Accepted Manuscript

Title: Fabrication of propylsulfonic acid functionalized SiO₂ core/PMO shell structured PrSO₃H-SiO₂@Si(R)Si nanospheres for the effective conversion of D-fructose into ethyl levulinate



Authors: Daiyu Song, Yingnan Sun, Qingqing Zhang, Panpan Zhang, Yihang Guo, Jiyan Leng

PII:	S0926-860X(17)30374-5
DOI:	http://dx.doi.org/doi:10.1016/j.apcata.2017.08.004
Reference:	APCATA 16359
To appear in:	Applied Catalysis A: General
Received date:	2-5-2017
Revised date:	19-7-2017
Accepted date:	2-8-2017

Please cite this article as: Daiyu Song, Yingnan Sun, Qingqing Zhang, Panpan Zhang, Yihang Guo, Jiyan Leng, Fabrication of propylsulfonic acid functionalized SiO2 core/PMO shell structured PrSO3H-SiO2@Si(R)Si nanospheres for the effective conversion of D-fructose into ethyl levulinate, Applied Catalysis A, Generalhttp://dx.doi.org/10.1016/j.apcata.2017.08.004

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Fabrication of propylsulfonic acid functionalized SiO₂ core/PMO shell structured PrSO₃H-SiO₂@Si(R)Si nanospheres for the effective conversion of D-fructose into ethyl levulinate

Daiyu Song^a, Yingnan Sun^a, Qingqing Zhang^a, Panpan Zhang^a, Yihang Guo^{a,*} Jiyan Leng^{b,*}

^a School of Environment, Northeast Normal University, Changchun 130117, P.R. China
^b First Hospital of Jilin University, Jilin University, Changchun 130021, PR China

*Corresponding authors.

Tel./fax: +86 431 89165626. E-mail: guoyh@nenu.edu.cn (Y. Guo)

Graphic Abstract



Propylsulfonic acid functionalized SiO₂ core/alkyl- or phenyl-bridged organosilica shell structured PrSO₃H-SiO₂@Si(R)Si (R = $-C_2H_4-$, $-C_6H_4-$ or $-C_6H_4-$ C₆H₄-) nanospheres exhibit excellent catalytic activity and stability for the ethanolysis of D-fructose to ethyl levulinate.

Highlights

- Propylsulfonic acid functionalized SiO₂ core/PMO shell nanospheres are prepared.
- PrSO₃H-SiO₂@Si(R)Si exhibit excellent catalytic activity in D-fructose ethanolysis.
- Strong Brønsted acid nature of as-prepared catalysts plays key role to the activity.
- Unique hydrophilicity core/hydrophobicity shell positively influences the activity.
- PrSO₃H-SiO₂@Si(R)Si can be reused at least 3 times without loss of activity.

Abstract

Propylsulfonic acid functionalized SiO₂ core/alkyl- or phenyl-bridged organosilica shell structured PrSO₃H-SiO₂@Si(R)Si (R = $-C_2H_4-$, $-C_6H_4-$ or $-C_6H_4-C_6H_4-$) nanospheres are facilely prepared by a CTAB-directed one-pot two-step condensation strategy. The morphological characteristics, textural properties, Brønsted acid nature and structure of the PrSO₃H-SiO₂@Si(R)Si nanospheres are well characterized. The materials are successfully applied in the catalytic transformation of D-fructose into the important organic chemical, ethyl levulinate, in the presence of ethanol as both reactant and solvent. The catalytic activity of the PrSO₃H-SiO₂@Si(R)Si nanospheres outperform commercially available Amberlyst-15, HY zeolite and HCl, mainly attributing to their strong Brønsted acid nature; additionally, unique core-shell structure with excellent porosity properties and well-adjusted hydrophilicity/hydrophobicity also give the positive influence on the ethanolysis activity, which can improve the accessibility of the reactants to the PrSO₃H sites and facilitate the multi-step ethanolysis reaction proceeding to the formation of the final product. The PrSO₃H-SiO₂@Si(R)Si nanospheres can be reused three times

without obvious activity loss, contributed from covalent bonding of the PrSO₃H groups with the silica and organosilica framework as well as hydrophobic PrSO₃H-functionalized organosilica shell.

Keywords: Solid acid, Biomass-derived platform molecule, Biofuel, D-fructose, Ethyl levulinate

1. Introduction

The utilization of abundant, naturally available and renewable biomass/derivatives for the sustainable production of fuels and chemicals is of great current interest due to growing concerns over the depletion of fossil resources and associated environmental issues [1-3]. In this research field, catalytic transformation of carbohydrates (monosaccharides or polysaccharides) such as Dfructose, glucose, sucrose and cellulose into the important chemical building blocks like 5hydroxymethylfurfural (5-HMF), 5-ethoxymethylfurfural (5-EMF), levulinic acid (LA) and alkyl levulinate (AL) have attracted particular attention since the feedstocks can be derived from lignocellulosic biomass [4-7]. Among the aforementioned chemical building blocks, ALs such as methyl, ethyl and *n*-butyl levulinate have strong potential to be applied in the perfume and flavor industries and as blending agents for diesel fuel formulation [8-10]; moreover, ethyl levulinate (EL) is the most suitable fuel blend which can be directly used in diesel engines [11]. EL can be synthesized from the acid-catalyzed esterification of levulinic acid with ethanol [12], however, high price of levulinic acid makes the processes uneconomical [13]. More economically alternative EL production process is the acid-catalyzed ethanolysis of various feedstocks such as furfuryl alcohol, monosaccharides or polysaccharides, and particularly, efficient conversion of

monosaccharides or polysaccharides to EL is the ultimate process for the production of biofuels and chemical buildings directly from lignocellulosic biomass [14]. Homogeneous liquid acids such as HCl, H₂SO₄ or *p*-toluenesulfonic acid can catalyze the conversion of monosaccharides or polysaccharides into ALs effectively due to their strong acidity and high acid site density. However, the employment of them in industry often faces problems of waste generation, equipment corrosion and recycling difficulty [15,16]. Heterogeneous acid catalysts such as sulfated metal oxides [9,17], acidic zeolites [18], sulfonic acid silicas [18] and resin sulfonic acids [17] have therefore received considerable attentions and applied in the above process. However, the applications of the reported solid acids are limited owing to the disadvantages of low surface area, worse accessibility to the acid sites, poor mechanical or thermal stability as well as inferior durability and reusability. Thus, the development of novel, robust and recyclable strong solid acid catalysts for direct synthesis of ALs from lignocellulosic biomass-derived carbohydrate remains a challenge [17].

Silicas (SiO₂) or periodic mesoporous organosilicas (PMOs) are the ideal catalyst supports with the advantages of tunable porosity properties, morphological characteristics and surface hydrophilicity/hydrophobicity as well as easy functionalization. SiO₂ or PMO nanopores, nanospheres, nanorods, nanofibers and nanotubes have been successfully constructed [19]. Functionalization of these supports with sulfonic acid groups can significantly improve the catalytic activity of SO₃H-based solid acids because the aforementioned properties can influence the accessibility to the acid sites [20-24]. In the search for novel solid acid catalysts for the transformation of D-fructose (FOS) into EL, herein, propylsulfonic acid functionalized silica core/alkyl- or phenyl-bridged organosilica shell structured nanospheres, PrSO₃H-SiO₂@Si(R)Si, (R = $-C_2H_{4-}$, $-C_6H_{4-}$ or $-C_6H_{4-}$), with interesting micro/mesoporous bimodal structure are

facilely prepared by a CTAB-directed one-pot two-step condensation strategy. In the PrSO₃H- $SiO_2 @Si(R)Si$ nanospheres, PrSO₃H functionalized SiO₂ core is more hydrophilic owing to the presence of abundant hydroxyl groups in the silica framework, while PrSO₃H functionalized PMO shell is more hydrophobic because of the presence of alkyl or phenyl moieties within PMO framework. Core-shell structured nanospheres with interior core and outer shell exhibit unique properties including accessible pore channels, low density, large surface area, high permeability and excellent loading capacity; meanwhile, their shell thickness can be well-adjusted, and both the cores and shells can be functionalized. Therefore, as-prepared PrSO₃H-SiO₂@Si(R)Si nanospheres are expected to exhibit excellent catalytic activity and reusability in direct ethanolysis of FOS to EL. During the PrSO₃H-SiO₂@Si(R)Si nanospheres-catalyzed FOS ethanolysis process, the influence of the shell thickness and core/shell compositions on the catalytic activity are studied. Subsequently, the mechanism of EL production from the PrSO₃H-SiO₂@Si(R)Si-catalyzed ethanolysis of FOS is reasonably put forward based on the identified intermediates. The excellent ethanolysis activity of the PrSO₃H-SiO₂@Si(R)Si nanospheres is explained in terms of the strong Brønsted acid nature, well-adjusted hydrophilicity/hydrophobicity and unique porosity and morphological properties. Finally, the reusability of the PrSO₃H-SiO₂@Si(R)Si is investigated.

2. Experimental

2.1. Materials

1,2-Bis(trimethoxysilyl)ethane (BTMSE, 97%), 1,4-bis-(triethoxysilyl)benzene (BTESB, 96%), 4,4'-bis(triethoxysilyl)-1,1'-biphenyl (BTESBP, 95%) and 3mercaptopropyltrimethoxysilane (MPTMS, 95%) were purchased from Sigma-Aldrich. Tetraethoxysilane (TEOS, 98%) and D-fructose (FOS, 98%) was purchased from Sinopharm

5

Chemical Reagent Co. Ltd.. Cetyltrimethylammonium bromide (CTAB, 99%) was purchased from Beijing Fine Chemical Co.. Ethyl levulinate (EL, > 98.0%) was purchased from TCI. Commercial available Amberlyst-15 and HY zeolite was purchased from Alfa Aesar. The above reagents were used without further purification.

2.2. Catalyst preparation

2.2.1. PrSO₃H-SiO₂@Si(Ph)Si nanospheres

Typically, CTAB (0.16 g) was dissolved in 30 mL ethanol and 75 mL water solution containing 1 mL 25% ammonia at 35 °C under stirring for 1 h. Then, TEOS (1.2 mmol) and MPTMS (0.212 mmol) were simultaneously added to the above clear solution. After stirring for 24 h at 35 °C, a mixture of BTESB (0.45, 0.6 or 0.75 mmol) and MPTMS (0.212 mmol) were rapidly added to the above suspension, and the resultant white suspension was stirred at 35 °C for 24 h. The final chemical composition of the precursor solution was 0.439CTAB: 1.2TEOS: (0.45, 0.6 or 0.75)BTESB: 0.424MPTMS: 6.5NH4OH: 514C2H5OH: 4167H2O: 100H2O2 (molar ratio). Subsequently, the white product was collected by centrifugation and washed with ethanol and dispersed in aqueous solution. The suspension was transferred to an autoclave and heated at 120 °C with a heating rate of 2 °C min⁻¹ for additional 5 h. The resulting white solid powder was collected by centrifugation and washed with boiling ethanol containing concentrated HCl (240 µL, 37%) for three times to remove CTAB in the product. The obtained product was washed with ethanol three times and then dispersed in 10 mL H_2O_2 aqueous solution at room temperature under stirring for 24 h. The product was washed with deionized water to remove residual H₂O₂ aqueous solution and then air-dried at 60 °C for 12 h. The corresponding product is denoted as PrSO₃H-SiO₂@Si(Ph)Si-1, PrSO₃H-SiO₂@Si(Ph)Si-2 and PrSO₃H-SiO₂@Si(Ph)Si-3, respectively, representing different contents of phenyl-bridged organosilica in the product.

2.2.2. PrSO₃H-SiO₂@Si(Ph-Ph)Si or PrSO₃H-SiO₂@Si(Et)Si nanospheres

The procedure is similar to that of the PrSO₃H-SiO₂@Si(Ph)Si nanospheres, however, BTESB was replaced by BTESBP (precursor of biphenyl-bridged organosilica) or BTMSE (precursor of ethyl-bridged organosilica). The final chemical composition of the precursor solution was 0.439CTAB: 1.2TEOS: 0.6BTESBP (or BTMSE): 0.424MPTMS: 6.5NH₄OH: 514C₂H₅OH: 4167H₂O: 100H₂O₂ (molar ratio).

2.2.3. PrSO₃H-Si(Et)Si@SiO₂ nanospheres

The procedure is similar to that of the $PrSO_3H$ -SiO₂@Si(Et)Si nanospheres, but BTMSE and TEOS was successively added to the preparation system. The final chemical composition of the precursor solution was 0.439CTAB: 1.2TEOS: 0.6BTMSE: 0.424MPTMS: 6.5NH₄OH: 514C₂H₅OH: 4167H₂O: 100H₂O₂ (molar ratio).

2.2.4. PrSO₃H-SiO₂ nanospheres

The procedure is similar to that of the $PrSO_3H-SiO_2@Si(Ph)Si$ nanospheres, but BTESB was not added in the preparation system. The final chemical composition of the precursor solution was $0.439CTAB: 1.2TEOS: 0.2MPTMS: 6.5NH_4OH: 514C_2H_5OH: 4167H_2O: 100H_2O_2$ (molar ratio).

2.2.5. PrSO₃H-Si(Ph)Si nanospheres

The procedure is similar to that of the PrSO₃H-SiO₂ nanospheres, however, TEOS was replaced by BTESB. The final chemical composition of the precursor solution was 0.439CTAB:0.6BTESB:0.2MPTMS:6.5NH₄OH:514C₂H₅OH:4167H₂O:100H₂O₂ (molar ratio).

2.3. Catalyst characterization

Transmission electron microscope (TEM) observations were performed on a JEM-2100F high resolution transmission electron microscope at an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) images were taken on a XL-30 ESEM FEG field emission scanning electron microscope. Nitrogen porosimetry measurement was performed on a Micromeritics ASAP 2020M surface area and porosity analyzer after the samples were outgassed under vacuum at 363 K for 1 h and 373 K for 12 h. The surface area (SBET) was calculated using the Brunauer-Emmett-Teller equation, pore diameters (D_p) was calculated using Barrett-Joyner-Halenda desorption branch of the isotherms, and pore volume (V_p) was accumulated up to $P/P_0 = 0.99$. ²⁹Si magic angle spinning (MAS) NMR and ¹³C cross polarization-magic angle spinning (CP-MAS) NMR spectra were recorded on a Bruker AVANCE III 400 WB spectrometer equipped with a 4 mm standard bore CP MAS probe head. The dried and finely powdered samples were packed in the ZrO₂ rotor closed with a Ke-F cap which was spun at 12 kHz rate. Chemical shifts for ²⁹Si MAS NMR and ¹³C CP-MAS NMR spectra were referenced to the signal of 3-(trimethylsilyl)-1propanesulfonic acid sodium salt standard ($\delta = 0.0$) and C₁₀H₁₆ standard (δ CH₂ = 38.5), respectively. The Brønsted acid-site density ($A_{titration}$, $\mu eq(H^+) g^{-1}$) was determined by titration with NaOH solution (0.0045 mol L^{-1}), and the detailed procedures were followed by the literature work [25].

2.4. Catalytic test

The catalysts were dried for 2 h at 120 °C in a vacuum before the catalytic tests.

Ethanolysis of FOS was carried out in an autoclave with a Teflon lining under the conditions of 140 °C, ethanol (68.95 mmol) to FOS (0.278 mmol) molar ratio of 248 and the ratio FOS/catalyst of 1 wt/wt, and stirring was applied throughout the reaction. The concentration of the produced EL was determined periodically on a Shimadzu 2014C gas chromatograph fitted with a HP-

INNOWAX capillary column and flame ionization detector. The injection port temperature was 250 °C, the oven temperature was maintained at 60 °C for 5 min, and then raised to 180 °C for 10 min at a heating rate of 8 °C min⁻¹. The GC injector temperature was 250 °C. Ethyl laurate was applied as an internal standard. The catalytic activity of the catalyst was evaluated quantitatively by the yield of EL (*Y*, %) and turnover frequency (TOF, h⁻¹), respectively. Herein, *Y* (%) = $(M_D/M_T) \times 100$, where M_D and M_T is the number of moles of EL produced and expected. TOF values were determined from the linear portion of the initial reaction rate profile for the yield of EL, which were normalized to the acid site density measured by acid-base titration. The intermediates produced during the catalytic process were identified by a mass spectrometry coupled with gas chromatography (HP6890GC-5973MSD) and a high-resolution electrospray ionization time-of-flight mass spectrometry equipped with high performance liquid chromatography (Agilent1200HPLC-micrOTOFESI-TOF-MS).

3. Results and discussion

3.1. Preparation of the PrSO₃H-SiO₂@Si(R)Si nanospheres

The PrSO₃H-SiO₂@Si(R)Si nanospheres are facilely and repeatedly prepared by a CTABdirected one-pot two-step condensation strategy followed by H_2O_2 post-oxidation process. As shown in Scheme 1, the PrSO₃H-SiO₂ core is obtained by a CTAB-directed hydrolysis/condensation of tetraethoxysilane (TEOS) with 3-mercaptopropyltrimethoxysilane (MPTMS) under ammonia environment. Specifically, when TEOS and MPTMS are mixed with aqueous ethanol solution containing CTAB and ammonia, they gradually hydrolyze to give the hydroxyl group-containing hydrolyzed precursors. Subsequently, the hydrolyzed precursors coassembly with spherical CTAB cation micelles (CTA⁺) *via* electrostatic interaction and condense

to form spherical propylthiol (SH) group-functionalized SiO₂ core. In the next step, spherical SH group-functionalized PMO shell is fabricated around the core after further adding bissilylated organic precursors (e.g. BTESB, BTESBP or BTMSE) and MPTMS into the reaction system with a time interval of 24 h. The successive growth of the core and shell is further facilitated under hydrothermal condition (120 $^{\circ}$ C, 5 h), leading to the formation of perfect spherical morphology with porous core and shell (see Fig. 1). Moreover, the shell thickness can be modulated by changing the starting amount of the bissilylated organic precursors, and the hydrophobicity of the shell can be adjusted by the introduction of different alkyl or phenyl moieties within the silica/carbon framework. Finally, propylsulfonic acid functionalized silica core/PMO shell nanospheres are obtained after removing CTAB by acidic boiling ethanol washing and oxidation of –SH groups by H₂O₂.

3.2. Catalyst characterization

3.2.1. Morphological characteristics and porosity properties

Morphological characteristics of as-prepared PrSO₃H-SiO₂@Si(R)Si are revealed by TEM (Fig. 1) and SEM observations (Fig. 2). The images shown in Fig. 1a and b indicate that the PrSO₃H-SiO₂ or PrSO₃H-Si(Ph)Si prepared by a CTAB-directed hydrolysis/condensation of TEOS or BTESB with MPTMS exhibit solid and monodispersed spherical morphology with porous structure and well-distributed particle size, and the estimated outer diameter of the PrSO₃H-SiO₂ and PrSO₃H-Si(Ph)Si particles are 155 and 140 nm (Table 1). After the formation of the PrSO₃H-SiO₂@Si(R)Si particles, their porous core-shell structure can be visibly observed (Fig. 1c-g), and the average core diameter is closed to the outer diameter of the PrSO₃H-SiO₂ or PrSO₃H-Si(Ph)Si nanospheres (Table 1). From the result shown in Fig. 1c, f and g it is found that the PrSO₃H-SiO₂@Si(R)Si nanospheres prepared at the same bissilylated organic precursor (BTESB, BTESBP

or BTMSE) adding amount possess the similar shell thickness (21, 23 and 23 nm), regardless of the structure of the incorporated functional organic moieties (R).

The core-shell structured PrSO₃H-SiO₂@Si(R)Si particles with opened porous structure favor the diffusion of the reactants and intermediates into the interior of the spheres, which can improve the accessibility of the active sites to the substrates. Moreover, the shell thickness is also one of the factors that influence the diffusion of the reactants and products. In order to evaluate the influence of the shell thickness on the catalytic activity of the PrSO₃H-SiO₂@Si(R)Si nanospheres, the shell thickness of the representative PrSO₃H-SiO₂@Si(Ph)Si is modulated by changing the starting amount of BTESB, which gives rise to the PrSO₃H-SiO₂@Si(Ph)Si-**1**, PrSO₃H-SiO₂@Si(Ph)Si-**2** and PrSO₃H-SiO₂@Si(Ph)Si-**3** nanospheres with the estimated shell thickness of 21, 25 and 30 nm, respectively (Fig. 1c–e and Table 1).

As for the PrSO₃H-functionalized ethyl-bridged organosilica core/SiO₂ shell structured PrSO₃H-Si(Et)Si@SiO₂ nanoparticles, its porous core-shell structure is also fabricated. The estimated core diameter and shell thickness are 165 and 21 nm, respectively (Fig. 1h).

From the SEM images shown in Fig. 2a and b it is found that the representative samples, PrSO₃H-SiO₂@Si(Ph)Si-**2** (outer diameter of 205 nm) and PrSO₃H-SiO₂@Si(Ph-Ph)Si (outer diameter of 206 nm), exhibit uniform and monodispersed spherical morphology; however, their core-shell structure is hardly observed by this method.

The results of nitrogen gas porosimetry measurement support the above TEM and SEM observations. From the nitrogen gas adsorption/desorption isotherms of three $PrSO_3H-SiO_2@Si(Ph)Si$ nanospheres with different shell thicknesses it is found that the samples exhibit interesting micro/mesoporosity with the characteristics of a rapid increasing nitrogen gas adsorbed amount at relative pressure (*P*/*P*₀) lower than 0.1 (Type I isotherm) and Type IV isotherm with a

large H1-type hysteresis loop at $P/P_0 = 0.4-1.0$ (Fig. 3a). The result signifies that the PrSO₃H-SiO₂@Si(Ph)Si nanospheres possess regular mesopores without interconnecting channels, regardless of the shell thickness. The pore size distribution curves indicate that the mesopores of three PrSO₃H-SiO₂@Si(Ph)Si nanospheres are well-distributed (Fig. 3b), and the average pore diameter is 3.8 (PrSO₃H-SiO₂@Si(Ph)Si-1), 3.8 (PrSO₃H-SiO₂@Si(Ph)Si-2) and 4.2 nm (PrSO₃H-SiO₂@Si(Ph)Si-3), respectively. From the determined textural parameters summarized in Table 1 it can be seen that three PrSO₃H-SiO₂@Si(Ph)Si nanospheres exhibit excellent porosity properties with extremely large BET surface area (866, 810 and 815 m² g⁻¹) and high pore volume (0.77, 0.73 and 0.62 cm³ g⁻¹), and the shell thickness of the nanospheres has little influence on their BET surface area. However, the pore volume is affected by the shell thickness in some extent, and the nanospheres with thicker shell thickness possesse lower pore volume. The extremely large BET surface area of the PrSO₃H-SiO₂@Si(Ph)Si nanospheres is contributed from the outer and inner surface of both the core and the shell as well as open porous structure of the nanospheres.

Similarly, the PrSO₃H-SiO₂@Si(Ph-Ph)Si and PrSO₃H-SiO₂@Si(Et)Si nanospheres also show the micro/mesoporosity properties to those of the PrSO₃H-SiO₂@Si(Ph)Si nanospheres, and their nitrogen gas adsorption/desorption isotherms display a rapid increasing nitrogen gas adsorbed amount at P/P_0 lower than 0.1 (Type I isotherm) and H2- or H4-type hysteresis loop at P/P_0 = 0.40–0.85 (Fig. 3c). Therefore, it is inferred that the PrSO₃H-SiO₂@Si(Ph-Ph)Si and PrSO₃H-SiO₂@Si(Et)Si nanospheres possess narrow mouth shaped mesopores. These two samples show very sharp pore size distribution curves, implying that they have uniform mesopores (Fig. 3d). The determined average pore diameter of them is 3.8 nm, and they still possess large BET surface area, i.e., 696 and 790 m² g⁻¹ for the PrSO₃H-SiO₂@Si(Ph-Ph)Si and PrSO₃H-SiO₂@Si(Et)Si, respectively (Table 1).

As for the PrSO₃H-Si(Et)Si@SiO₂ nanospheres composed of PrSO₃H-functionalized ethylbridged organosilica core and silica shell, it still exhibits micro/mesoporosity with very small hysteresis loop (Fig. 3c); meanwhile, its pore size distribution curve becomes wider, together with low pore volume (Fig. 3d). However, its BET surface area (777 m² g⁻¹, Table 1) is still large. The individual PrSO₃H-SiO₂ and PrSO₃H-Si(Ph)Si nanospheres also show micro/mesoporosity properties, evidenced by the nitrogen gas adsorption/desorption isotherms and pore size distribution curves presented in Fig. 3e and f; additionally, both of them possess extremely small hysteresis loop. Owing to having plentiful pores within the nanospheres, the PrSO₃H-SiO₂ has extremely larger BET surface area (1060 m² g⁻¹) than that of the PrSO₃H-Si(Ph)Si (757 m² g⁻¹), but their pore diameter is the same (3.9 nm, Table 1). As expected, after the formation of the coreshell structured PrSO₃H-SiO₂@Si(Ph)Si-**1** nanospheres, its BET surface area (866 m² g⁻¹) is larger than that of PrSO₃H-Si(Ph)Si but smaller than PrSO₃H-SiO₂.

3.2.2 Composition and structure

The formation of the inorganic-organic silica framework and the incorporation of PrSO₃H groups within the framework of the PrSO₃H-SiO₂@Si(R)Si nanospheres were studied by ²⁹Si MAS NMR (Fig. 4a) and ¹³C CP-MAS NMR spectra (Fig. 4b-d).

In the ²⁹Si MAS NMR spectrum of the representative sample, $PrSO_3H-SiO_2@Si(Ph)Si-2$, three characteristic resonances are found at -56, -60 and -69 ppm, respectively, which are originated from the organosiloxane species including T¹ [C–Si(OSi)(OH)₂], T² [C–Si(OSi)₂(OH)] and T³ [C–Si(OSi)₃] within the carbon/silica framework of the shell [26,27]; additionally, the other four characteristic resonances detected at -80, -94, -102 and -111 ppm are assigned to the inorganic silica species including Q¹ [Si(OSi)(OH)₃], Q² [Si(OSi)₂(OH)₂], Q³ [Si(OSi)₃(OH)] and Q⁴ [Si(OSi)₄] from the core of nanospheres, respectively [27]. The result indicates that the silica core

and organosilica shell of the PrSO₃H-SiO₂@Si(R)Si nanospheres are fabricated by using current preparation route.

In the ¹³C CP-MAS NMR spectrum of the PrSO₃H-SiO₂@Si(Ph)Si-**2** nanospheres (Fig. 4b), the detected three signals at 11, 17 and 53 ppm belong to the C^1-C^3 species of the PrSO₃H groups, implying that the PrSO₃H groups are successfully introduced within the silicon/carbon framework [28]. Additionally, the other predominant signal found at 132 ppm is due to the carbon species (C⁴) of phenyl-bridged silsesquioxane framework of the shell [17,24,29].

Similarly, in the ¹³C CP-MAS NMR spectra of the PrSO₃H-SiO₂@Si(Ph-Ph)Si (Fig. 4c) and PrSO₃H-SiO₂@Si(Et)Si nanospheres (Fig. 4d), three characteristic resonances originated from PrSO₃H groups can also be found at 11, 17 and 53 ppm. As for the other four strong signals found at 143.0, 134.6, 130.3 and 126.2 ppm in Fig. 4c, they are assigned to C^4-C^7 species of biphenyl-bridged silsesquioxane framework of the shell [24], while the strongest signal detected at 5.1 ppm in Fig. 4d attributes to C^4 species of ethyl-bridged silsesquioxane framework of the shell [28,30]. As for the signal found at 58.2 ppm in Fig. 4b, c and d, it is assigned to the residual carbon species of the ethoxy groups, which are formed during the boiling ethanol washing step [12,21,31].

Combination of the ²⁹Si MAS NMR and ¹³C CP-MAS NMR spectra it is concluded that PrSO₃H group-functionalized silica core/alkyl- or phenyl-bridged organosilica shell are created in the PrSO₃H-SiO₂@Si(R)Si nanospheres by using CTAB-directed one-pot two steps sol-gel process, and its core and shell are composed of covalently bonded $-Si-O_{1.5}-Si-PrSO_3H$ and $O_{1.5}-Si-R-Si-O_{1.5}-Si-PrSO_3H$ (R = $-C_6H_4-/-C_6H_4-/-C_2H_4-$) framework, respectively (Scheme 1).

3.2.3. Brønsted acid site density

The Brønsted acid site density ($A_{titration}$, $\mu eq g^{-1}$) of as-prepared PrSO₃H-SiO₂@Si(R)Si nanospheres is determined by titration with dilute NaOH solution. As shown in Table 1, three

PrSO₃H-SiO₂@Si(Ph)Si nanospheres possess similar Brønsted acid-site density (522–540 µeq g⁻¹), and the shell thickness has a slight influence on this value. As for the PrSO₃H-SiO₂@Si(Ph-Ph)Si (508 µeq g⁻¹) and PrSO₃H-SiO₂@Si(Et)Si (571 µeq g⁻¹) nanospheres, their Brønsted acid-site density is similar to that of the PrSO₃H-SiO₂@Si(Ph)Si-**1** nanospheres. The PrSO₃H-Si(Et)Si@SiO₂ nanospheres has the highest Brønsted acid-site density (621 µeq g⁻¹) among all tested PrSO₃H-based nanospheres. Additionally, the soilid PrSO₃H-Si(Ph)Si and PrSO₃H-SiO₂ nanospheres have somewhat higher Brønsted acid-site density (585 and 603 µeq g⁻¹) than that of the PrSO₃H-SiO₂@Si(R)Si nanospheres.

3.3. Catalytic performance

The catalytic performance including activity, reaction mechanism and reusability of the PrSO₃H-SiO₂@Si(R)Si nanospheres is studied in the synthesis of EL from ethanolysis of FOS under the conditions of ethanol-to-FOS molar ratio of 248, the ratio FOS/catalyst of 1 wt/wt and 140 °C.

3.3.1. Catalytic activity

Firstly, influence of ethanol-to-FOS molar ratio on the ethanolysis activity of the PrSO₃H-SiO₂@Si(Ph)Si is studied by selecting the PrSO₃H-SiO₂@Si(Ph)Si-**2** as the representative catalyst, and the result is presented in Fig. 5a. It shows that after the reaction proceeds for 4 h, the yield of EL increases from 24.9, 32.4 to 35.6% as increasing ethanol-to-FOS molar ratio from 124, 186 to 248. In the PrSO₃H-SiO₂@Si(Ph)Si-catalysed FOS ethanolysis reaction, ethanol is used as both the reactant and solvent, and higher ethanol-to-FOS molar ratio (e.g. 248) can facilitate the conversion process of FOS–5-HMF–5-EMF–EL, giving rise to higher EL yield. Otherwise, at lower ethanol-to-FOS molar ratio (e.g. 124), more oligomeric byproducts may be produced owing

to self-polymerization of some intermediates (e.g. 5-HMF), accompanying with the decreased EL yield. Much higher ethanol-to-FOS molar ratio (higher than 248) may dilute the substrate and thereby decreasing the yield of EL; meanwhile, excessive ethanol may lead to the above process uneconomic. Therefore, in the subsequent catalytic test, ethanol-to-FOS molar ratio is set at 248.

Subsequently, influence of the shell thickness on the ethanolysis activity is studied by selecting the PrSO₃H-SiO₂@Si(Ph)Si nanospheres as the representative catalysts. From the result shown in Fig. 5b it can be seen that the yield of EL has a slight decrease with increasing the shell thickness from 21, 25 to 30 nm, and it is 62.5 (PrSO₃H-SiO₂@Si(Ph)Si-1), 60.6 (PrSO₃H-SiO₂@Si(Ph)Si-2) and 58.8% (PrSO₃H-SiO₂@Si(Ph)Si-3) after the reaction carried out for 12 h. As for the corefree PrSO₃H-Si(Ph)Si and shell-free PrSO₃H-SiO₂@Si(Ph)Si. Under the same conditions, the yield of EL is 50.8 and 47.7%, respectively, for the PrSO₃H-Si(Ph)Si- and PrSO₃H-SiO₂catalyzed FOS ethanolysis reaction. The result suggests that permeable and porous hydrophilic silica core/hydrophobic PMO shell structure of the PrSO₃H-SiO₂@Si(R)Si nanospheres play an important role in the enhancement of the ethanolysis activity.

Next, the catalytic activity of the PrSO₃H-SiO₂@Si(Ph)Si nanospheres with different R moieties within the shell framework is tested. From the result shown in Fig. 6a it is found that the tested catalysts follow the ethanolysis activity order of $PrSO_3H-SiO_2@Si(Ph-Ph)Si > PrSO_3H-SiO_2@Si(Ph)Si-2 > PrSO_3H-SiO_2@Si(Et)Si > PrSO_3H-Si(Et)Si@SiO_2$. After the ethanolysis reaction proceeded for 12 h, the yield of EL reaches 62.6, 60.6, 59.3 and 53.9%, respectively, for the $PrSO_3H-SiO_2@Si(Ph-Ph)Si-$, $PrSO_3H-SiO_2@Si(Ph)Si-2-$, $PrSO_3H-SiO_2@Si(Et)Si-$ and $PrSO_3H-SiO_2@Si(Ph-Ph)Si-$, $PrSO_3H-SiO_2@Si(Ph)Si-2-$, $PrSO_3H-SiO_2@Si(Et)Si-$ and $PrSO_3H-SiO_2@Si(Ph-Ph)Si-$, $PrSO_3H-SiO_2@Si(Ph)Si-2-$, $PrSO_3H-SiO_2@Si(Et)Si-$ and $PrSO_3H-SiO_2@Si(Ph)Si-2-$ and $PrSO_3H-SiO_2@Si($

Since the tested PrSO₃H-SiO₂@Si(Ph)Si nanospheres possess different Brønsted acid site densities, their ethanolysis activity is further compared in terms of TOF values determined from the linear portion of the initial reaction rate profile for the yield of EL, which are normalized by the acid site density. As displayed in Fig. 6b, the catalysts follow the TOF value order of PrSO₃H-SiO₂@Si(Ph-Ph)Si (0.86 h⁻¹) > PrSO₃H-SiO₂@Si(Ph)Si-**2** (0.81 h⁻¹) > PrSO₃H-SiO₂@Si(Et)Si (0.68 h⁻¹) > PrSO₃H-SiO₂ (0.62 h⁻¹), in line with the activity revealed by the yield of EL (Fig. 6b).

Finally, the catalytic activity of the PrSO₃H-SiO₂@Si(Ph)Si-2 is further compared with some reference acid catalysts including HCl, HY zeolite and Amberlyst-15. Fig. 7a displays the ethanolysis activity of the tested catalysts revealed by the yield of EL, showing that they follow the activity order of Amberlyst-15 > $PrSO_3H-SiO_2@Si(Ph)Si-2 > HCl > HY$ zeolite. For the Amberlyst-15-, PrSO₃H-SiO₂@Si(Ph)Si-2-, HCl- and HY zeolite-catalyzed ethanolysis reaction, the yield of EL reached 75.5, 60.6, 53.4 and 30.9%, respectively, after the reaction proceeded for 12 h. Considering the difference of Brønsted acid site density among the tested acid catalysts, the corresponding TOF values are determined and presentated in Fig. 7b, showing that they follow the TOF order of $PrSO_3H-SiO_2@Si(Ph)Si-2$ (0.81 h⁻¹) > HY zeolite (0.31 h⁻¹) > Amberlyst-15 (0.14) h^{-1}) > HCl (0.02 h^{-1}). Therefore, the ethanolysis activity of the PrSO₃H-SiO₂@Si(Ph)Si-2 nanosphere outferforms these commerical acid catalysts, attributing to its unique hydrophilic core/hydrophobic shell structure and excellent porosity properties such as large BET surface area $(810 \text{ m}^2 \text{ g}^{-1})$ and high pore volum $(0.73 \text{ cm}^3 \text{ g}^{-1})$. In the case of Amberlyst-15 and HCl, they have high EL yield but low TOF value, which is due to their high Brønsted acid site density. Moreover, the mechanical stability of Amberlyst-15 is poor at higher temperature (e.g. 140 °C), leading to it difficultly being recycled. Homogeneous HCl suffers from disadvantages such as corrosion,

difficulty in separation and acid-waste generation, resulting in it uncompetitive with respect to heterogeneous acid catalysts. The lowest ethanolysis activity of microporous HY zeolite is due to its small micropore, leading to poor accessibility of the reactants to the acid sites.

3.3.2. Possible reaction mechanism

During the process of ethanolysis of FOS to EL catalyzed by the PrSO₃H-SiO₂@Si(R)Si nanospheres, the intermediates including ethyl fructoside (Compound 1), 5-HMF (Compound 2), 5-EMF (Compound 3), 5-hydroxymethylfurfural diethylacetal (Compound 4) and 5ethoxymethylfurfural diethylacetal (Compound 5) are identified through GC-MS and LC-MS analysis (Scheme 2). Based on the identified intermediates and the relevant literature work, the reaction mechanism of the PrSO₃H-SiO₂@Si(R)Si-catalyzed ethanolysis of FOS to EL is tentatively proposed and illustrated in Scheme 2 [32,33]. Firstly, FOS molecules are activated by the PrSO₃H sites of the PrSO₃H-SiO₂@Si(R)Si nanospheres, and the activated FOS molecules are attacked by ethanol molecules to form ethyl fructoside, accompanying with the release of water. Further release of both water and ethanol molecules from the activated ethyl fructoside gives rise to 5-HMF. 5-HMF molecules are activated by the PrSO₃H sites, and the activated 5-HMF molecules are attacked by ethanol molecules to form 5-EMF or 5-hydroxymethylfurfural diethylacetal and water. 5-EMF may also be yielded directly from the release of water from the activated FOS molecule. Next, 5-EMF or 5-hydroxymethylfurfural diethylacetal are further attacked by ethanol molecules to form 5-ethoxymethylfurfural diethylacetal and water (Step I). In the other parallel pathway, the activated FOS molecules are isomerized by ethanol followed by the release of water to form 5-HMF (Step II). During the above FOS-5-HMF-5-EMF dehydration stage, permeable hydrophobic shell of the PrSO₃H-SiO₂@Si(R)Si nanospheres is favorable to

selectively create an unsuitable environment for water, leading to it easy desorption from the catalyst surface. As a consequence, the formation of 5-HMF and 5-EMF is facilitated.

Subsequently, the formation of EL (Compound 6) may undergo the following three possible approaches: (i) protonation of epoxy groups of 5-EMF by the PrSO₃H sites gives rise to cyclic oxonium of 5-EMF, and the latter suffers from the ring-opening reaction under the attack of water and ethanol molecules to produce EL; (ii) the activated 5-hydroxymethylfurfural diethylacetal is attacked by water molecules, and EL is formed *via* the ring-opening reaction; and (iii) under the attack of water molecules, the activated 5-ethoxymethylfurfural diethylacetal suffers from the ring-opening reaction to form EL. During the above 5-EMF–EL stage, water yielded from the dehydration of FOS participates in the ring-opening reaction of the intermediates, and therefore, in order to increase the accessibility of the intermediates to the acid sites, core of the PrSO₃H-SiO₂@Si(R)Si nanospheres should be more hydrophilic than its shell, which can provide a more suitable environment for the rehydration of hydrophilic intermediates.

3.3.3. Discussion

The excellent ethanolysis activity of the PrSO₃H-SiO₂@Si(R)Si nanospheres is attributed to their strong Brønsted acid nature, unique core-shell structure with excellent porosity properties and well-adjusted hydrophilicity/hydrophobicity.

The strong Brønsted acid nature of the PrSO₃H-SiO₂@Si(R)Si nanospheres plays the key role to the synthesis of EL from FOS based on the above reaction mechanism discussion. Moreover, in the PrSO₃H-SiO₂@Si(R)Si nanospheres, both the core and shell are functionalized by the PrSO₃H groups, which can provide more acid sites for the ethanolysis reaction. This is another reason that ensures the target reaction proceeds at a fast rate.

Additionally, the unique core-shell structure of the PrSO₃H-SiO₂@Si(R)Si nanospheres gives a positive influence on their ethanolysis activity. On the one hand, the PrSO₃H-SiO₂@Si(R)Si nanospheres exhibit interesting micro/mesoporous bimodal structure, leading to them excellent porosity properties and better dispersion of the PrSO₃H sites throughout the core and shell. The large BET surface area and high pore volume can increase the population of the PrSO₃H sites, while the opened porous structure can reduce the diffusion limit of the reactants to the interior of the spheres, leading to the increased accessibility of FOS molecules to the PrSO₃H sites throughout the core and shell. Both of the advantages can improve the catalytic activity of multi-step ethanolysis reaction. For the reference acid catalyst Amberlyst-15, although it has extremely high Brønsted acid site density, its TOF value is lower than the PrSO₃H-SiO₂@Si(Ph)Si nanosphere, which is attributed to its smaller BET surface area (50 m² g⁻¹) or less exposed acid sites. In the case of HY zeolite, its microporous structure limits the accessibility of the acid sites to the bulky FOS molecules, leading to severe diffusion limit and thereby poor ethanolysis activity. The above results further confirm that the porosity properties of the solid acids influence their catalytic activity except for the Brønsted acid nature.

The another contribution of the core-shell structured PrSO₃H-SiO₂@Si(R)Si nanospheres to the ethanolysis activity is that they have permeable shell, which can facilitate mass transfer of the reactants. The PrSO₃H-SiO₂@Si(Ph)Si-1 nanosphere with the thinnest shell among three PrSO₃H-SiO₂@Si(Ph)Si nanospheres exhibits the highest ethanolysis activity, attributing to the shortest mass transfer distance and thereby the increased accessibility of the PrSO₃H groups to the reactants.

Finally, the PrSO₃H-SiO₂@Si(R)Si nanospheres with more hydrophilic PrSO₃H-functionalized silica core and more hydrophobic PrSO₃H-functionalized organosilica shell have a considerable

influence on the ethanolysis activity. The conversion of FOS into EL in the presence of ethanol is a continuous process of multi-step reaction. In the first stage, FOS dehydration or etherification produces 5-HMF or ethyl fructoside, and then 5-EMF, 5-hydroxymethylfurfural diethylacetal and 5-ethyloxymethylfurfural diethylacetal are obtained. The process accompanies with the release of water and formation of some hydrophilic oligomeric byproducts such as diethyl ether and 5,5'oxybis(methylene)bis-2-furfural (identified by GC-MS and LC-MS). In the next stage, EL is formed via the ring opening reactions of the aforementioned intermediates with the help of the yielded water in the first stage. Well-adjusted hydrophilicity/hydrophobicity of the PrSO₃H-SiO₂@Si(R)Si nanospheres can match the above reaction process. In the first stage, the hydrophobic PrSO₃H-functionalized organosilica shell may avoid the adsorption of water and hydrophilic oligomeric byproducts on the catalyst surface, which can further facilitate the mass transfer of the intermediates to the interior of hydrophilic PrSO₃H-functionalized silica core besides the shell. Accordingly, the ring opening reactions of the intermediates with the assistance of water proceed effectively on the hydrophilic core, leading to considerably higher EL yield with respect to shell-free PrSO₃H-SiO₂ and PrSO₃H-Si(Et)Si@SiO₂ (hydrophilic shell and hydrophobic core) nanospheres. The lower catalytic activity of the PrSO₃H-SiO₂ nanospheres is due to the strong interaction of the PrSO₃H sites with water and hydrophilic oligomeric byproducts, which is confirmed by the following recycling test (Fig. 8). Additionally, slight activity difference among three PrSO₃H-SiO₂@Si(R)Si nanospheres with different bridging organic groups (e.g. ethyl, phenyl and biphenyl) within the shell framework is mainly due to their different hydrophobicity. The PrSO₃H-SiO₂@Si(Ph-Ph)Si nanosphere with the highest hydrophobicity exhibits the highest ethanolysis activity although its BET surface area and acid site density are the lowest.

3.3.4. Regeneration and reusability

The reusability of the supported catalysts is one of the important properties that determines their practical applications. To explore the catalytic stability of the incorporated PrSO₃H groups and the reusability of as-prepared PrSO₃H-SiO₂@Si(R)Si nanospheres, the PrSO₃H-SiO₂@Si(Ph)Si-2 nanosphere is selected and reused for three times in ethanolysis of FOS. As a comparison, the reusability of shell-free PrSO₃H-SiO₂ nanosphere is also investigated under the same conditions. As shown in Fig. 8a, the PrSO₃H-SiO₂ nanosphere exhibits an obvious activity loss during three consecutive cycles, and the yield of EL decreased from 47.7% (the first cycle) to 29.9% (the third cycle). In the case of the PrSO₃H-SiO₂@Si(Ph)Si-2 nanosphere, it shows excellent catalytic stability, and the yield of EL is 60.6 (1st cycle), 58.5 (2nd cycle) and 58.8% (3rd cycle), respectively, under the same conditions. The result implies that the reusability of the PrSO₃H-SiO₂@Si(R)Si nanosphere is superior to the shell-free PrSO₃H-SiO₂ nanosphere. The excellent reusability of the PrSO₃H-SiO₂@Si(R)Si nanosphere is firstly due to the covalent bonding between the PrSO₃H groups with silica or PMO framework, which can avoid the leakage of the PrSO₃H groups during the catalytic recycle process. Additionally, the hydrophobic PrSO₃H-Si(R)Si shell can prevent the adsorption of the hydrophilic oligomeric byproducts on the catalyst surface and maintain high accessibility of the reactants and intermediates to the PrSO₃H sites of the core, and therefore the deactivation of the catalyst hardly occurred in current catalytic system. However, the hydrophilic oligomeric byproducts can be easily adsorbed on the surface of hydrophobic shell-free PrSO₃H-SiO₂ nanopheres, leading to it poor reusiability. To further support the above explanation, TEM image (Fig. 8b) and ¹³C CP-MAS NMR spectrum (Fig. 8c) of the third used PrSO₃H-SiO₂@Si(Ph)Si-2 catalyst are presented, showing that both the morphology and chemical structure of the catalyst remain intact. The result also implies that the catalyst possesses excellent mechanical stability under vigorous stirring and solvothermal conditions. Importantly, the

adsorption of the oligomeric byproducts on the catalyst surface and obvious block of the micro/mesoporous channel are hardly observed. Therefore, the $PrSO_3H-SiO_2@Si(R)Si$ nanospheres can work effectively as the recyclable solid acid catalysts in the conversion of FOS to EL.

4. Conclusions

The CTAB-directed one-pot two-step co-condensation strategy was designed for the preparation of propylsulfonic acid functionalized silica core/PMO shell structured nanospheres. The shell thickness of the PrSO₃H-SiO₂@Si(R)Si nanospheres can be regulated by changing the starting amount of the bissilvlated organic precursors, while the hydrophobicity of the shell can be adjusted by the introduction of different alkyl or phenyl moieties within the silica/carbon framework. The PrSO₃H-SiO₂@Si(R)Si nanospheres exhibited excellent acid catalytic activity in the synthesis of EL from ethanolysis of FOS, which is mainly attributed to the strong Brønsted acid nature; additionally, the unique core-shell structure of the PrSO₃H-SiO₂@Si(R)Si nanospheres with micro/mesoporosity and permeable shell gives a positive influence on their catalytic activity, which can improve the accessibility of to the PrSO₃H sites throughout the core and shell; finally, well-adjusted surface hydrophilicity/hydrophobicity of the PrSO₃H-SiO₂@Si(R)Si nanospheres can avoid the adsorption of water and hydrophilic oligomeric byproducts on the shell, which can further facilitate the mass transfer of the intermediates to the interior of hydrophilic PrSO₃Hfunctionalized silica core and thereby ensuring the formation of EL with considerably high yield. As-prepared PrSO₃H-SiO₂@Si(R)Si nanospheres also show excellent catalytic stability in the target reaction, which is due to the covalent bonding the PrSO₃H groups with the silica or

silica/carbon framework; meanwhile, the hydrophobic PrSO₃H-Si(R)Si shell can prevent the catalyst deactivation originating from the adsorption of the hydrophilic oligomeric byproducts.

Acknowledgements

This work is supported by the Natural Science Fund Council of China (21573038).

References

- [1] C. Chatterjee, F. Pong, A. Sen, Green Chem. 17 (2015) 40-71.
- [2] E. Ahmad, M.I. Alam, K.K. Pant, M.A. Haider, Green Chem. 18 (2016) 4804-4823.
- [3] F. Liu, C. Liu, W. Kong, C. Qi, A. Zheng, S. Dai, Green Chem. 18 (2016) 6536-6544.
- [4] A. Corma, S. Iborra, A. Velty, Chem. Rev. 107 (2007) 2411-2502.
- [5] J.-P. Lange, R. Price, P.M. Ayoub, J. Louis, L. Petrus, L. Clarke, H. Gosselink, Angew.Chem. Int. Ed. 49 (2010) 4479-4483.
- [6] P. Lanzafame, D.M. Temi, S. Perathoner, G. Centi, A. Macario, A. Aloise, G. Giordano, Catal. Today 175 (2011) 435-441.
- [7] S. Saravanamurugan, O. NguyenVanBuu, A. Riisager, ChemSusChem 4 (2011) 723-726.
- [8] D.J. Hayes, Catal. Today 145 (2009) 138-151.
- [9] L. Peng, L. Lin, H. Li, Q. Yang, Appl. Energ. 88 (2011) 4590-4596.
- [10] A. Démolis, N. Essayem, F. Rataboul, ACS Sustain. Chem. Eng. 2 (2014) 1338-1352.
- [11] B.C. Windom, T.M. Lovestead, M. Mascal, E.B. Nikitin, T.J. Bruno, Energ. Fuel. 25(2011) 1878-1890.
- [12] F. Su, L. Ma, D. Song, X. Zhang, Y. Guo, Green Chem. 15 (2013) 885-890.
- [13] G.F. Wang, Z. Zhang, L. Song, Green Chem. 16 (2014) 1436-1443.
- [14] E. Ahmad, M.I. Alam, K.K. Pant, M.A. Haider, Green Chem. 18 (2016) 4804-4823.
- [15] M. Karaki, A. Karout, J. Toufaily, F. Rataboul, N. Essayem, B. Lebeau, J. Catal. 305 (2013)204-216.
- [16] X. Zhang, Y. Zhao, Q. Yang, J. Catal. 320 (2014) 180-188.

- [17] C.-H. Kuo, A.S. Poyraz, L. Jin, Y. Meng, L. Pahalagedara, S.-Y. Chen, D.A. Kriz, C. Guild,A. Gudz, S.L. Suib, Green Chem. 16 (2014) 785-791.
- [18] S. Saravanamurugan, A. Riisager, Catal. Commun. 17 (2012) 71-75.
- [19] J.G. Croissant, X. Cattoen, M. Wong Chi Man, J.-O. Durand, N.M. Khashab, Nanoscale 7(2015) 20318-20334.
- [20] X. Zhang, F. Su, D. Song, S. An, B. Lu, Y. Guo, Appl. Catal. B: Environ. 163 (2015) 50-62.
- [21] J. Liu, S. Bai, H. Zhong, C. Li, Q. Yang, J. Phys. Chem. C 114 (2010) 953-961.
- [22] L. Wang, F.-S. Xiao, Green Chem. 17 (2015) 24-39.
- [23] F. Su, Y. Guo, Green Chem. 16 (2014) 2934-2957.
- [24] S. An, Y. Sun, D. Song, Q. Zhang, Y. Guo, Q. Shang, J. Catal. 342 (2016) 40-54.
- [25] J.A. Melero, G.D. Stucky, R. van Grieken, G. Morales, J. Mater. Chem. 12 (2002) 1664-1670.
- [26] Y. Chen, P. Xu, H. Chen, Y. Li, W. Bu, Z. Shu, Y. Li, J. Zhang, L. Zhang, L. Pan, X. Cui,
- Z. Hua, J. Wang, L. Zhang, J. Shi, Adv. Mater. 25 (2013) 3100-3105.
- [27] Z. Teng, X. Su, Y. Zheng, J. Zhang, Y. Liu, S. Wang, J. Wu, G. Chen, J. Wang, D. Zhao,
- G. Lu, J. Am. Chem. Soc. 137 (2015) 7935-7944.
- [28] S. An, D. Song, B. Lu, X. Yang, Y.H. Guo, Chem. Eur. J. 21 (2015) 10786-10798.
- [29] Y. Goto, S. Inagaki, Chem. Commun. (2002) 2410-2411.
- [30] M.H. Tucker, A.J. Crisci, B.N. Wigington, N. Phadke, R. Alamillo, J. Zhang, S.L. Scott,
- J.A. Dumesic, ACS Catal. 2 (2012) 1865-1876.
- [31] D. Song, S. An, Y. Sun, Y. Guo, J. Catal. 333 (2016) 184-199.
- [32] J. Chen, G. Zhao, L. Chen, RSC Adv. 4 (2014) 4194-4202.

- [33] T. Flannelly, S. Dooley, J.J. Leahy, Energ. Fuel. 29 (2015) 7554-7565.
- [34] Y.-B. Huang, Y. Fu, Green Chem. 15 (2013) 1095-1111.
- [35] Z. Zhang, Z.K. Zhao, Carbohyd. Res. 344 (2009) 2069-2072.

Fig. 1 TEM images of the PrSO₃H-SiO₂ (a), PrSO₃H-Si(Ph)Si (b), PrSO₃H-SiO₂@Si(Ph)Si-1 (c), PrSO₃H-SiO₂@Si(Ph)Si-2 (d), PrSO₃H-SiO₂@Si(Ph)Si-3 (e), PrSO₃H-SiO₂@Si(Ph-Ph)Si (f), PrSO₃H-SiO₂@Si(Et)Si (g) and PrSO₃H-Si(Et)Si@SiO₂ nanospheres (h).



Fig. 2 SEM images of the PrSO₃H-SiO₂@Si(Ph)Si-**2** (a) and PrSO₃H-SiO₂@Si(Ph-Ph)Si nanospheres (b).



Fig. 3 Nitrogen gas adsorption–desorption isotherms (a, c, e) and BJH pore size distribution profiles (b, d, f) of various PrSO₃H-functionalized silica nanospheres.



Fig. 4 ²⁹Si MAS NMR spectrum (a) of the PrSO₃H-SiO₂@Si(Ph)Si-**2** and ¹³C CP-MAS NMR spectra of the (b) PrSO₃H-SiO₂@Si(Ph)Si-**2**, (c) PrSO₃H-SiO₂@Si(Ph-Ph)Si and (d) PrSO₃H-SiO₂@Si(Et)Si nanospheres.



Fig. 5 (a) Influence of ethanol-to-FOS molar ratio on the ethanolysis activity of the PrSO₃H-SiO₂@Si(Ph)Si-**2.** the ratio FOS/catalyst of 1 wt/wt, 4 h, 140 °C; (b) ethanolysis activity comparison of various PrSO₃H-SiO₂@Si(Ph)Si as well as PrSO₃H-Si(Ph)Si and PrSO₃H-SiO₂ nanospheres. Ethanol-to-FOS molar ratio of 248, the ratio FOS/catalyst of 1 wt/wt, 140 °C.



Fig. 6 Comparison of the ethanolysis activity of the $PrSO_3H-SiO_2@Si(Ph)Si$ nanospheres with different core or shell compositions revealed by the yield of EL (a) and TOF (b). FOS 0.278 mmol, ethanol 68.95 mmol, the ratio FOS/catalyst of 1 wt/wt, 140 °C.



Fig. 7 Comparison of the ethanolysis activity of the $PrSO_3H$ -SiO₂@Si(Ph)Si-2 nanospheres with commercial solid acids revealed by the yield of EL (a) and TOF (b). FOS 0.278 mmol, ethanol 68.95 mmol, the ratio FOS/catalyst of 1 wt/wt, 140 °C.



Fig. 8 Reusability of the PrSO₃H-SiO₂@Si(Ph)Si-**2** and PrSO₃H-SiO₂ nanospheres in ethanolysis of FOS to EL (a). TEM image (b) and ¹³C CP-MAS NMR spectrum (c) of the third used PrSO₃H-SiO₂@Si(Ph)Si-**2** nanosphere. FOS 0.278 mmol, ethanol 68.95 mmol, the ratio FOS/catalyst of 1 wt/wt, 140 °C.



Scheme 1. Illustration of CTAB-templated preparation and network structure of the PrSO₃H-SiO₂@Si(R)Si nanospheres, $R = -C_2H_4-$, $-C_6H_4-$ or $-C_6H_4-C_6H_4-$.



Scheme 2. Mechanism of EL production from the ethanolysis of FOS catalyzed over the $PrSO_3H-SiO_2@Si(R)Si$ nanospheres.



Table 1. Textural parameters, Brønsted acid site density, average core diameter (*d*) and average shell thickness (δ) of various propylsulfonic acid functionalized silica nanospheres. For comparison, the textural parameters and Brønsted acid site density of Amberlyst-15 and HY zeolite are also presentated.

Catalyst	$S_{\rm BET}$	$D_{ m p}$	Vp	$A_{ ext{titration}}$	d	δ
	$(m^2 g^{-1})$	(nm)	$(cm^3 g^{-1})$	$(\mu eq g^{-1})$	(nm)	(nm)
PrSO ₃ H-SiO ₂ @Si(Ph)Si-1	866	3.8	0.77	540	155	21
$PrSO_{3}H\text{-}SiO_{2}@Si(Ph)Si\text{-}\textbf{2}$	810	3.8	0.73	535	155	25
$PrSO_{3}H\text{-}SiO_{2}@Si(Ph)Si\text{-}\textbf{3}$	815	4.2	0.62	522	155	30
PrSO ₃ H-SiO ₂ @Si(Ph-Ph)Si	696	3.8	0.48	508	160	23
PrSO ₃ H-SiO ₂ @Si(Et)Si	790	3.8	0.38	571	160	23
PrSO ₃ H-Si(Et)Si@SiO ₂	777	3.9	0.47	621	165	21
PrSO ₃ H-Si(Ph)Si	757	3.9	0.46	585	140	n.d.
PrSO ₃ H-SiO ₂	1060	3.9	0.60	603	155	n.d.
Amberlyst-15 ^a	50	n.d.	n.d.	4800	n.d.	n.d.
HY zeolite	573 ^{<i>b</i>}	1.3 ^b	0.29^{b}	647	n.d.	n.d.

^{*a*} Data was from ref 34. ^{*b*} Data was from ref 35.