pore diameter than PS-SO₃H/C₈-SiO₂-x (x=0.05,PS-SO₃H/C₈F-SiO₂-0.10 0.10)HNs, and HNs (Table 1). PS-SO₃H/C₈-SiO₂-0.05 with less octyl group has larger BET surface ares and pore diameter than PS-SO₃H/C₈-SiO₂-0.10 with higher octyl group. The BET surface area and diameter the of PS-SO₃H/SiO₂< pore decreases in order PS-SO₃H/C₈F-SiO₂-0.10< PS-SO₃H/C₈-SiO₂-0.05< PS-SO₃H/C₈-SiO₂-0.10.

As shown in Fig. 4A, the FT-IR spectra of all PS-SO₃H/SiO₂ HNs clearly displays vibration peaks at 1020 cm⁻¹ and 573 cm⁻¹, respectively assigned to of S=O [6, 38] symmetric stretching vibration and S-C stretching vibration [39], which confirms the successful incorporation of sulfonic acid group onto aromatic ring during sulfonation process. The vibration peaks in the range of 900 cm⁻¹ to 650 cm⁻¹ are from the C–H bending vibration and C=C stretching vibration of phenyl groups. Compared with PS-SO₃H/SiO₂ HNs, the intensified vibration peaks at 2930cm⁻¹ (CH₂,v_{as}) [34] for PS-SO₃H/C₈-SiO₂-x (x=0.05, 0.10) HNs and the new peak at 1240 cm⁻¹ (CF₂,CF₃,v_{as})

[6, 7] for PS-SO₃H/C₈F-SiO₂-0.10 clearly show the existence of octyl and 1H,1H,2H,2H-perfluorinated octyl groups as the surface modified samples (Fig. 4A).

The solid-state ¹³C CP/MAS NMR spectra of PS-SO₃H/SiO₂ HNs and PS-SO₃H/C₈-SiO₂-0.10 HNs are presented in Fig. 4B. The strong signals at 40 ppm and 43 ppm are attributed to the aliphatic carbon chain on aromatic ring. The chemical shifts at 127 ppm, 141 ppm (incorporated with SO₃H) [5, 33] and 152 ppm (incorporated with vinyl) could be assigned to aromatic rings. In addition, the new chemical shifts at 13.1 ppm, 21.6 ppm, 28.5 ppm and 31.5 ppm in the ¹³C CP/MAS NMR spectrum of PS-SO₃H/C₈-SiO₂-0.10 HNs is from carbon species of octyl groups. The combined results of FT-IR and ¹³C CP/MAS NMR confirm the successful formation of organo-modified hybrid solid acids.

The sulfur content and acid exchange capacity was measured respectively by element analysis and acid-base titration methods (Table 1). The sulfur contents of samples vary in the range of 3.24 mmol/g to 2.85 mmol/g. The acid exchange capacity of samples in the range of 1.25 mmol/g to 0.97 mmol/g is much lower than sulfur content. The inconsistence between acid exchange capacity and sulfur content suggests that some sulfonic acid sites are buried in the silica shell and cannot be accessed during the acid-base titration process. The acid exchange capacity of the samples decreases with the content of octyl group increasing, probably due to the decrease in both the surface area and pore diameter. PS-SO₃H/C₈F-SiO₂-0.10 gives the lowest sulfur content and acid exchange capacity among all the samples.

The organic groups incorporated into the mesoporous silica shell of $PS-SO_3H/C_8-SiO_2-x$ (x=0.05, 0.10) and $PS-SO_3H/C_8F-SiO_2-0.10$ could adjust hydrophobic and hydrophilic properties of the hybrid solid acids. All hollow

nanospheres before sulfonation, except PS/SiO₂ HNs, located on the interface between water and n-hexane, however, all samples uniformly dispersed in the water after sulfonation (Fig. 5). The distribution phenomenon of samples before sulfonation confirms that the incorporation of organic groups indeed could modify the surface properties of HNs. After sulfonation, the incorporation of sulfonic acid groups onto the PS distributed in the mesopore of silica shell could increase the surface hydrophilicity of the samples. This could be confirmed by the decrease in water contact angle of the samples before and after sulfonation. Thus, the samples could be well dispersed in water phase. The water contact angle of the hybrid solid acids increases in the order of PS-SO₃H/C₈-SiO₂-0.10 > PS-SO₃H/C₈F-SiO₂-0.10 > PS-SO₃H/C₈-SiO₂-0.05 > PS-SO₃H/SiO₂ (Table 1). This shows that octyl and perfluorinated octyl groups could increase the surface hydrophobicity of the hybrid solid acids.

The catalytic performance of hybrid solid acids with different surface properties was tested in both the esterification of lauric acid and ethanol and the transesterification of tripalmitin and methanol (Table 2). The esterification of lauric acid and ethanol produce ethyl laurate as the only organic product with water as byproduct. Water usually acts as a byproduct in various acid-catalyzed reactions, which can easily poison the acid sites and result in opposite reactions, so the surface properties of solid acid catalysts are quite important for achieving excellent catalytic performance.

In the esterification of lauric acid and ethanol, Amberlyst-15 shows the lowest activity due to the low BET surface area (the BET surface area of Amberlyst-15 is only 41.8 m²/g) that causes most of the acid sites buried in the bulk polymer beads, while liquid acid (H₂SO₄) shows the highest activity with turnover frequency (TOF)

of 36.7 h⁻¹. Under similar reaction conditions, all PS-SO₃H/SiO₂ HNs catalysts are more active than Amberlyst-15, which is mainly attributed to the high surface area of hybrid solid acids benefiting higher exposure degree of acid sites. As the surface hydrophobicity increases, the TOF of the hybrid solid acids increases from 15.2 h⁻¹ to 27.5 h⁻¹, showing the surface hydrophobicity could increase the catalytic activity. PS-SO₃H/C8F-SiO₂-0.10HNs affords the highest TOF (27.5 h⁻¹) among all the solid hybrid solid acids, indicating the unique properties of fluorine in catalytic reactions. [5-7]

The kinetic curves for the esterification and transterification reaction catalyzed by different types of catalysts are displayed in Fig. 6. Though H₂SO₄ affords the highest initial rate among all catalysts tested, the reaction rate decreases sharply after 1 h, suggesting the deactivation of the liquid acid catalysts probably due to H₂O formed during the catalytic process. As a result, the final product yield is less than 85%. PS-SO₃H/SiO₂ without organic groups in the shell affords 90% yield. As the surface hydrophobicity increases, the product yield increases, which suggests that solid acids with hydrophobic organic groups in the shell could protect the sulfonic acid sites from deactivation by water. Among all solid acid catalysts, PS-SO₃H/C₈-SiO₂-0.10 HNs takes the shortest reaction time to achieve 96% yield though its TOF is not the highest. This is probably related with its surface hydrophobicity and relatively larger BET surface area. Compared with PS-SO₃H/2.5PMA-C₈-SiO₂ with poly(methyl acrylate) (PMA) and octyl modified shell [33], the solid catalysts, PS-SO₃H/C₈-SiO₂-0.10 and PS-SO₃H/C₈F-SiO₂-0.10, reported in this work show much higher TOF and slightly higher product yield. This is mainly attributed to the strong surface hydrophobicity and larger BET surface area of the solid acids prepared using co-condensation method.

The transesterification of tripalmitin with methanol has been widely investigated for the production of biodiesel. [40] Liquid acid, H₂SO₄, could smoothly catalyze the transesterification reaction to afford 52.3% yield of biodisel. However, Amberlyst-15 gives very low biodiesel yield of 17.3%. Compared with lauric acid, tripalmitin with larger molecular size is more difficult to diffuse through Amberlyst-15 with low BET surface area. As a result, Amberlyst-15 only shows low activity in the transesterification reaction. On the contrary, all hybrid solid acids could efficiently catalyze the transesterification reaction to afford much higher yield than H₂SO₄, showing the mesopore in the silica shell allows the free diffusion of tripalmitin to access the acid sites. It is also observed that the hybrid solid acids with stronger surface hydrophobicity afford higher biodiesel yield and TOF. It should be noted that PS-SO₃H/C₈-SiO₂-0.10 HNs and PS-SO₃H/C₈F-SiO₂-0.10 HNs are even more active than H₂SO₄. The high activity of hybrid solid acids is probably due to its enrichment effect for hydrophobic tripalmitin.

Based on the kinetic curves for the transesterification reaction (Fig. 6B), H₂SO₄ with higher initial reaction rate also affords much slower reaction rate after 2.5 h, similar to those observed in the esterification reaction, showing the deactivation of liquid acids during the transesterification reaction. The initial reaction rate of PS-SO₃H/SiO₂ HNs is also identical to that of PS-SO₃H/C₈-SiO₂-0.05 HNs, but the reaction rate of the later sample is faster than the former sample after 7.5 h. This further confirms the incorporation of organic groups in the silica shell could protect the sulfonic acid sites from deactivation.

The above catalytic results suggest that hybrid solid acids with surface hydrophobicity show high activity in both the esterification of lauric acid and ethanol and the transesterification of tripalmitin and methanol. This is probably related to the

anti-poisoning effect of acid sites by water and enrichment effects for hydrophobic substrates derived from the increased surface hydrophobicity.

The reusability of hybrid solid acids was tested with PS-SO₃H/C₈-SiO₂-0.10 HNs as model catalysts and esterification of lauric acid and ethanol as model reaction. As shown in Fig. 7, the catalytic activity of PS-SO₃H/C₈-SiO₂-0.10 HNs gradually decreases in the course of repeating use, but the decrease is not so obvious. After 10 cycles, the conversion only decreases from 97.5 to 86.2 %, and the activity of the catalyst could still retain 88 % of the fresh one. It should be noted that the reaction time is extended from 6 h to 8 h after the 8th cycle. Also, the product yield was measured for 20 min run for evaluating the stability of PS-SO₃H/C₈-SiO₂-0.10 (Fig. 7). The data for the 20 min run show the obvious decrease in product yield for the first two cycles. The product yield remains constant for the next three cycles and an obvious decrease in product yield was observed for the sixth run. The above results show the gradual deactivation of the catalyst during the recycle process. For understanding the decrease in activity of the hybrid solid acids during recycle process, the used PS-SO₃H/C₈-SiO₂-0.10 HNs was characterized by acid titration, elemental analysis, TEM technique (Fig. 7B) and N₂ sorption analysis (Table 1). The sulphur content and acid exchange capacity of PS-SO₃H/C₈-SiO₂-0.10 were measured after 10 cycles. It was found that sulphur content and acid exchange capacity of used PS-SO₃H/C₈-SiO₂-0.10 were 3.08 and 2.35 mmol/g, respectively. The sulfur content is almost the same as that of fresh catalyst, suggesting negligible leaching of PS-SO₃H during the recycle process. It is noteworthy to mention that acid exchange capacity of the used PS-SO₃H/C₈-SiO₂-0.10 is much higher than that of fresh one (2.35 versus 1.13 mmol/g). The TEM image (Fig. 7B) show that used PS-SO₃H/C₈-SiO₂-0.10 still keeps the original hollow nanostructure with no significant changes in shell thickness

and particle size. However, the BET surface area decreases sharply from 262 m²/g to 130 m²/g after 7 cycles and to 27 m²/g after 10 cycles (Table 1). The above results suggest that the swelling of PS-SO₃H in the silica shell occurs during the recycle process. The swelling of PS-SO₃H increases the exposure degree of acid sites, as a result, the activity of the catalyst only decreases slightly during recycle process though the BET surface area decreases sharply. The fact that no obvious leaching of PS-SO₃H was observed during the recycle process shows that the octyl group incorporated in the silica shell could efficiently prevent the leaching of PS-SO₃H. [33] Based on the elemental analysis, acid exchange capacity and TEM characterization, the gradual deactivation of PS-SO₃H/C₈-SiO₂-0.10 is probably due to the combined effect of PS-SO₃H swelling and decrease in BET surface area.

4. Conclusion

In summary, we report the successful synthesis of highly efficient solid acid catalyst with controllable surface wettability and unique hollow nanostructure via one-pot co-condensation method. The surface properties and the catalytic performance of the solid acids could be facilely tuned by incorporation of octyl or 1H,1H,2H,2H-perfluorooctyl in the silica shell. Compared with post-synthesis grafting method, the co-condensation method could result in the formation of silica hollow nanospheres with both high content of organic groups and open mesoporous structure. The primary results suggest that stronger surface hydrophobicity could increase the catalytic activity of the solid acid catalysts and also could prevent the acid sites from deactivation by water formed during the catalytic process. PS-SO₃H/C₈-SiO₂-0.10 HNs with optimized surface hydrophobicity and mesoporous structure show much higher activity than H₂SO₄ or Amberlyst-15 in the esterification

and transesterification reactions and is among the most efficient solid acids reported in the literature. The octyl groups in the silica shell could prevent the leaching of PS-SO₃H during the catalytic process, as a result, the solid acids could be recycled though gradually deactivation was observed.

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Fig. 1. (A) Schematic illustration of the synthetic route of $PS-SO_3H/SiO_2$ HNs with $PS-SO_3H/C_8-SiO_2-0.10$ as a model and the corresponding TEM images of (B) $PS@C_8-SiO_2-0.10$ CSNs and (C) $PS/C_8-SiO_2-0.10$ HNs.



Fig. 2. (A) TEM images of (a) PS-SO₃H/SiO₂ HNs, (b) PS-SO₃H/C₈-SiO₂-0.05 HNs, (c) PS-SO₃H/C₈-SiO₂-0.10 HNs and (d) PS-SO₃H/C₈F-SiO₂-0.10 HNs, Scale bar: 200 nm, (B) SEM images and (C) HRTEM images and corresponding element mapping image analysis of PS-SO₃H/C₈-SiO₂-0.10 HNs (silica and sulfur along the area 1 shown in (C)).



Fig. 3. N₂ adsorption–desorption isotherms of (a) PS-SO₃H/SiO₂ HNs, (b) PS-SO₃H/C₈-SiO₂-0.05 HNs, (c) PS-SO₃H/C₈-SiO₂-0.10 HNs and (d) PS-SO₃H/C₈F-SiO₂-0.10 HNs.



Fig. 4. (A) FT-IR spectra of (a) PS-SO₃H/SiO₂ HNs, (b) PS-SO₃H/C₈-SiO₂-0.05 HNs, (c) PS-SO₃H/C₈-SiO₂-0.10 HNs and (d) PS-SO₃H/C₈F-SiO₂-0.10 HNs, (B) ¹³ C NMR of (a) PS-SO₃H/SiO₂ HNs and (c) PS-SO₃H/C₈-SiO₂-0.10 HNs.



Fig. 5. Pictures of samples dispersed in water and n-hexane: (a) PS/SiO_2 HNs, (b) $PS/C_8-SiO_2-0.05$ HNs, (c) $PS/C_8-SiO_2-0.10$ HNs, (d) $PS/C_8F-SiO_2-0.10$ HNs, (e) $PS-SO_3H/SiO_2$ HNs, (f) $PS-SO_3H/C_8-SiO_2-0.05$ HNs, (g) $PS-SO_3H/C_8-SiO_2-0.10$ HNs, and (h) $PS-SO_3H/C_8F-SiO_2-0.10$ HNs.



Fig. 6. The kinetic curves for the esterification (A) and transterification (B) reaction catalyzed by PS-SO₃H/SiO₂ HNs, PS-SO₃H/C₈-SiO₂-0.05 HNs, PS-SO₃H/C₈-SiO₂-0.10 HNs, PS-SO₃H/C₈F-SiO₂-0.10 HNs, H₂SO₄ and Amberlyst-15.



Fig. 7. (A) The yield obtained at different reaction times on PS-SO₃H/C₈-SiO₂-0.10 HNs in the esterification of lauric acid with ethanol during recycle experiments (the reaction time is prolonged from 6h to 8 h after the 8th cycle) and (B) TEM images of PS-SO₃H/C₈-SiO₂-0.10 HNs after the (a) 7th and (b) 10th recycle.

Sample	S_{BET} $(m^2/g)^{[a]}$	Vt (cm ³ /g) ^[b]	D _{DFT} (nm) ^[c]	Water contact angle ^[d]	Acid exchange capacity (mmol/g) ^[e]	S content (mmol/g) ^[f]
PS-SO ₃ H/SiO ₂	318	0.39	3.2	37.5 (31.5)	1.25±0.04	3.24±0.015
PS-SO ₃ H/C ₈ -SiO ₂ -0.05	210	0.13	2.2	52.3 (60.3)	1.18±0.05	3.21±0.009
PS-SO ₃ H/C ₈ -SiO ₂ -0.10	222	0.21	1.4	70.8 (92.3)	1.13±0.02	3.20±0.002
PS-SO ₃ H/C ₈ F-SiO ₂ -0.10	262	0.19	2.7	62.8 (103.7)	0.97±0.03	2.85±0.016
PS-SO ₃ H/C ₈ -SiO ₂ -0.10 ^[g]	130	0.10		-	-	-
PS-SO ₃ H/C ₈ -SiO ₂ -0.10 ^[h]	27	0.02	1.6	-	2.35	3.08

Table 1. Physical parameters of PS-SO₃H/SiO₂ HNs, PS-SO₃H/C₈-SiO₂-x HNs and PS-SO₃H/C₈F-SiO₂-0.10 HNs.

[a] S_{BET} is the BET specific surface area. [b] V_t is the total pore volume determined at relative pressure 0.99. [c] D_{DFT} is pore diameter determined from the adsorption branch calculated based on the NLDFT. [d] data in parentheses refers to the sample before sulfonation. [e] based on acid–base titration, the error bar is calculated based on three parallel experiments. [f] based on elemental analysis, the error bar is calculated based on three parallel experiments. [g] after recycled for seven times in esterification reaction. [h] after recycled for ten times in esterification reaction

C	Este	rification ^[a]	Transesterification ^[b]		
Sample	Yield (%)	TOF $(h^{-1})^{[c]}$	Yield (%)	TOF $(h^1)^{[c]}$	
H_2SO_4	84.4±2.2	36.7±0.6	52.3±1.4	3.21±0.44	
Amberlyst-15	53.3±1.2	6.9±0.6	17.3±1.8	0.24±0.17	
PS-SO ₃ H/SiO ₂	91.5±3.8	15.2±0.6	80.9±4.2	2.82±0.52	
PS-SO ₃ H/C ₈ -SiO ₂ -0.05	93.2±5.7	16.7±0.2	86.8±2.8	3.55±0.47	
PS-SO ₃ H/C ₈ -SiO ₂ -0.10	96.7±2.9	23.7±1.0	95.9±3.7	4.69±0.20	
PS-SO ₃ H/C ₈ F-SiO ₂ -0.10	97.2±2.0	27.5±0.5	96.2±1.2	4.76±0.08	
PS-SO ₃ H/2.5PMA-C ₈ -SiO	94.7±0.1	19.1±0.1			

Table 2. Catalytic activity of PS-SO₃H/SiO₂-x HNs in the esterification of lauric acid and ethanol and in the transesterification of tripalmitin and methanol.

[a] Reaction condition: 2 mmol of lauric acid, 10 mmol of ethanol, 0.04 mmol of H⁺, 80 °C, 6 h; The selectivity to ethyl laurate is 99.9%. The error bar is calculated based on three parallel experiments. [b] Reaction condition: 0.52 mmol of tripalmitin, 2 mL of methanol, 0.04mmol of H⁺, 80 °C, 21 h; The selectivity to methyl palmitate is nearly 100%. The error bar is calculated based on three parallel experiments. [c] The TOF was defined as mmol product obtained per acid site per hour with yield about 15%. [d] Data taken from ref. [33].