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PS-SO₃H@phenylenesilica with yolk-double-shell nanostructures as efficient and stable solid acid catalysts



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ABSTRACT

Efficient and stable solid acids have been successfully synthesized by sulfonation of polystyrene (PS) in the hollow interiors of silica-based hollow nanostructures. It was found that larger and smaller inner void spaces result in the formation of PS-SO₃H@phenylenesilica respectively with double-shell (DSNs) and yolk-double-shell nanostructure (YDSNs). PS-SO3H@phenylenesilica with DSNs and YDSNs nanostructure shows comparable activity and is more active than Amberlyst-15 in the esterification reaction. PS-SO₃H@phenylenesilica with YDSNs nanostructure affords higher activity than that with DSNs nanostructure in the Friedel-Crafts alkylation of toluene with 1-hexene, which is mainly attributed to the fact that the unique YDSNs nanostructure could slow down the swelling rate of PS-SO₃H during the catalytic process. More importantly, PS-SO₃H@phenylenesilica with YDSNs nanostructure showed much higher recycle stability than Amberlyst-15 in the Friedel-Crafts alkylation of toluene with 1-hexene, probably due to the high thermal stability of the sulfonic acid group and the unique YDSNs nanostructure.

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1. Introduction

Acid-catalyzed reactions have been widely used in the production of chemicals. The homogenous mineral liquid acids, such as HCl, H₂SO₄, and HF, are efficient acid catalysts due to their uniform acid sites and strong acid strength. However, the employment of liquid acids in industry often faces problems of wastewater generation, equipment corrosion, and recycling difficulty [1–9]. The development of solid acids as replacements for liquid acids has received growing research attention recently due to strict environmental legislation and the requirement of green processes for chemicals production in industry.

Ion-exchange resins, such as Amberlyst-15, are very attractive solid acid catalysts because they are convenient to use and invariably exhibit high concentrations of acid sites [10–15]. However, they generally have low degrees of exposure of acid sites due to low surface area and low thermal stability. Silica/ion-exchange resins have been prepared for improving both the accessibility of acid sites and the thermal stability of ion-exchange resins [16-18]. In addition to silica/ion-exchange resins, sulfonic acid group-functionalized mesoporous silicas have been widely studied and successfully applied to many acid-catalyzed reactions [19-23]. These hybrid solid acids with larger surface areas show higher activity than the parent ion-exchange resins. However, they are not active enough for catalyzing reactions requiring high acid strength.

The solid acids generally show lower acid strength than their homogeneous counterparts [24-26]. One reason is the low concentration of acid sites on the solid surface, which could not generate the cooperative effects among acid sites that homogeneous acids do. In our previous report, we found that the acid strength of sulfonated polystyrene could be greatly enhanced by compressing it in a confined nanospace, showing that high acid concentration could increase the acid strength of solid acids [27]. Compared with traditional methods for the preparation of hybrid composites of silica/ion-exchange resins by mixing silica and ion-exchange resins together either chemically or physically, the encapsulation method provides a new approach to crowding sulfonated polystyrene within a confined nanospace. This may generate a solid acid with both high acid concentration and high stability. Moreover, the acid concentrations of solid catalysts can be adjusted via tuning the volume of the nanospace, which may have a big influence on the catalytic performance of solid acids.

Here, we report the preparation of solid acids with sulfonated polystyrene encapsulated within mesoporous benzene-silica hollow nanospheres. By adjusting the volume of hollow nanospace, sulfonated polystyrene hollow nanospheres and nanospheres





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could be formed within the confined nanospace. The catalytic performance of solid acids was tested in a series of important acid-catalyzed reactions such as esterification of fatty acids and Friedel–Crafts alkylation of toluene and compared with the performance of sulfonated benzene–silica hollow nanospheres, Amberlyst-15, and liquid acid. The relation of activity to the acid strength of solid acids was also investigated.

2. Experimental

2.1. Chemicals and reagents

All reagents were of analytical grade and used as purchased without further purification. 1,4-Bis-(trimethoxysilyl)benzene (BTEB), cetyltrimethylammonium bromide (CTAB), and triethylphosphine oxide were purchased from Sigma–Aldrich Company Ltd. (USA). Fluorocarbon surfactant, FC-4, was bought from YickVic Chemicals (Hong Kong). Tetraethoxysilane (TEOS) was obtained from Nanjing Shuguang Chemical Group (China). Other reagents were purchased from Shanghai Chemical Reagent, Inc., of the Chinese Medicine Group.

2.2. Catalyst preparation

2.2.1. Preparation of PS-SO₃H@phenylenesilica yolk-double-shell nanospheres (YDSNs)

In the first step, PS@phenylenesilica yolk-shell nanospheres (YSNs) were prepared. In a typical run, an aqueous solution (60 mL) and ethanol (20 mL) with CTAB (0.2 g), PS template spheres (0.2 g), and NH₃·H₂O (0.7 mL, 25 wt%) was stirred at 50 °C for 0.5 h. Then TEOS (0.4 g) was added and the mixture was stirred for 2 h, followed by the addition of an aqueous solution (3 g) containing FC4 (0.04 g), CTAB (0.08 g), and NH₃·H₂O (0.2 mL, 25 wt%). Then BTEB (0.50 mL) in ethanol solution (2 mL) was added under vigorous stirring to the above synthesis medium. The temperature was raised to 80 °C and maintained for 4 h under stirring. After that, the mixture was transferred into a Teflon-lined autoclave and aged at 100 °C under static conditions for 36 h. The white powder was collected by filtration and dried at room temperature. To remove the surfactant, the as-synthesized materials (1 g) were dispersed in 200 mL of ethanol containing 1.5 g of concentrated HCl aqueous solution and the mixture was heated at 70 °C for 12 h. After filtration and drying at 60 °C overnight, PS@phenylenesilica YSNs was obtained.

PS-SO₃H@phenylenesilica with yolk–double-shell nanostructure (YDSNs) was generated by the following sulfonation reaction of PS@phenylenesilica YSNs. The sulfonation of PS@phenylenesilica (1.0 g) was similar to our previously reported method using chlorosulfonic acid (10 mL) as sulfonation reagent and dichloromethane as solvent (50 mL) at 0 °C for 12 h under argon. The obtained nanospheres were denoted as PS-SO₃H@phenylenesilica YDSNs.

2.2.2. Preparation of PS@phenylenesilica double shell nanospheres (DSNs)

The preparation route was almost the same as that for $PS-SO_3$ -H@phenylenesilica YDSNs, except that 0.65 g TEOS was used instead of 0.4 g for the formation of PS@phenylenesilica-L YSNs (L was used for differentiating with PS@phenylenesilica prepared using 0.4 g of TEOS).

The following sulfonation of PS@phenylenesilica-L YSNs results in the formation of PS-SO $_3$ H@phenylenesilica DSNs.

2.2.3. Preparation of SO₃H-phenylenesilica hollow nanospheres (HNs)

PS@phenylenesilica YSNs was calcined in air at 350 °C for 2 h to remove PS cores. The resultant phenylenesilica HNs were

sulfonated in the same way as described above for the generation of SO₃H-phenylenesilica HNs.

2.3. Characterization

The nitrogen sorption experiments were performed at 77 K using a Micromeritics ASAP 2020. The BET surface area was calculated from the adsorption data at a relative pressure P/P_0 in the range of 0.04-0.2. Pore size distributions were determined from the desorption branch using the Barret-Joyner-Halenda (BJH) and Horvath-Kawazone (HK) method. Pore volume was estimated at a 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. Before the measurement, the sample was dispersed in ethanol and deposited on a holev carbon film on a Cu grid. High-resolution transmission electron microscopy (HR-TEM) was performed on an FEI Tecnai G2 F30 S-Twin at an acceleration voltage of 300 kV. Before the measurement, the sample was dispersed in ethanol and deposited on a holey carbon film on a Cu grid. High-resolution scanning electron microscopy (HR-SEM) was undertaken on a HITACHI S-4800 operating at an accelerating voltage of 1-20 kV. FT-IR spectra were collected with a Nicolet Nexus 470 IR spectrometer (KBr pellets were prepared) in the range of 400–4000 cm⁻¹. Elemental analyses were determined by means of an Elementary Vario EL III analyzer. The thermogravimetric analysis (TGA) was performed using a NETZSCH STA 449F3 analyzer from 30 to 900 °C with a heating rate of 10 °C/min under air atmosphere. 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 and ²⁹Si signals were referenced to tetramethylsilane (TMS). The experimental parameters are as follows: 8 kHz spin rate, 3 s pulse delay, 4 min contact time, and 1000 scans.

The acid strength of the solid acid catalysts was monitored by reference to the ³¹P NMR chemical shift of triethylphosphine oxide (TEPO) chemically adsorbed on acid sites. ³¹P NMR spectra were obtained 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 µs and a 30 s recycle delay. The chemical shifts spectra were referenced to 85 wt% phosphoric acid external standard.

The acid exchange capacity of solid acids was determined by acid-base titration with NaOH solution.

2.4. Catalytic reactions

2.4.1. Esterification of lauric acid with ethanol

Typically, the desired amount of solid acids (0.05 mmol H^+) was added into a two-necked round flask equipped with a reflux condenser and a magnetic stirrer. Then 10 mmol of ethanol and 2 mmol of lauric acid were added to the flask and the mixture was stirred at 80 °C for 6 h. The activity in esterification was evaluated by yield of ethyl laurate. Reaction products were analyzed using a gas chromatograph (GC Agilent-6890A) equipped with an FID as well as a PEG capillary column using tetradecane as internal standard.

2.4.2. Friedel-Crafts alkylation of 1-hexene with toluene

A mixture of 1-hexene (2 mmol), toluene (24 mmol), dodecane (0.10 g, internal standard), and the solid acids (0.1 mmol H^+) was added in a round-bottomed flask (10 mL) equipped with a reflux condenser and a magnetic stirrer. The reaction mixture was heated to 120 °C. The activity in Friedel–Crafts alkylation was evaluated by conversion of 1-hexene. Samples were taken out at desired

intervals and analyzed using a gas chromatograph (GC Agilent-7890A) equipped with an FID as well as a PEG capillary column using dodecane as internal standard.

2.4.3. Recycling the solid acids

Friedel–Crafts alkylation of 1-hexene with toluene was used as a model reaction to test the stability of solid acids. After reaction, the solid acids were separated from the reaction system by filtration, thoroughly washed with ethanol, and dried overnight under vacuum at 60 °C. Then the recovered solid acids were used directly in the next run.

3. Results and discussion

3.1. Preparation and characterization of PS-SO₃H@phenylenesilica YDSNs and PS-SO₃H@phenylenesilica DSNs

The overall process for the synthesis of PS-SO₃H@phenylenesilica YDSNs and PS-SO₃H@phenylenesilica DSNs is illustrated in Scheme 1. Initially, PS@SiO₂ core-shell nanospheres with different thicknesses of the SiO₂ layer surrounding PS spheres were used as starting materials for the synthesis of PS@phenylenesilica with volk-shell nanostructures according to an organosilane-assisted etching method [28] using 1,4-bis-(trimethoxysilyl)benzene (BTEB) as organosilane precursor. As shown in Fig. 1A, the particle size of PS@phenylenesilica YSNs was about 367 nm. By adjusting the amount of sacrificed SiO₂ layer, the particle size of yolk-shell nanostructures could be enlarged to 387 nm for PS@phenylenesilica-L YSNs. Notably, the inner void space between PS and the benzene-silica shell is not completely empty and some cotton like particles exist, which are probably the silica residues. This is quite different from the PS@ethane-silica volk-shell nanostructures with empty inner void space using 1,2-bis-(trimethoxysilyl)ethane as organosilane precursor [27]. This may be related to different hydrolysis and condensation rates of the organosilane precursor. The sulfonation of PS@phenylenesilica YSNs and PS@phenylenesilica-L YSNs could directly introduce sulfonic acid groups onto PS.

3.2. Morphology and structure characterizations

Base on the TEM image shown in Fig. 1, the sulfonation of PS@phenylenesilica YSNs and PS@phenylenesilica-L YSNs results in the formation of PS-SO₃H@phenylenesilica yolk-double-shell nanostructures (YDSNs) and PS-SO₃H@phenylenesilica double-shell



Scheme 1. General procedure for the synthesis of PS-SO₃H@phenylenesilica YDSNs and DSNs.

nanostructures (DSNs), respectively. Both PS-SO₃H@phenylenesilica YDSNs and PS-SO₃H@phenylenesilica DSNs have uniformly dispersed spherical morphology with particle size 367 and 387 nm respectively, as evidenced by the HR-SEM characterizations (Fig. S1 in the Supplementary Material). The fact that sulfonated samples have particle size and morphology similar to those of parent samples suggests that PS@phenylenesilica YSNs has enough mechanical stability to survive the sulfonation process. Notably, PS-SO₃H@phenylenesilica YDSNs have double shells surrounding the core. The inner and outer shell thickness of PS-SO₃H@phenylenesilica YDSNs was ~30 nm and the particle size of the inner core was about 160 nm. PS-SO₃H@phenylenesilica DSNs have particle size 387 nm with inner and outer shell thickness 55 and 25 nm, respectively.

HR-TEM element mapping analysis was used to illustrate the location of sulfur and silica in PS-SO₃H@phenylenesilica YDSNs and PS-SO₂H@phenylenesilica DSNs (Fig. 2). The element mapping image of the sulfur shows that the PS-SO₃H is located mostly in the core and inner shell for PS-SO₃H@phenylenesilica YDSNs and mainly in the inner shell for PS-SO₃H@phenylenesilica DSNs. To further clarify the location of PS-SO₃H, PS-SO₃H@phenylenesilica YDSNs and PS-SO₃H@phenylenesilica DSNs were calcined in air at 350 °C to remove PS-SO₃H. According to the TEM images shown in Fig. 1, both samples have similar double-shell hollow nanostructures after calcination with particle size identical to that of the samples before calcination. The formation of a double-shell nanostructure after calcination suggests that a thin layer of silica fused with PS-SO₃H for both PS-SO₃H@phenylenesilica YDSNs and PS-SO₃H@phenylenesilica DSNs, as demonstrated in Scheme 1, which is probably formed by the condensation of silica residue during the sulfonation process. When the samples before and after calcination are compared, it can be figured out that PS-SO₃H mainly locates in the inner shell and core, which is consistent with the results of HR-TEM.

 N_2 adsorption–desorption isotherms of PS-SO₃H@phenylenesilica YDSNs and PS-SO₃H@phenylenesilica DSNs are type IV, with a sharp capillary condensation step and an H3 hysteresis loop starting from a relative pressure P/P_0 of 0.40 (Fig. 3A), showing that both samples have mesoporous structures. The H3 hysteresis loop is from the inner void space. PS-SO₃H@phenylenesilica YDSNs and PS-SO₃H@phenylenesilica DSNs have high BET surface area (406.1 and 422.0 m²/g), large pore volume (0.35 and 0.41 cm³/g), and coexistence of mesopores and micropores (Fig. 3B and Table 1). The surface area of the solid acids is much larger than that of commercial Amberlyst-15, which will benefit the diffusion of guest molecules during the catalytic process.

3.3. Characterizations of chemical composition, thermal stability, and acidity

The chemical composition of solid acids with different nanostructures was carefully characterized by FT-IR and solid NMR technique (Fig. 4). The FT-IR spectra of PS-SO₃H@phenylenesilica YDSNs and PS-SO₃H@phenylenesilica DSNs exhibit a broad intense peak around 1300–1000 cm⁻¹ corresponding to the Si–O–Si stretch vibration characteristic of silica-based materials. The peaks attributed to sulfonic acid groups at 581 and 1415 cm⁻¹ appeared in the FT-IR spectra of PS-SO₃H@phenylenesilica YDSNs and PS-SO₃-H@phenylenesilica DSNs. The ¹³C CP-MAS NMR spectra of PS-SO₃-H@phenylenesilica YDSNs and PS-SO₃-H@phenylenesilica DSNs clearly display the signal at around 142 ppm assigned to the aromatic carbon coordinated with sulfonic acid groups. These results confirm the successful formation of PS-SO₃H via sulfonation.

Two sets of chemical shifts in the range of -35 to -90 ppm and -85 to -120 ppm, respectively, attributed to T and Q sites of silicon species could be clearly observed in 29 Si MAS NMR spectra



Fig. 1. TEM images of PS-SO₃H@phenylenesilica and the corresponding parent materials: PS@phenylenesilica YSNs (A) and PS-SO₃H@phenylenesilica YDSNs before (B) and after calcination (C); PS@phenylenesilica-L YSNs (D) and PS-SO₃H@phenylenesilica DSNs before (E) and after calcination (F). Scale bar, 200 nm.



Fig. 2. HR-TEM images of PS-SO₃H@phenylenesilica YDSNs (A) and PS-SO₃H@phenylenesilica DSNs (B) and corresponding element mapping image analysis of silica and sulfur along the area 1 shown in (A) and (B).

of PS-SO₃H@phenylenesilica YDSNs and PS-SO₃H@phenylenesilica DSNs, showing that both materials are hybrids of benzene–silicas (mainly distributed in the outer shell) and pure silicas (both in the outer shell and in the inner shell). T/(T + Q) for PS-SO₃H@phenylenesilica YDSNs and PS-SO₃H@phenylenesilica DSNs is respectively 0.61 and 0.68, calculated by the integration of the peak

area. These results show that the hybrid solid acids were composed of sulfonic acid groups, silicas, and phenylenesilica.

Based on the acid–base titration method, PS-SO₃H@phenylenesilica YDSNs and PS-SO₃H@phenylenesilica DSN have acid exchange capacity respectively of 1.0 and 1.2 mmol/g, much lower than the S content from elemental analysis results (Table 1). This

Fig. 3. N₂ adsorption-desorption isotherms (A) and the corresponding pore size distributions (B) of PS-SO₃H@phenylenesilica YDSNs (a), PS-SO₃H@phenylenesilica DSNs (b), and PS-SO₃H@phenylenesilica YDSNs after being used for the 9th cycle in the Friedel-Crafts alkylation reaction (c).

| Table 1 |
|---|
| Textural parameters, acidity, and sulfur content of solid acid catalyst |

| Sample | S_{BET}^{a} (m ² /g) | $V_t^{\rm b}$ (cm ³ /g) | $D_{\rm BJH}^{\rm c}({\rm nm})$ | $D_{\rm HK}^{\rm c}({\rm nm})$ | Acid exchange capacity (mmol/g) ^d | S content (mmol/g) ^e |
|-------------------------------|--|------------------------------------|---------------------------------|--------------------------------|--|---------------------------------|
| Amberlyst-15 | 41.8 ± 0.15 | 0.31 | 40 | - | 4.7 ± 0.06 | 4.9 ± 0.03 |
| | | | | | $(3.6 \pm 0.04)^{t}$ | (3.9 ± 0.06) |
| PS-SO₃H@phenylenesilica YDSNs | 406.1 ± 3.4 | 0.35 | 2.1 (2.0) | 1.3 | 1.0 ± 0.03 | 2.3 ± 0.05 |
| | (235.6 ± 3.2) | (0.16) | | | $(2.1 \pm 0.06)^{\rm f}$ | (2.1 ± 0.05) |
| PS-SO₃H@phenylenesilica DSNs | 422.0 ± 1.3 | 0.41 | 2.1 | 1.2 | 1.2 ± 0.03 | 2.1 ± 0.03 |
| SO3H-phenylenesilica HNs | 438.0 ± 3.4 | 0.49 | 2.1 | - | 0.49 ± 0.02 | 0.5 ± 0.03 |

^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_{BJH} and D_{HK} are BJH mesopore diameter and HK micropore diameter calculated by the desorption branches of the nitrogen sorption isotherms.

^d based on acid-base titration.

^e based on elemental analysis.

^f Data in parentheses for Amberlyst-15 and PS-SO₃H@phenylenesilica YDSNs were obtained respectively after four and nine cycles in the Friedel–Crafts alkylation reaction.

shows that some of the acid sites in the solid acids could not be accessed during the titration process [27]. The control sample, SO₃H-phenylenesilica HNs, has comparable BET surface area and pore diameter but much lower acidity than PS-SO₃H@phenylenesilica YDSNs and DSNs (TEM; see Fig. S2 in the Supplemental Material). This shows that SO₃H groups could be incorporated into benzene-silica during the sulfonation process, similarly to the previous report [29]. This result also suggests that SO₃H groups also exist in the shells of PS-SO₃H@phenylenesilica YDSNs and DSNs.

The thermal stability of solid acids was investigated by TG analysis (Fig. 4). PS-SO₃H@phenylenesilica YDSNs and PS-SO₃H@ phenylenesilica DSNs exhibit similar TG curves with two step weight losses at 300–450 and 450–700 °C due to the destruction of sulfonated polystyrene frameworks and benzene–silica, respectively [30,31]. PS-SO₃H@phenylenesilica YDSNs and PS-SO₃H@phenylenesilica DSNs show higher thermal stability than Amberlyst-15, with decomposition temperature around 200 °C, probably due to the protective effect of the outer silica shells of the unique hollow nanostructures.

The acid strength of solid acids was investigated using TEPO (triethylphosphine oxide) as a base probe molecule in combination with the ³¹P MAS NMR technique [32–36] (Fig. 5). Amberlyst-15 exhibits the chemical shift at 89.4 ppm that was assigned to TEPO adsorbed on sulfonic acid group sites [27]. PS-SO₃H@phenylenesilica YDSNs with chemical shift at 85.0 ppm have lower acid strength than PS-SO₃H@phenylenesilica DSNs with chemical shift at 87.0 ppm. Our previous studies show that the acid strength of PS-SO₃H could be enhanced or weakened by controlling its aggregation and swelling state in a confined nanospace. Based on the TEM images, the volume of PS after sulfonation for PS-SO₃H@phenylenesilica DSNs is $10.8 \times 10^{-21} \text{ m}^3$ and $9.6 \times 10^{-21} \text{ m}^3$, respectively. This could

explain the lower acid strength of PS-SO₃H@phenylenesilica YDSNs. PS-SO₃H@phenylenesilica YDSNs and PS-SO₃H@ phenylenesilica DSNs both have lower acid strength than Amberlyst-15. As a comparison, the acid strength of SO₃H-phenylenesilica HNs (Fig. S2) was also characterized using the same method. SO₃Hphenylenesilica HNs with acid exchange capacity of 0.47 mmol/g exhibit chemical shift at 61.9 ppm. The low acid strength of SO₃H-phenylenesilica HNs is probably due to the low acid concentration [26].

3.4. Catalytic results

The catalytic performance of solid acids with different nanostructures and acid strength was tested in acid-catalyzed liquid phase reactions and compared with that of concentrated H₂SO₄ and Amberlyst-15 (Table 2). Two types of reactions, esterification of fatty acid with ethanol and liquid-phase Friedel–Crafts alkylation, were chosen to clarify the influence of the nanostructure, acid strength, and thermal stability of solid acids on their catalytic performance.

3.4.1. Esterification of fatty acid with ethanol

All solid acids tested could catalyze the esterification of lauric acid and ethanol with ethyl laurate as the only organic product. 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. Liquid acid, H₂SO₄, affords high activity with TOF of 40.7 h⁻¹. Under the same reaction conditions, PS-SO₃H@phenylenesilica YDSNs and PS-SO₃H@phenylenesilica DSNs with TOF of ~24.1 h⁻¹ exhibit comparable activity, probably due to the similar composition and nanostructure of the two materials. Notably,





Fig. 4. FT-IR spectra (A), ¹³C CP-MAS NMR spectra (B), solid-state ²⁹Si NMR spectra (C), and TG curves (D) of PS-SO₃H@phenylenesilica YDSNs (a), PS-SO₃H@phenylenesilica DSNs (b), and Amberlyst-15 (c).



Fig. 5. ³¹P MAS NMR spectra (A) of PS-SO₃H@phenylenesilica YDSNs (a), PS-SO₃H@phenylenesilica YDSNs after being used for the 9th cycle in the Friedel–Crafts alkylation reaction (b), PS-SO₃H@phenylenesilica DSNs (c), and SO₃H-phenylenesilica HNs (d); (B) KN criterion plot of f_w (g^{-1}) versus r (mol h^{-1} g^{-1}) for the esterification of lauric acid and ethanol at 50 and 80 °C.

SO₃H-phenylenesilica HNs with TOF of $37.7 h^{-1}$ are more active than PS-SO₃H@phenylenesilica YDSNs and PS-SO₃H@phenylenesilica DSNs. Differently from PS-SO₃H@phenylenesilica YDSNs and PS-SO₃H@phenylenesilica DSNs, SO₃H-phenylenesilica HNs prepared by sulfonation of phenylenesilica HNs have a uniform distribution of acid sites in the shells. Thus, the high activity of SO₃H-phenylenesilica HNs is mainly attributed to a high exposure of acid sites and a short diffusion length of the reactants and products. The hybrid solid catalysts afford a higher yield of ethyl laurate than H₂SO₄. This is probably related to the fact that benzene-silica

provides a hydrophobic microenvironment, which may help to slow the reaction rate of the reverse hydrolysis reaction and prevent the poison of sulfonic acid groups by water. The fact that the activity of solid acids has no direct relation to their acid strength suggests that the exposure of acid sites is more important than the acid strength in the esterification reaction.

3.4.2. Koros-Nowak (KN) criterion test

In order to establish that the measured catalytic activity is independent of transport phenomena, the Koros–Nowak (KN) criterion

Table 2

The catalytic performance of acid catalysts in the esterification reaction and the Friedel-Crafts alkylation reaction:



| Catalysts | Esterification ^a | | Friedel–Crafts alkylation ^b | |
|--|-----------------------------|----------------|--|----------------|
| | TOF $(h^{-1})^{c}$ | Yield (%) | TOF $(h^{-1})^{c}$ | Conv. (%) |
| H ₂ SO ₄ | 40.7 ± 0.3 | 80.4 ± 0.3 | 4.0 ± 0.1 | 10.0 ± 0.8 |
| Amberlyst-15 ^d | 3.3 ± 0.1 | 41.2 ± 0.9 | 23.7 ± 0.2 | 98.3 ± 0.5 |
| PS-SO ₃ H@phenylenesilica YDSNs | 24.1 ± 0.1 | 85.6 ± 0.8 | 11.5 ± 0.2 | 94.9 ± 0.5 |
| PS-SO ₃ H@phenylenesilica DSNs | 20.5 ± 0.2 | 83.8 ± 0.4 | 7.3 ± 0.1 | 31.3 ± 1.0 |
| SO ₃ H-phenylenesilica HNs | 37.7 ± 0.6 | 86.3 ± 0.8 | - | 5.6 ± 0.2 |

^a The esterification reaction: 80 °C, 6 h, 0.04 mmol of acid sites, 2 mmol of lauric acid and 10 mmol ethanol.

^b The Friedel–Crafts alkylation reaction: 120 °C, 6 h, 5 mmol % of acid sites, 2 mmol of 1-hexene, and 24 mmol of toluene.

^c For the calculation of TOFs, the acid sites (H^*) were measured by the acid-base titration method.

^d The conversion of 1-hexene for Amberlyst-15 was obtained at 2 h.

test modified by Madon-Boudart has been employed [37,38]. PS-SO₃H@phenylenesilica YDSNs was used as a model sample for the esterification of lauric acid and ethanol. The reaction rates in the kinetic regime should be proportional to the concentration of active sites (H⁺ in the present case). Hence a series of batch experiments were performed following identical reaction conditions at 50 and 80 °C. The KN criterion has been explained by plotting the reaction rate (*r*) in mol h⁻¹ g⁻¹ of catalyst versus the weight of H⁺ (f_w) in g⁻¹, as shown in Fig. 5B. The value of the slope calculated from the graph in Fig. 5B is 0.97 and 1.06 at 50 and 80 °C, respectively. Because the calculated values of the slope are close to unity, it can be concluded that the rate of transport has no influence on the reaction rates.

3.4.3. Friedel-Crafts alkylation

The catalytic performance of solid acids was also tested in liquid-phase Friedel–Crafts alkylation of toluene with 1-hexene at S/C of ~20. Friedel–Crafts alkylations are industrially important reactions used to produce numerous chemical compounds. Classical Friedel–Crafts chemistry often relies on liquid acid catalysts, such as AlCl₃ and HF, because high acid strength is needed to catalyze this reaction. Due to the severe drawbacks of liquid acids, the development of solid acids is an urgent need. To avoiding oligomerization of alkenes, a molar ratio of toluene/1-hexene of 12 was used. Only 10% 1-hexene conversion was found on H₂SO₄, showing that H₂SO₄ has poor activity at low concentrations. Amberlyst-15 affords the highest activity among all the catalysts tested. Within 2 h, 98.3% of 1-hexene was converted to several isomers of Me-C₆H₄–C₆H₁₃. A small amount of dialkylated product (dihexylbenzene isomers) was observed as well.

Under similar reaction conditions, PS-SO₃H@phenylenesilica YDSNs and PS-SO₃H@phenylenesilica DSNs with TOF respectively of 11.5 and 7.3 h⁻¹ are less active than Amberlyst-15 with TOF of 23.7 h⁻¹. With reaction time prolonged to 6 h, 94.9% conversion of 1-hexene could be obtained on PS-SO₃H@phenylenesilica YDSNs. PS-SO₃H@phenylenesilica DSNs only give 31.3% conversion of 1-hexene. Under similar reaction conditions, SO₃H-phenylenesilica HNs show very low activity, with 1-hexene conversion of only 5.6%. Thus, the distinct difference in catalytic performance of the solid acid catalysts is not related to the exposure degree of acid sites. It has been shown in previous work that higher acid strength was needed for Friedel–Crafts alkylation. So the catalytic activity of solid acids in alkylations could be correlated to the strength of their acid sites [27]. Based on these results, Amberlyst-15 indeed has higher acid strength than PS-SO₃H@ phenylenesilica YDSNs and PS-SO₃H@phenylenesilica DSNs. So it is reasonable that Amberlyst-15 shows higher activity. However, PS-SO₃H@phenylenesilica YDSNs with lower acid strength than PS-SO₃H@phenylenesilica DSNs show higher activity.

To clarify the reason for the low activity of PS-SO₃H@phenylenesilica DSNs, the catalytic reaction was stopped after 4 h and solid catalysts were taken out and analyzed with TEM. The TEM image shows that the double-shell nanostructure changed completely to a hollow nanostructure (Fig. 6A) and the volume of sulfonated polystyrene calculated based on the TEM image was increased from the original 9.6×10^{-21} m³ to 17.4×10^{-21} m³. As we have reported, the swelling of PS-SO₃H could decrease the acid strength of solid acids. So the low activity of PS-SO₃H@phenylenesilica DSNs is possibly due to the decreased acid strength caused by the swelling of PS-SO₃H during the catalytic process. PS-SO₃H@phenylenesilica YDSNs exhibit high stability and the yolk–double-shell nanostructure could be retained during the catalytic process, which we will discuss later.

3.4.4. Stability of solid acid catalysts

One of the important advantages for solid acids is recyclability. In view of their good performance, PS-SO₃H@phenylenesilica YDSNs were chosen for a stability test in Friedel–Crafts alkylation of toluene with 1-hexene. As a comparison, the recyclability of Amberlyst-15 was investigated under the same conditions. As shown in Fig. 7, Amberlyst-15 exhibited a very high deactivation rate during four successive cycles. The conversion of 1-hexene decreased from 97.8% in the first cycle to 45.0% for the fourth cycle. For PS-SO₃H@phenylenesilica YDSNs, the conversion of 1-hexene was quite steady in the first seven cycles. An obvious decrease in conversion was observed for the 8th run; however, 70% conversion of 1-hexene could still be obtained for the ninth run. The result suggests that PS-SO₃H@phenylenesilica YDSNs are more stable than Amberlyst-15.

To understand the reason for the deactivation, the sulfur content of both PS-SO₃H@phenylenesilica YDSNs and Amberlyst-15 was analyzed after the recycle reaction (Table 1). The sulfur content of Amberlyst-15 decreased from 4.9 to 3.9 mmol/g after four reaction cycles, indicating that about 20% of sulfonic acid groups were leached during the recycle process. So leaching of sulfonic acid groups may be the main reason for the deactivation of



Fig. 6. TEM image of PS-SO₃H@phenylenesilica DSNs taken out at 4 h during the Friedel–Crafts alkylation (A) and PS-SO₃H@phenylenesilica YDSNs after first (B) and ninth cycles (C). Scale bar, 200 nm.



Fig. 7. Recycling ability of PS-SO₃H@phenylenesilica YDSNs (gray) and Amberlsyt-15 (black) in F-C alkylation of toluene with 1-hexene.

Amberlyst-15. For PS-SO₃H@phenylenesilica YDSNs, the sulfur content remained almost unchanged even after nine cycles, suggesting much higher stability of the sulfonic acid groups. However, the acid exchange capacity of PS-SO₃H@phenylenesilica YDSNs increases from 1.0 to 2.1 mmol/g after nine cycles, suggesting that the nanostructure of PS-SO₃H@phenylenesilica YDSNs might change during the continuous recycling process.

As shown in Fig. 6, the nanostructure of PS-SO₃H@phenylenesilica YDSNs did not change after the first run. However, swelling of the core was clearly observed after nine cycles. This could explain the increase in acid exchange capacity after reuse. ³¹P NMR characterization (Fig. 5) also shows an upfield of chemical shift from 85.1 to 80.0 ppm after nine cycles, showing a decrease in acid strength after reuse. Based on TEM images, the volume of PS-SO₃H increases from 10.8×10^{-21} to 15.1×10^{-21} m³ after nine cycles. The gradual swelling of PS-SO₃H is the main reason for the slow decrease in acid strength. Obvious decreases in BET surface area and pore volume were observed for PS-SO₃H@phenylenesilica YDSNs after reuse, probably due to pore blockage by the swelling PS-SO₃H. The combined results show that the decrease in acid strength and BET surface area caused by gradual swelling of PS-SO₃H is the main reason for the deactivation of PS-SO₃H@phenylenesilica YDSNs.

4. Conclusions

In summary, PS-SO₃H@phenylenesilica with DSNs and YDSNs nanostructure was successfully synthesized. It was found that acid strength of solid acids is directly related to the swelling and aggregation of PS-SO₃H in a confined nanospace. PS-SO₃H@phenylenesilica

DSNs with PS-SO₃H in a more aggregated state show higher acid strength than PS-SO₃H@phenylenesilica YDSNs with PS-SO₃H in a less aggregated state. PS-SO₃H@phenylenesilica DSNs and PS-SO₃-H@phenylenesilica YDSNs show comparable activity in esterification reactions due to the similar nanostructure and compositions. However, PS-SO₃H@phenylenesilica YDSNs are more active than PS-SO₃H@phenylenesilica DSNs in the Friedel–Crafts alkylation of toluene with 1-hexene. This is due to the fact that the unique YDSNs nanostructure affords superior resistance to the swelling of PS-SO₃H during the catalytic process. Meanwhile, PS-SO₃H@phenylenesilica YDSNs show much higher stability than Amberlyst-15 in the Friedel–Crafts alkylation of toluene with 1-hexene. Our findings suggest that increasing antiswelling ability of PS-SO₃H in confined nanospaces may result in a highly efficient and stable solid acid catalyst.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2014.09.018.

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