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Sustainable production of biodiesel and transformation of glycerol to glycerol laurate esters over inner diameter-controlled sulfonic acid functionalized ethyl-bridged-organosilica nanotubes



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ABSTRACT

Solid acid-catalyzed biodiesel production from inedible oils offers a promising mean to reduce the cost of feedstocks and avoid the competition with edible oil market. Here we demonstrate a series of inner diametercontrolled sulfonic acid functionalized ethyl-bridged-organosilica nanotubes ($Ar/PrSO_3H$ -Si(Et)Si) by a toluene swollen mixed Pluronic surfactant micelle-templating co-condensation route for transesterification of tripalmitin or plant oils with methanol to produce fatty acid methyl esters and esterification of glycerol with lauric acid to produce mono- and di-glycerol esters. By combination of superstrong Brønsted acidity, unique hollow tubular nanostructure, excellent porosity properties and hydrophobic surface, the $Ar/PrSO_3H$ -Si(Et)Si nanotubes display higher catalytic activity as compared with acidic resin and zeolite. Additionally, the inner diameters and lengths of $Ar/PrSO_3H$ -Si(Et)Si nanotubes influence the activity obviously. The $Ar/PrSO_3H$ -Si(Et)Si is nanotubes also show excellent catalytic reusability, attributing to covalent bonding of $Ar/PrSO_3H$ groups within silica/carbon framework and surface hydrophobicity of the catalysts.

1. Introduction

Heterogeneous acid-catalyzed synthesis of bio-derived fuels and chemicals offers a promising and sustainable means to reduce current fossil fuel dependency and to control greenhouse gas and particulate emissions [1-12]. Biodiesel, a kind of bio-derived fuel with main composition of C12-C22 fatty acid methyl esters (FAMEs), has the potential to play an important role in meeting renewable fuel targets [13-21]. Biodiesel is produced via the base- or acid-catalyzed transesterification of triglyceride (TG) components of lipids with methanol, and the process accompanies with the formation of glycerol as a potentially valuable byproduct. Growing trend towards green chemistry and sustainable technology has driven to develop new catalytic systems for biodiesel production, in which valorization of glycerol, reducing waste and producing additional value-added products should be considered [22]. For this purpose, environmentally-benign heterogeneous acid catalytic system is preferential because the soap and hazardous materials are avoided during biodiesel synthesis process; meanwhile, the system can boost the transformation of glycerol into high-value added building-block chemicals [23-25]. For instance,

acid-catalyzed synthesis of valuable glycerol esters by esterification of glycerol with short- or long-chain fatty acids is one of the important utilizations of glycerol [26–33].

It should admit that solid acid catalyzed-transesterification process need longer reaction time and higher temperature, and therefore the development of efficient solid acids for efficient transesterification of TG to produce FAMEs and transformation of byproduct, glycerol, into highvalue added chemicals is a challenge. Among various types of heterogeneous acid catalysts for transesterification of TG components and esterification of glycerol, mesoporous sulfonic acid functionalized silicas are popular candidates [34–38]. However, fundamental problems in this type of solid acid catalysts still need to be addressed [39]. One of the problems is diffusion and mass-transport limitation for bulky TGs or long-chain fatty acids because of their smaller mesopore diameter as well as long and isolated parallel channels, which may limit the accessibility of the acid sites to the substrate molecules. Therefore, the pore size of mesoporous sulfonic acid functionalized silicas is one of the key factors to limit the catalytic activity for these reactions. To overcome these problems, it is one of the effective strategies that the morphology and pore size of the silicas-based solid acids should be controlled

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Received 15 June 2020; Received in revised form 4 November 2020; Accepted 12 December 2020 Available online 19 December 2020 0926-860X/© 2020 Elsevier B.V. All rights reserved. carefully. This can not only improve porosity properties and thereby high distribution of the acid sites, but also effectively alleviate diffusion and mass-transport limitation of the bulky or long-chain reactant molecules. Both factors can significantly increase the accessibility of the acid sites. Additionally, the surface of sulfonic acid functionalized mesoporous silicas is hydrophilic, which is problematic for TG transesterification due to preferential in-pore diffusion and adsorption of methanol and glycerol molecules. The results may lead to deactivation of the catalysts. In the case of esterification of glycerol with long-chain fatty acids, hydrophilic catalyst may prevent these hydrophobic acids from adsorption on its surface, significantly decelerating the formation of glycerol esters. Another serious problem is catalyst deactivation resulting from the leaching of sulfonic acid residues under harsh conditions. As a consequence, design of novel sulfonic acid functionalized silica catalysts with the simultaneous control over porosity properties and surface hydrophilicity/hydrophobicity is thus highly desirable.

Bearing this in mind, here arenesulfonic or propylsulfonic acid functionalized ethyl-bridged-organosilica nanotubes (Ar/PrSO₃H–Si(Et) Si) are designed for transesterification of tripalmitin or plant oils with methanol to produce FAMEs and esterification of glycerol with lauric acid to produce mono- and di-glycerol esters. Organosilicas, prepared through surfactant-micelle-templating strategy, have attracted a great deal of attention in a large number of scientific disciplines such as catalysis, adsorption and drug delivery [40-42]. Under properly adjusted composition ratio of the framework precursor to the surfactant, the surfactant-micelle-templating strategy can produce not only periodic mesoporous organosilicas [43,44] but also hollow nanospheres [45,46] and nanotubes [47,48]. Functionalization of organosilicas with catalytically active organic functional groups is an emergent field of heterogeneous catalysis, and the resulting catalysts show unique properties such as homogeneous dispersion of covalently-bonded active sites throughout the silica/carbon framework, large channel structure as well as tunable surface hydrophilicity/hydrophobicity-,[4,30,49-53]. Motivation of design one-dimensional tubular nanocatalysts depends on their fascinating advantages including large fraction of voids in the interior, flexible structure as well as distinct inner and outer surfaces, and they can serve as the nanoreactors to allow free diffusions and fast mass-transport of reactants and products and thereby the enhanced catalytic performance [54-58]. Design of the Ar/PrSO₃H-Si(Et)Si nanotubes follows the successful experience of construction of less aggregated silica and organosilica nanotubes with widely adjustable inner diameters [48,59], and the preparation process includes one-step toluene swollen mixed Pluronic surfactant micelle-templating co-condensation strategy. We pay particular attention on tuning of the inner diameters and lengths of the Ar/PrSO₃H-Si(Et)Si nanotubes in a wide range; meanwhile, the influence of inner diameter, length, surface hydrophobicity and porosity properties on the acid catalytic performance of the nanotube catalysts in transesterification of tripalmitin with cheaper, more reactive and volatile methanol (with respect to ethanol) and esterification of glycerol with lauric acid is studied. Finally, the catalytic performance of the Ar/PrSO₃H-Si(Et)Si nanotubes is further studied on the synthesis of FAMEs from plant oils (rapeseed oil, sunflower oil and yellowhorn seed oil) to evaluate the possibility of practical applications of the Ar/PrSO₃H-Si(Et)Si nanotubes in biodiesel production from low-grade, highly-acidic and water-containing virgin plant oils.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation of inner diameter-controlled propylsulfonic acid functionalized ethyl-bridged-organosilica nanotubes (PrSO₃H–Si(Et)Si)

Mixed Pluronic poly(ethylene oxide)-poly(propylene oxide)-poly (ethylene oxide) (PEO-PPO-PEO) triblock copolymers including P123 (EO₂₀PO₇₀EO₂₀) and F127 (EO₁₀₆PO₇₀EO₁₀₆) were used as the structure directing agents. Typically, P123 (0.25 g) and F127 (0.25 g) were dissolved in a HCl solution (2.0 mol L⁻¹, 30 mL) at room temperature under stirring until a homogeneous aqueous P123-F127 solution formed. Subsequently, toluene (0.1, 0.3, 0.5, 1.0 and 1.5 mL, respectively, or 0.03, 0.09, 0.16, 0.32 and 0.47 mol L⁻¹), 1,2-bis(trimethoxysilyl)ethane (BTMSE, 97 %, 0.85 mL), 3-mercaptopropyltrimethoxysilane (MPTMS, 95 %, 0.15 mL) and H₂O₂ (0.7 mL) were added dropwise to the above acidic P123-F127 solution successively at an interval of 45 min, and the resulting suspension was further stirred at room temperature for another 24 h. The final suspension was transferred into an autoclave and heated at 130 °C with a heating rate of 2 °C min⁻¹ for 24 h. After cooling to room temperature, the white solid was obtained by filtration and then being air-dried at 80 °C overnight. Finally, P123 and F127 were removed from the solid by extraction with boiling ethanol completely. The surfactant-free product was obtained after being air-dried at 80 °C for 12 h, and it is denoted as $PrSO_3H$ -Si(Et)Si-x. Herein, x = 1, 2, 3, 4and 5, respectively, corresponding to initial concentration of toluene in the preparation system of 0.03, 0.09, 0.16, 0.32 and 0.47 mol L^{-1} .

2.1.2. Preparation of inner diameter-controlled arenesulfonic acid functionalized ethyl-bridged-organosilica nanotubes (ArSO₃H–Si(Et)Si)

The preparation followed a route similar to the *Pr*SO₃H–Si(Et)Si-**x** but replacement of MPTMS for 2-(4-chlorosulfonylphenyl)ethyl trimethoxysilane (CSPTMS, 50% in dichloromethane, 0.4 mL) in the absence of H₂O₂, and the product is denoted as *Ar*SO₃H–Si(Et)Si-**x** (**x** = **1**, **2**, **3**, **4** and **5**).

2.2. Catalyst characterization

FESEM and TEM images were obtained using XL-30 ESEMFEG field emission scanning electron microscope and JEM-2100 F high resolution transmission electron microscope. Nitrogen porosimetry measurement was undertaken on a Micromeritics ASAP 2020 PLUS HD88 surface area and porosity analyser. X-ray photoelectron spectroscopy (XPS) spectra were recorded on an Axis Ultra DLD instrument with a monochromated Al–K α source at a residual gas pressure of below 10^{-8} Pa. ^{13}C cross polarization-magic angle spinning (CP-MAS) NMR and ²⁹Si MAS NMR spectra were carried out on a Bruker AVANCE III 400 WB spectrometer. Sulfur element contents or ArSO3H/PrSO3H loadings were determined by an ICAP6300-Thermoscientific ICP-OES. The quantification of the Brønsted acid site density (μ eq(H⁺) g⁻¹) of as-prepared catalysts was also carried out through ion exchange with 2 mol L⁻¹ of NaCl solution (10 mL) followed by titration with 0.0098 mol L^{-1} of NaOH standard solution. Ammonia temperature programmed desorption (NH₃-TPD) analysis was carried out on a Micromeritics Autochem II 2920 instrument.

2.3. Catalytic tests

Transesterification of tripalmitin (TP) or plant oils (rapeseed oil, sunflower oil and yellowhorn seed oil) with methanol (MeOH) was carried out in a closed autoclave under the conditions of 100 °C, MeOH (50 mmol)-to-TP (1.1 mmol) molar ratio of 45:1, catalyst weight ratio of 4 wt% (relative to the reactants) and 600 rpm. The concentrations of the yielded methyl palmitate (MP) and other FAMEs were determined by a Shimadzu 2014C gas chromatograph (GC), and ethyl laurate was applied as an internal standard. The concentration of TP was determined by an Agilent Technologies 1200HPLC equipped with an Alltech ELSD 2000ES evaporative light-scattering detector (ELSD) and a Vision HT-C18 column, and the composition of flow phase was acetonitrile: isopropanol = 50: 50 (v/v). The intermediates generated were identified by a thermoscientific Q EXACTIVE Focus high performance liquid chromatography equipped with mass spectrometer, while various FAMEs produced in transesterification of plant oils were identified by a HP6890GC-5973MSD analysis.

Esterification of glycerol (Gly) with lauric acid (LA) was conducted

under the conditions of 140 °C, Gly (33.5 mmol)-to-LA (11.2 mmol) molar ratio of 3:1, 2 wt% catalyst (relative to total reactants) and 600 rpm. The produced glycerol monolaurate (MLG), glycerol dilaurate (DLG) and glycerol trilaurate (TLG) were simultaneously monitored by an Agilent Technologies 1260HPLC equipped with a Vision HT-C18 column and a ELSD, and the composition of flow phase was dichloromethane: acetonitrile = 35: 65 (v/v). The concentration of LA was determined by gas chromatography after methylation.

All of the above concentration data were obtained by repeating the catalytic tests for three times.

3. Results and discussion

3.1. Preparation of the inner diameter-controlled Ar/PrSO₃H–Si(Et)Si nanotubes

The inner diameter-controlled Ar/PrSO₃H-Si(Et)Si nanotubes are successfully achieved via one-step toluene swollen mixed P123 (EO₂₀PO₇₀EO₂₀) and F127 (EO₁₀₆PO₇₀EO₁₀₆) micelle-templating cohydrolysis and -condensation of both BTMSE and MPTMS/CSPTMS as the precursors of silica/carbon framework and Ar/PrSO₂H groups in a strong acid media. The key factors for the construction of less aggregated Ar/PrSO₃H-Si(Et)Si nanotubes are carefully controlled composition ratio of P123 to F127 as well as lower composition ratio of bridged organosilanes to the copolymer surfactants. As illustrated in Scheme 1, under the conditions of pH < 1, P123 to F127 wt ratio of 1:1 and total organosilanes to total copolymer surfactants molar ratio of 32:1, amphiphilic copolymer surfactants P123 and F127 self-assemble into cylindrical micelles through hydrogen bonding and hydrophobic/hydrophilic interactions in the beginning of the preparation process. In these cylindrical micelles, hydrophilic EO blocks with longer and shorter chains presented in F127 and P123 form a hydrophilic corona, in which co-hydrolysis and -condensation reactions of BTMSE and MPTMS/ CSPTMS happen. During the above process, EO blocks are protonated to hydronium ions, and the positively charged EO blocks interact with the hydrolyzed BTMSE and MPTMS/CSPTMS species (e.g., --CH2CH2Si (OSi)(OH)₂ or ---CH₂CH₂Si(OSi)₂(OH) via hydrogen bonding. Consequently, cylindrical silica/carbon framework functionalized with Ar/ PrSO₃H groups is constructed, in which PrSO₃H groups are introduced to the silica/carbon framework *via in situ* approach in the presence of H_2O_2 , while ArSO₃H groups are directly incorporated to the framework. At sufficiently low (BTMSE and MPTMS/CSPTMS) to (P123 + F127) molar ratio (32:1), long PEO blocks of F127 are not embedded completely in the silica/carbon framework, and their free ends are present at the boundary. Meanwhile, the presence of both longer and shorter PEO chains in the corona decreases the crowding of the PEO chains, thus

reducing the driving force for the formation of high-surface-curvature spherical micelles [48]. Accordingly, open and tubular nanostructures are stabilized because the aggregation and cross-linking between nanotubes are inhibited. On the other hand, the hydrophobic PPO blocks in P123 and F127 form a hydrophobic core of the micelles, which can permit uptaking the swelling agent toluene. After hydrothermal treatment at 130 °C, the Ar/PrSO₃H-functionalized silica/carbon framework is reinforced further. The tubular Ar/PrSO₃H-functionalized silica/carbon framework is finally created by boiling ethanol extraction for removal of the copolymer surfactants. In the Ar/PrSO₃H-functionalized silica/carbon framework, ethyl groups are covalently bonded to two silicon atoms to form -Si-C-C-Si linkages, while Ar/PrSO3H groups are linked to the framework via Si-C-C-Si-O-Si-Ar/PrSO₃H covalent bonds (Scheme 1). As a result, both ethyl and Ar/PrSO3H groups homogeneously disperse throughout the silica/carbon framework. Additionally, the inner diameters and lengths of the Ar/PrSO₃H-Si(Et)Si nanotubes can be easily adjusted in a wide range by changing the swelling agent concentration.

3.2. Characterization of Ar/PrSO₃H-Si(Et)Si nanotubes

3.2.1. Morphological characteristics

The tubular nanostructures of the Ar/PrSO₃H-Si(Et)Si catalysts prepared at different initial concentrations of toluene are revealed by both TEM and SEM observations (Fig. 1). The TEM images clearly indicate that ten samples are all composed of perfect tubular nanostructures, and the nanotubes are curved and less aggregated; additionally, their inner diameters and lengths are tunable widely. For five PrSO₃H-Si(Et)Si nanotubes, their inner diameters increase from 5, 9, 11, 18-22 nm as increasing initial concentration of toluene in the preparation system from 0.03, 0.09, 0.16, 0.32 to 0.47 mol L^{-1} (Fig. 1a-e and Table 1). In the cases of five ArSO₃H-Si(Et)Si nanotubes, the corresponding inner diameters are 5, 11, 16, 25 and 38 nm, respectively (Fig. 1f-j and Table 1). The result indicates that the ArSO₃H-Si(Et)Si nanotubes exhibit much wider range of inner diameter, which is due to the fact that the stronger hydrophobicity of bulky ArSO₃H groups is more favorable for the uptake of toluene molecules. From Fig. 1 it is also found that the nanotubes become shorter gradually with the increase of their inner diameters, originating from continuous swelling of toluene. Therefore, the inner diameters and lengths of the Ar/PrSO₃H-Si(Et)Si nanotubes can be well-adjusted in a wide range by changing initial concentration of toluene. Additionally, the wall of the smallest PrSO₃H-Si(Et)Si-1 (2 nm) and ArSO₃H-Si(Et)Si-1 (3 nm) is the thinnest among their counterparts; however, other four PrSO₃H-Si(Et)Si (4 nm) and four ArSO₃H-Si(Et)Si (5 nm) nanotubes possess the same wall thickness, regardless of their inner diameters and lengths (Table 1). The



Scheme 1. Morphology evolution and framework structure of the Ar/PrSO₃H–Si(Et)Si nanotubes.



Fig. 1. TEM and SEM images of *Pr*SO₃H–Si(Et)Si-1 (a, a'), *Pr*SO₃H–Si(Et)Si-2 (b, b'), *Pr*SO₃H–Si(Et)Si-3 (c, c'), *Pr*SO₃H–Si(Et)Si-4 (d, d'), *Pr*SO₃H–Si(Et)Si-5 (e, e'), *Ar*SO₃H–Si(Et)Si-1 (f, f'), *Ar*SO₃H–Si(Et)Si-2 (g, g'), *Ar*SO₃H–Si(Et)Si-3 (h, h'), *Ar*SO₃H–Si(Et)Si-4 (i, i') and *Ar*SO₃H–Si(Et)Si-5 (j, j').

SEM observations further confirm the TEM results, suggesting that the swelling agent-based control of the inner nanotube diameters and lengths of the $Ar/PrSO_3H$ –Si(Et)Si are achievable *via* the mixed-micelle-templating strategy (Fig. 1a'–j').

3.2.2. Porosity properties

The tubular nanostructures of the Ar/PrSO₃H-Si(Et)Si render them excellent porosity properties, which are clearly verified by the nitrogen gas porosimetry measurement. As shown in Fig. 2a and b, ten Ar/ PrSO3H-Si(Et)Si nanotubes all exhibit type IV isotherm, reflecting their mesoporosity; however, their capillary condensations happen at different P/P_0 regions, which are closely related to the inner diameters of the nanotubes. For the PrSO₃H-Si(Et)Si-1 and ArSO₃H-Si(Et)Si-1 with the smallest inner diameters among various PrSO3H-Si(Et)Si and ArSO₃H–Si(Et)Si nanotubes, they have two capillary condensation steps occurring at $P/P_0 = 0.55-0.80$ and 0.80-0.99, respectively, together with two predominant hysteresis loops. The first capillary condensation step at $P/P_0 = 0.55-0.80$ is originated from the interior channel of the Ar/PrSO₃H-Si(Et)Si-1 nanotubes, while the additional capillary condensation step close to the saturation vapor pressure is associated with the voids between the nanotubes. Continuous increasing the concentration of toluene leads to the first capillary condensation step of the resulting $Ar/PrSO_3H$ -Si(Et)Si nanotubes gradually shifts to higher P/P_0 region, implying that the pore diameter or interior channel of the nanotubes increase gradually. Additionally, for the Ar/PrSO₃H-Si(Et)Si-2, Ar/PrSO₃H–Si(Et)Si-3, Ar/PrSO₃H–Si(Et)Si-4 and Ar/PrSO₃H–Si(Et) Si-5, their secondary capillary condensation steps disappear. This is due

to the void space between the larger nanotubes are too large to be filled by capillary condensation at the highest P/P_0 (~1.0) [59,60]. BJH pore size distribution profiles show that the pore diameters of five $PrSO_3H$ –Si (Et)Si nanotubes center at 6.4, 11.4, 11.4, 24.0 and 24.0 nm (Fig. 2c and Table 1), respectively, while five $ArSO_3H$ –Si(Et)Si nanotubes exhibit more broad pore diameter distribution ranging from 6.3, 10.9, 19.0, 21.0–33.5 nm (Fig. 2d and Table 1). The change trend of pore diameter of the $Ar/PrSO_3H$ –Si(Et)Si nanotubes is similar to that of their inner diameters.

The calculated textural parameters are summarized in Table 1. The Si (Et)Si-3 support (Fig. S1 of SI) possesses the largest BET surface area (649 $\text{m}^2 \text{g}^{-1}$) and the highest pore volume (2.4 $\text{m}^3 \text{g}^{-1}$) among all tested samples, contributed from inner tube voids, outer surface of the tubes and voids between tubes. After covalently bonding of PrSO₃H or ArSO₃H groups on the framework of the support, both BET surface area and pore volume of the resulting $PrSO_3H$ –Si(Et)Si-3 (478 m² g⁻¹ and 1.1 cm³ g⁻¹) or $ArSO_3H$ –Si(Et)Si-3 (546 m² g⁻¹ and 1.0 cm³ g⁻¹) decrease significantly. The result suggests that the most of -SO₃H groups are positioned at the inner surface of the nanotubes, leading to clogging of part of the inner tube voids. However, the Ar/PrSO3H-Si(Et)Si nanotubes still possess relatively large BET surface areas (456-623 m² g⁻¹) and high pore volumes $(1.0-1.7 \text{ cm}^3 \text{ g}^{-1})$; additionally, their BET surface area and pore volume are related to the inner diameter. The PrSO₃H-Si(Et)Si-1 and ArSO₃H-Si(Et)Si-1 with the smallest inner diameter among PrSO₃H-Si(Et)Si and ArSO₃H-Si(Et)Si nanotubes have the largest BET surface area (530 and 623 m² g⁻¹). This is due to the fact that much smaller nanotubes can provide obviously higher volume-to-surface

Table 1

Textural parameters, wall thickness (δ), inner diameter (D_1) and Brønsted acid site density (A) of various $Ar/PrSO_3H$ –Si(Et)Si nanotube catalysts.

Catalysts	S _{BET} (m ²	V _p (cm ³	D _p (nm)	D _I ^a (nm)	δ ^a (nm)	$A^{\rm b}$ (μ eq	А ^с (µеq
	g^{-1})	g ⁻¹)				(SO ₃ H)	(H ⁺)
						g ⁻¹)	g ⁻¹)
Si(Et)Si-3	649	2.4	10.3/	12	3	-	-
			50.0				
PrSO ₃ H–Si	530	1.2	3.8/	5	2	1160	1052
(Et)Si-1			6.4				
PrSO ₃ H–Si	477	1.0	4.3/	9	4	1035	990
(Et)Si-2			11.4				
PrSO ₃ H–Si	478	1.1	3.8/	11	4	1017	952
(Et)Si-3			11.4				
PrSO ₃ H–Si	468	1.1	4.0/	18	4	997	990
(Et)Si-4			24.0				
PrSO ₃ H–Si	456	1.1	3.6/	22	4	916	932
(Et)Si-5			24.0				
ArSO ₃ H–Si	623	1.2	3.9/	5	3	1026	1020
(Et)Si-1			6.3				
ArSO ₃ H–Si	543	1.1	3.8/	11	5	993	1010
(Et)Si-2			10.9				
ArSO ₃ H–Si	546	1.0	4.2/	16	5	961	961
(Et)Si-3			19.0				
ArSO ₃ H–Si	552	1.3	3.6/	25	5	981	971
(Et)Si-4			21.0				
ArSO ₃ H–Si	585	1.7	3.4/	38	5	997	980
(Et)Si-5			33.5				
ArSO ₃ H–Si	624	1.4	3.7/	5	3	986	975
(Et)Si-			6.1				
1 ³⁰⁰⁰							

^a Estimated by TEM images.

^b Determined by ICP-OES over fresh catalysts.

^c Determined by an acid-base titration over fresh catalysts.

^d After being used for five times.

ratio. As for other four *Pr*SO₃H–Si(Et)Si (477–456 m² g⁻¹) or *Ar*SO₃H–Si (Et)Si (543–585 m² g⁻¹) nanotubes, changes of their BET surface areas are inconspicuous.

3.2.3. Structural information

The formation of silica/carbon framework and successful incorporation of *Ar/Pr*SO₃H groups within the framework during one-step swollen mixed P123 and F127 micelle-templating co-condensation route are studied by XPS and MAS NMR, and the *Pr*SO₃H–Si(Et)Si-1 and *Ar*SO₃H–Si(Et)Si-1 are selected as the representative samples.

As shown in Fig. 3a, the S 2p XPS of both samples are deconvoluted into two peaks centering at 169.0 and 170.0 eV, characteristic of S $2p_{3/2}$ and S $2p_{1/2}$ spin-orbit components of $-SO_3H$ groups [4,23]; additionally, the absence of the peak at *ca*. 164.0 eV implies that sulphur species from -SH groups is absent, and -SH groups are completely oxidized to $-SO_3H$ groups by H_2O_2 during current one-step preparation process [51]. Fig. 3b presents C 1s XPS of the samples. For the *Pr*SO₃H–Si(Et)Si-1 nanotubes, the spectrum is deconvoluted into two peaks centering at 284.7 and 285.7 eV, respectively, attributing to carbon species from -C-C and C–S bonds [26]. In the case of the *Ar*SO₃H–Si(Et)Si-1, the above two XPS signals still can be observed; additionally, another weak signal at 284.5 eV emerges, attributing to carbon species from C=C bonds (phenyl rings) [51,61]. The above XPS analysis suggests that the presence of *Ar*/*Pr*SO₃H groups within the silica/carbon framework of the nanotubes.

In the ¹³C CP-MAS NMR spectrum of the *Pr*SO₃H–Si(Et)Si-1 (Fig. 3c), the strongest signal at 5.3 ppm is attributed to carbon species from the bridging ethyl units of the framework (C¹). The other three signals with chemical shifts of 12.5 (C²), 19.1 (C³) and 54.6 ppm (C⁴) are assigned to the carbon species from *Pr*SO₃H groups [26,56,62]. A series of weak peaks with chemical shifts in the range of 58.7–105.7 ppm are assigned to carbon species of the residual trace P123 and F127. In the ¹³C CP-MAS



Fig. 2. Nitrogen gas adsorption-desorption isotherms (a, b) and BJH pore size distribution profiles (c, d) of various Ar/PrSO₃H–Si(Et)Si nanotube catalysts.



Fig. 3. S 2p (a) and C 1s (b) XPS spectra, ¹³C CP-MAS NMR (c, d) and ²⁹Si MAS NMR (e, f) spectra of the PrSO₃H–Si(Et)Si-1 and ArSO₃H–Si(Et)Si-1 nano-tube catalysts.

NMR spectrum of the *Ar*SO₃H–Si(Et)Si-**1** (Fig. 3d), the strongest signal corresponding to the carbon species of bridging ethyl groups is still identified at 5.3 ppm (C^1). The other five signals with the chemical shifts of 15.8, 29.2, 127.6, 140.5 and 148.3 ppm are originated from the carbon species of *Ar*SO₃H groups (C^2 – C^6 in Fig. 3d). A weak signal detected at 58.3 ppm is due to carbon species of the residual trace P123 and F127.

In the ²⁹Si MAS NMR spectrum of the *Pr*SO₃H–Si(Et)Si-1 (Fig. 3e), two characteristic resonance signals at 63.9 and 70.0 ppm are identified, which are assigned to —-CH₂CH₂Si(OSi)₂(OH) (T²) and —CH₂CH₂Si (OSi)₃ (T³) sites within the ethyl-bridged-organosilica framework. Similarly, T² and T³ sites appear at 62.0 and 67.2 ppm for the *Ar*SO₃H–Si (Et)Si-1 nanotubes (Fig. 3f). Both ²⁹Si MAS NMR and ¹³C CP-MAS NMR spectra further evidence that *Ar/Pr*SO₃H groups functionalized ethylbridged-organosilica is fabricated by current preparation route.

3.2.4. Brønsted acid nature

The Brønsted acid strength of the *Ar/Pr*SO₃H–Si(Et)Si nanotubes is studied by NH₃–TPD analysis, and the *Pr*SO₃H–Si(Et)Si-1 and *Ar*SO₃H–Si(Et)Si-1 are selected as the representative samples. As shown in Fig. 4, the NH₃–TPD profiles of both samples exhibit two peaks in the range of 100–800 °C. The first peak is found at *ca.* 260 °C for both samples, while the second peak is identified at 547 °C for the *Pr*SO₃H–Si (Et)Si-1 and 603 °C for the *Ar*SO₃H–Si(Et)Si-1, respectively. Moreover, the peak intensities of the *Ar*SO₃H–Si(Et)Si-1 are stronger than those of the *Pr*SO₃H–Si(Et)Si-1. The first peak is attributed to desorption of NH₃ from the weak Brønsted acid sites, herein, protons from SiO–H groups, while the second peak is originated from desorption of NH₃ from the strong Brønsted acid sites, herein, protons from *Pr*SO₃H or *Ar*SO₃H groups. The result suggests that both *Pr*SO₃H–Si(Et)Si-1 and *Ar*SO₃H–Si (Et)Si-1 are strong Brønsted acid; additionally, *Ar*SO₃H–Si(Et)Si-1



Fig. 4. NH₃-TPD profiles of the *Pr*SO₃H-Si(Et)Si-1 and *Ar*SO₃H-Si(Et)Si-1 nanotube catalysts.

possesses stronger Brønsted acid nature than PrSO₃H-Si(Et)Si-1. Difference of Brønsted acid strength between two samples is due to their different microenvironment of the SO₃H sites. Namely, phenyl in ArSO₃H groups can provide stronger electron withdrawing environments as compared with propyl in PrSO₃H groups, and therefore ArSO₃H-Si(Et)Si exhibits stronger proton releasing ability than PrSO₃H-Si(Et)Si nanotubes [63]. The Brønsted acid site densities of various Ar/PrSO3H-Si(Et)Si nanotubes are determined by both ICP-OES and acid-base titration. As listed in Table 1, both methods give the similar results, and the determined Brønsted acid site densities are ca. 1000 μ eq g⁻¹ for all samples. The data are consistent with those of their theoretical values (10 mol%). It is therefore reasonably inferred that the most of Ar/PrSO₃H groups in the initial preparation systems are incorporated to the ethyl-bridged-organosilica framework. Additionally, the PrSO₃H-Si(Et)Si-1 and ArSO₃H-Si(Et)Si-1 nanotubes possess the highest Brønsted acid site density among their counterparts, contributed from their largest BET surface areas.

3.3. Catalytic tests

3.3.1. Catalytic activity and selectivity

The heterogeneous acid catalytic activity of as-prepared ten Ar/ PrSO₃H-Si(Et)Si nanotubes is firstly evaluated by transesterification of TP with MeOH to produce MP. In the search for the optimum reaction conditions to produce MP with high yield, the influence of the stirring speed, reaction temperature and MeOH-to-TP molar ratio (n_{MeOH} : n_{TP}) on the yield of MP is studied by using the ArSO₃H–Si(Et)Si-1 nanotubes as the representative catalyst. Transesterification of TG with MeOH is a complex process with multiple steps, accompanying with the production of intermediates including diglyceride and monoglyceride and then FAMEs. Here, LC-MS analysis is applied to identified the intermediates and product yielded during the process of the ArSO₃H-Si(Et)Si-1 nanotubes-catalyzed transesterification of TP with MeOH performing at 100 °C and *n*_{MeOH}:*n*_{TP} molar ratio of 15:1 and 45:1. As shown in Fig. S2 of SI, glycerol dipalmitin (DPG), glycerol monopalmitate (MPG) and MP are all found in current catalytic systems, confirming that the production of MP via transesterification of TP suffers from a multiple-step process (Scheme S1 of SI). The transesterification reaction therefore needs higher activation energy and proceeds at a slower rate, and reaction temperature and n_{MeOH} : n_{TP} molar ratio are both important parameters that influence the catalytic activity of TP transesterification significantly.

At first, the influence of stirring speed on the transesterification activity of the *Ar*SO₃H–Si(Et)Si-1 nanotubes is studied under the conditions of 100 °C and n_{MeOH} : n_{TP} molar ratio of 45:1. As shown in Fig. S3a of SI, the reaction rate is consistent and the yield of MP is the same in $ArSO_{3}H$ -Si(Et)Si-1 nanotubes-catalyzed TP transesterification reaction performing at 450, 600 and 750 rpm, respectively. As a result, the reaction rate is not affected by changing stirring speed in the range of 450–750 rpm, reflecting little mass transfer limitation of the $Ar/PrSO_{3}H$ -Si(Et)Si nanotube catalyst systems. For subsequent catalytic tests, the stirring speed is set at 600 rpm.

The influence of reaction temperature on the transesterification activity of the *Ar*SO₃H–Si(Et)Si-1 nanotubes is tested *via* changing temperature from 65, 80–100 °C at n_{MeOH} : n_{TP} molar ratio of 45:1. As shown in Fig. 5a, the conversion of TP and yield of MP increase markedly with the reaction temperature. For instance, over period of 6 h, the conversion of TP enhances from 41.3 (65 °C), 48.5 (80 °C) to 76.8 % (100 °C); correspondingly, the yield of MP increases from 29.8, 37.8–68.0%. This is due to the fact that higher reaction temperature can facilitate the transesterification reaction proceeding at a faster rate.

At the reaction temperature of 100 °C, the influence of n_{MeOH} : n_{TP} molar ratio on the transesterification activity of the $ArSO_{3}H$ –Si(Et)Si-1 nanotubes is studied subsequently. Practically, the transesterification of TP with MeOH frequently performs at higher n_{MeOH} : n_{TP} molar ratio to boost the formation of MP. As shown in Fig. 5b, with increasing the n_{MeOH} : n_{TP} molar ratio, the conversion of TP increases from 33.5 (15:1), 57.7 (30:1) to 76.8 % (45:1), respectively, after the transesterification reaction proceeds for 6 h, and the corresponding yield of MP increases from 28.8, 48.5–68.0%. The result is explained below. Transesterification of TP with MeOH is a reversible reaction, and excessive MeOH can accelerate the reaction equilibrium in a positive shift and thereby promote the conversion of TP to MP. Additionally, excessive MeOH can dilute TP and thus increasing the diffusion rate of TP molecules, which can also facilitate the formation of MP. Therefore, a higher n_{MeOH} : n_{TP} molar ratio of 45:1 is set for the next catalytic tests.

Besides the optimum reaction conditions of 100 °C and n_{MeOH} : n_{TP} molar ratio of 45:1, the influence of the controlled inner diameters of various Ar/PrSO3H-Si(Et)Si nanotubes on transesterification activity is further studied, and for comparison, commercially available Amberlyst-15 resin and acidic ZSM-5 zeolite are also tested under the identical reaction conditions. As shown in Fig. 5c-f, five ArSO₃H-Si(Et)Si nanotubes all exhibit considerably high transesterification activity, and they follow the activity order of $ArSO_{3}H$ -Si(Et)Si-1 $\approx ArSO_{3}H$ -Si(Et)Si-5 > $ArSO_{3}H-Si(Et)Si-4 > ArSO_{3}H-Si(Et)Si-3 > ArSO_{3}H-Si(Et)Si-2$. For example, the conversion of TP reaches 99.9 (ArSO₃H-Si(Et)Si-1), 97.9 (ArSO3H-Si(Et)Si-5), 93.5 (ArSO3H-Si(Et)Si-4), 91.0 (ArSO3H-Si(Et)Si-3) and 86.9 % (ArSO₃H-Si(Et)Si-2), respectively, after the reaction proceeds for 12 h (Fig. 5c); meanwhile, the yield of MP reaches 97.9 (ArSO3H-Si(Et)Si-1), 96.9 (ArSO3H-Si(Et)Si-5), 91.6 (ArSO3H-Si(Et)Si-4), 88.3 (ArSO₃H-Si(Et)Si-3) and 83.4 % (ArSO₃H-Si(Et)Si-2) (Fig. 5e). In the cases of five PrSO₃H-Si(Et)Si nanotubes, they all possess lower transesterification activity than their corresponding ArSO3H-Si(Et)Si counterparts; however, they still follow the activity order of PrSO₃H-Si $(Et)Si\textbf{-1}\approx \textit{PrSO}_{3}H\textbf{-Si}(Et)Si\textbf{-5} > \textit{PrSO}_{3}H\textbf{-Si}(Et)Si\textbf{-4} > \textit{PrSO}_{3}H\textbf{-Si}(Et)Si\textbf{-3}$ > PrSO₃H–Si(Et)Si-2. Over period of 12 h, the conversion of TP reaches 86.0 (PrSO₃H–Si(Et)Si-1), 84.1 (PrSO₃H–Si(Et)Si-5), 75.7 (PrSO₃H–Si (Et)Si-4), 71.1 (PrSO₃H-Si(Et)Si-3) and 68.4 % (PrSO₃H-Si(Et)Si-2), respectively (Fig. 5d). At the same reaction time, the yield of MP is 81.7 (PrSO₃H-Si(Et)Si-1), 79.0 (PrSO₃H-Si(Et)Si-5), 72.7 (PrSO₃H-Si(Et)Si-4), 69.0 (PrSO₃H-Si(Et)Si-3) and 67.0 % (PrSO₃H-Si(Et)Si-2), respectively (Fig. 5f). Both Amberlyst-15 and ZSM-5 show poor transesterification activity under the same reaction conditions, and the corresponding conversion of TP and yield of MP is 46.5 and 42.9 as well as 32.0 and 29.4 %, respectively (Fig. 5d and f).

Next, the heterogeneous acid catalytic performance of the $Ar/PrSO_3H$ –Si(Et)Si nanotubes is tested by esterification of Gly with LA to produce glycerol laurate esters. The esterification of Gly with fatty acid is an equilibrium limitation and multi-step reaction. Generally, when Gly is esterified with long-chain fatty acid, *e.g.*, LA, the main products are mono- and di-glycerol esters, and it is difficult to produce tri-glycerol ester with long-chain fatty acid. Moreover, long-chain mono- and di-



Fig. 5. Influence of temperature (a), $n_{\text{MeOH}:n_{\text{TP}}}$ molar ratio (b) on the catalytic activity of the *Ar*SO₃H–Si(Et)Si-1 in transesterification of TP with MeOH. Reaction conditions for (a): 50 mmol MeOH, 1.1 mmol TP, $n_{\text{MeOH}:n_{\text{TP}}} = 45:1, 6$ h; (b) 100 °C, 6 h. Transesterification activity of various *Ar/Pr*SO₃H–Si(Et)Si nanotubes and reference acid catalysts (c–f). 50 mmol MeOH, 1.1 mmol TP, $n_{\text{MeOH}:n_{\text{TP}}} = 45:1, 100$ °C, 12 h. 4 wt% catalyst; 600 rpm.

glycerol esters have widely applied in the fields of foods, pharmaceuticals and cosmetics, and thus complete esterification of Gly with longchain fatty acid to tri-glycerol ester is undesired [64–68].

Since the yield and selectivity of glycerol laurate esters are influenced by not only the nature of the catalysts but also the reaction parameters such as temperature and reactant molar composition [30], the influence of these parameters is considered. At first, the influence of stirring speed on the esterification activity of the *Ar*SO₃H–Si(Et)Si-1 nanotubes is studied under the conditions of 140 °C and n_{Gly} : n_{LA} ratio of 3:1. As shown in Fig. S3b of SI, the total yields of MLG and TLG is the same (*ca.* 95 %, 60 min) in *Ar*SO₃H–Si(Et)Si-1 nanotubes-catalyzed esterification of Gly with LA performing at 450, 600 and 750 rpm, respectively. As a result, the esterification reaction rate is not affected by changing stirring speed in the range of 450–750 rpm, reflecting little mass transfer limitation of the *Ar*/*Pr*SO₃H–Si(Et)Si nanotube catalyst systems in Gly esterification reaction. Thus, the stirring speed is set at 600 rpm for the next catalytic tests.

Fig. 6a displays the influence of temperature on the catalytic activity of the *Ar*SO₃H–Si(Et)Si-1 in esterification of Gly with LA carried out at

Gly-to-LA molar ratio (n_{Gly} : n_{LA}) of 3:1. In this catalytic system, three glycerol laurate esters including MLG, DLG and TLG are found. With the increase of the reaction temperature from 110, 140–170 °C, the conversion of LA reaches 24.5, 95.6 and 94.3 %, respectively; meanwhile, the produced TLG is still in trace amount (lower than 6.0 %). Additionally, the yield of MLG is considerably lower (lower than 15.0 %), and the most of the yielded glycerol laurate ester is DLG at higher reaction temperature (140 and 170 °C). For example, after the reaction performs for 60 min, the yield of DLG is 85.6 % (140 °C) and 76.6 % (170 °C), respectively, while the total yields of MLG and TLG is 10.1 % (140 °C) and 21.0 % (170 °C). Accordingly, the subsequent esterification reaction is tested at 140 °C.

The influence of n_{Gly} : n_{LA} molar ratio on the esterification activity and selectivity of the $ArSO_3H$ –Si(Et)Si-1 nanotubes is shown in Fig. 6b. At 140 °C and 60 min, conversion of LA is close to 1.0 % at various n_{Gly} : n_{LA} ratios. Changing n_{Gly} : n_{LA} ratio from 3:1 to 1:3, the selectivity to MLG has somewhat increase (from 8.5–18.3 %); meanwhile, the selectivity to TLG increase obviously (from 2.0–29.2 %). The above changes accompany with the decrease of the selectivity to DLG (from 89.5–52.5 %).



Fig. 6. Influence of temperature (a) and $n_{Gly}:n_{LA}$ molar ratio (b) on the catalytic activity and selectivity of the $ArSO_3H$ –Si(Et)Si-1 nanotubes in the esterification of Gly with LA. Reaction conditions for (a): 33.5 mmol Gly, 11.2 mmol LA, $n_{Gly}:n_{LA} = 3:1$, 60 min; (b) 140 °C, 60 min. (c–f) Esterification activity comparison of various $Ar/PrSO_3H$ –Si(Et)Si nanotubes and reference catalysts. 33.5 mmol Gly, 11.2 mmol LA, $n_{Gly}:n_{LA} = 3:1$, 140 °C, 2 wt% catalyst; 600 rpm.

This is due to the fact that higher $n_{Gly}:n_{LA}$ molar ratio (or excessive Gly) can not only speed the reaction rate but also shift the reaction towards the formation of DLG, whereas lower $n_{Gly}:n_{LA}$ molar ratio (or excessive LA) is favorable for the formation of deep esterification product (TLG). Considering that the highest selectivity to MLG and DLG is obtained and thereby the highest total yields of MLG and DLG (93.7 %) at $n_{Gly}:n_{LA}$ molar ratio of 3:1, the optimal $n_{Gly}:n_{LA}$ molar ratio of 3:1 is chosen for subsequent catalytic tests.

Under the optimum reaction conditions of n_{Gly} : n_{LA} molar ratio of 3:1 and 140 °C, the esterification activity of various $Ar/PrSO_3H$ –Si(Et)Si nanotubes are tested to explore the influence of inner diameter on the esterification activity. As shown in Fig. 6c and e, the $ArSO_3H$ –Si(Et)Si-1 exhibits apparently higher esterification activity than its other four counterparts; and the other four $ArSO_3H$ –Si(Et)Si nanotubes follow the esterification activity order of $ArSO_3H$ –Si(Et)Si-5 > $ArSO_3H$ –Si(Et)Si-4 > $ArSO_3H$ –Si(Et)Si-3 > $ArSO_3H$ –Si(Et)Si-2. Over period of 60 min, the conversion of LA reaches 95.6 ($ArSO_3H$ –Si(Et)Si-1), 78.8 ($ArSO_3H$ –Si (Et)Si-5), 73.7 ($ArSO_3H$ –Si(Et)Si-4), 66.6 ($ArSO_3H$ –Si(Et)Si-3) and 62.4 % ($ArSO_3H$ –Si(Et)Si-2), respectively (Fig. 6c). At the same reaction time, the total yields of MLG and DLG are 93.7 ($ArSO_3H$ –Si(Et)Si-1), 76.9 ($ArSO_3H$ –Si(Et)Si-5), 72.1 ($ArSO_3H$ –Si(Et)Si-4), 64.9 ($ArSO_3H$ –Si(Et)Si**3**) and 61.4 % (*A*rSO₃H–Si(Et)Si-**2**), respectively. In the cases of five *P*rSO₃H–Si(Et)Si nanotubes, they all exhibit lower esterification activity than their corresponding *A*rSO₃H–Si(Et)Si counterparts, similar to their catalytic behavior in transesterification reaction; additionally, they still follow the activity order of *P*rSO₃H–Si(Et)Si-**1** > *P*rSO₃H–Si(Et)Si-**5** > *P*rSO₃H–Si(Et)Si-**4** > *P*rSO₃H–Si(Et)Si-**3** > *P*rSO₃H–Si(Et)Si-**2**. The conversion of LA reaches 66.5 (*P*rSO₃H–Si(Et)Si-**1**), 58.9 (*P*rSO₃H–Si(Et)Si-**5**), 55.9 (*P*rSO₃H–Si(Et)Si-**4**), 50.1 (*A*rSO₃H–Si(Et)Si-**3**), 49.2 % (*P*rSO₃H–Si(Et)Si-**2**), 33.4 (Amberlyst-15) and 22.6 % (ZSM-5), respectively, after the reaction proceeds for 60 min (Fig. 6d). At the same reaction time, the corresponding total yields of MLG and DLG are 64.8, 57.7, 54.3, 48.8 and 47.8 %, respectively (Fig. 6f). As for two reference solid acids, their esterification activity is considerably lower, and only the total yields of MLG and DLG of 29.6 % (Amberlyst-15) and 20.3 % (ZSM-5) are obtained under the same reaction conditions (Fig. 6f).

From the results shown in Fig. 6c–f it is found that under the conditions of 140 °C and n_{Gly} : n_{LA} molar ratio of 3:1 (Gly is excessive), asprepared $Ar/PrSO_3H$ -Si(Et)Si nanotube-catalyzed esterification reaction rate maintains constant basically within 60 min, although the proportion of Gly and LA may changes over time. However, under the same reaction conditions, Amerlyst-15 resin- or ZSM-5 zeolite-catalyzed esterification reaction rate becomes slow gradually (Fig. 6d and f). The result reflects that the Ar/PrSO3H-Si(Et)Si nanotubes are more catalytically active than both reference solid acid catalysts. Additionally, the product yield, represented by the total yields of MLG and DLG, increases linearly within 60 min in Ar/PrSO₃H-Si(Et)Si nanotube systems (Fig. 6e and f). As shown in Fig. S4 of SI, taking ArSO₃H-Si(Et)Si-1 nanotubes as the representative catalyst, changes of the selectivity of the ArSO₃H-Si (Et)Si nanotubes to each product like MLG, DLG and TLG with the reaction time follow the trend described below. Increasing the reaction time from 20 to 60 min, the selectivity of the ArSO₃H-Si(Et)Si-1 nanotubes to MLG (from 18 to 8.5 %) and TLG (from 5.0-2.0 %) decreases gradually, whereas the selectivity to DLG increases obviously (from 77.0-89.5 %); meanwhile, DLG is always a main product within 60 min, and change of total selectivity of the ArSO₃H-Si(Et)Si-1 nanotubes to MLG and DLG has only a slight increase with the time, e.g., from 95.0 (20 min), 97.8 (40 min) to 98.0 % (60 min). The above result is originated from higher n_{Glv} : n_{LA} molar ratio (3:1) in the initial reaction system, and thus Gly is always excessive although the n_{Gly} : n_{LA} molar ratio may have some change over time, which is greatly favorable for the formation of DLG rather than TLG.

To evaluate the intrinsic catalytic activity of as-prepared Ar/ PrSO₃H-Si(Et)Si nanotubes in both target reactions, their Brønsted acid site densities are considered. Accordingly, TOF values of various Ar/ PrSO₃H–Si(Et)Si nanotubes are presented (Fig. 7). Here, TOF values are determined from the linear portion of the initial reaction rate profiles for the yields of MP (transesterification reaction) and DLG (esterification reaction), which are normalized to the acid site densities determined by acid-base titration. Fig. 7a displays the TOF values of ten Ar/PrSO₃H-Si (Et)Si nanotubes and reference catalysts in TP transesterification reaction, showing that five ArSO₃H-Si(Et)Si nanotubes follow the TOF value order of $ArSO_3H$ –Si(Et)Si-1 (2.9 min⁻¹) > $ArSO_3H$ –Si(Et)Si-5 (2.8 min^{-1}) > ArSO₃H-Si(Et)Si-4 (2.4 min^{-1}) > ArSO₃H-Si(Et)Si-3 (2.3 min^{-1}) > ArSO₃H–Si(Et)Si-2 (1.8 min^{-1}). In the cases of five PrSO₃H–Si (Et)Si nanotubes, they follow the TOF value order of PrSO₃H-Si(Et)Si-1 $(1.9 \text{ min}^{-1}) > PrSO_3H-Si(Et)Si-5 (1.8 \text{ min}^{-1}) > PrSO_3H-Si(Et)Si-4 (1.7 \text{ min}^{-1}) > PrSO_3H-Si(Et)Si-4 (1.7$ min^{-1}) > PrSO₃H-Si(Et)Si-3 (1.6 min^{-1}) > PrSO₃H-Si(Et)Si-2 (1.5 min^{-1}). As for ZSM-5 (0.2 min^{-1}) and Amberlyst-15 (0.9 min^{-1}), their TOF values are very small.

Fig. 7b shows the TOF values of ten *Ar/Pr*SO₃H–Si(Et)Si nanotubes and reference catalysts in esterification of Gly with LA reaction. It shows that five *Ar*SO₃H–Si(Et)Si nanotubes follow the TOF value order of *Ar*SO₃H–Si(Et)Si-1 (8.7 min⁻¹) > *Ar*SO₃H–Si(Et)Si-5 (7.7 min⁻¹) > *Ar*SO₃H–Si(Et)Si-4 (6.8 min⁻¹) > *Ar*SO₃H–Si(Et)Si-3 (6.0 min⁻¹) > *Ar*SO₃H–Si(Et)Si-2 (4.8 min⁻¹); and five *Pr*SO₃H–Si(Et)Si nanotubes follow the TOF value order of *Pr*SO₃H–Si(Et)Si-1 (5.7 min⁻¹) > *Pr*SO₃H–Si(Et)Si-5 (5.5 min⁻¹) > *Pr*SO₃H–Si(Et)Si-4 (5.4 min⁻¹) > $PrSO_3H$ –Si(Et)Si-**3** (5.3 min⁻¹) > $PrSO_3H$ –Si(Et)Si-**2** (5.0 min⁻¹). The TOF values of both ZSM-5 (0.9 min⁻¹) and Amberlyst-15 (3.0 min⁻¹) are smaller than all tested $Ar/PrSO_3H$ –Si(Et)Si nanotubes.

The above activity order of various Ar/PrSO₃H-Si(Et)Si nanotubes revealed by TOF values are in line with those revealed by the yield of MP or DLG, confirming that the Ar/PrSO₃H-Si(Et)Si-1 nanotubes exhibits the highest catalytic activity, due to their increased accessibility of the acid sites. More importantly, the accessibility of the acid sites can be improved by adjusting the inner diameter of the Ar/PrSO3H-Si(Et)Si nanotubes. The Ar/PrSO3H-Si(Et)Si-1 nanotubes with the smallest inner diameter possess the highest BET surface area, giving rise to a high exposing degree of the acid sites and thereby increasing availability of acid sites. As for four pairs of the Ar/PrSO3H-Si(Et)Si nanotubes, they have the similar BET surface area but different inner diameters. The Ar/ PrSO₃H-Si(Et)Si-5 nanotubes exhibit higher activity than other three counterparts, due to that the largest inner diameter decreases diffusion and mass-transport limitation of bulky reactant molecules and also can create high accessibility of the acid sites. Additionally, ArSO₃H-Si(Et)Si nanotubes possess higher TOF value and thereby higher catalytic activity than their corresponding PrSO₃H-Si(Et)Si nanotubes. It is due to that the formers possess not only higher BET surface area and inner diameter but also stronger Brønsted acid strength.

To explain the above catalytic results, possible reaction mechanism of the Ar/PrSO₃H-Si(Et)Si nanotube-catalyzed transesterification of TP with MeOH is put forward following Eley-Rideal-type hypothesis [69, 70]. As illustrated in Scheme S1 of SI, in current reaction system, transesterification of TP with MeOH suffers from three successive steps. Specifically, in TP-MeOH biphasic system, the mass transfer of protons from Ar/PrSO₃H groups and reactants through TP-MeOH interface is clearly essential to obtain fast reaction rate. At first, carbonyl groups of TP molecules are activated by protons from Ar/PrSO₃H groups, giving rise to oxonium ions that are readily attacked by the nucleophilic oxygen atoms of MeOH molecules. After nucleophilic addition of MeOH to oxonium ions in TP, DPG is produced, accompanying with the formation of MP and release of protons. Further activation of DLG by protons from Ar/PrSO₃H groups and subsequent attack by MeOH can produce MLG, and the process also accompanies with the formation of MP and release of protons. Finally, MLG is activated by protons from Ar/PrSO₃H groups and then attack by MeOH, leading to produce Gly, together with the formation of MP and release of protons. It is assumed that the nucleophilic addition of MeOH to oxonium ions in TP molecules is the rate determining step in the overall transesterification, because the mass transfer of MeOH through TP-MeOH two-phase interface happens prior to the nucleophilic addition reaction. Since hydrophobic Ar/PrSO₃H-Si (Et)Si nanotubes can stabilize Pickering emulsion in two-phase system and minimize the mass transfer limitation, the TP transesterification



Fig. 7. Catalytic activity comparison of various Ar/PrSO₃H–Si(Et)Si nanotubes as well as reference acid catalysts by TOF values in transesterification of TP with MeOH (a) and esterification of Gly with LA (b). 50 mmol MeOH, 1.1 mmol TP, n_{MeOH} : n_{TP} = 45:1, 100 °C, 4 wt% catalyst, 1.5 h; 33.5 mmol Gly, 11.2 mmol LA, n_{Gly} : n_{LA} = 3:1, 140 °C, 2 wt% catalyst, 20 min; 600 rpm.

reaction is facilitated correspondingly. Similar to transesterification reaction, esterification of Gly with LA also starts from the protonation of carbonyl groups of LA molecules by the $Ar/PrSO_3H$ sites, followed by nucleophilic addition of oxygen atoms of glycerol molecules with oxonium ions in LA [71].

On the basis of the above reaction mechanism, the transesterification/esterification activity of the $Ar/PrSO_3H$ –Si(Et)Si nanotubes strongly depends on their Brønsted acid nature; additionally, the morphological characteristics, porosity properties and surface hydrophobicity influence the accessibility of the acid sites to bulky reactant molecules and thus the activity in some extent.

Firstly, the intrinsic strong Brønsted acid nature of the $Ar/PrSO_3H$ -Si (Et)Si nanotubes plays the key role to boost the target reactions. With the assistance of the protons from the $Ar/PrSO_3H$ -Si(Et)Si nanotubes, superstrong Brønsted acidity with high acid site density can activate sufficiently the bulky reactant molecules and further assure the transesterification/esterification reaction proceeds rapidly. Lower transesterification/esterification activity of the $PrSO_3H$ -Si(Et)Si nanotubes than the corresponding $ArSO_3H$ -Si(Et)Si counterparts is due to their weaker Brønsted acid strength.

Secondly, the morphological characteristics and porosity properties of the Ar/PrSO₃H-Si(Et)Si nanotubes influence their transesterification/ esterification activity obviously. One-dimensional tubular Ar/ PrSO₃H-Si(Et)Si nanocatalysts possess outstanding advantages such as open and flexible structure, thin wall, tunable inner diameter and length, high dispersity, high pore volume as well as large BET surface area, and the most of the acid sites situate at the interior of the nanotubes. These acid site-confined nanotubes with large inner diameter can serve as the nanoreactors to allow free diffusion and fast mass-transport of the reactants and products, particularly for bulky reactants (TP and Gly) and products (MP, MLG and DLG). In addition, large BET surface area of the nanotubes can help the Ar/PrSO₃H groups homogeneously dispersed throughout the silica/carbon framework, giving rise to high population of the exposed acid sites confined in the surface of the nanotubes and thus of high accessibility of the acid sites to the reactants. These advantages positively influence the catalytic activity of the Ar/ PrSO₃H-Si(Et)Si nanotubes. Although the Ar/PrSO₃H-Si(Et)Si-1 nanotubes show the smallest inner diameter of the tubes (5 nm) among ten asprepared Ar/PrSO₃H-Si(Et)Si nanotubes, their inner diameter and pore diameter are still large enough for free diffusion and fast mass-transport of bulky reactants (TP and Gly) and products (MP, MLG and DLG) within the nanotubes. The highest transesterification and esterification activity of the Ar/PrSO₃H–Si(Et)Si-1 nanotube among their counterparts is due to their largest BET surface area. In the cases of other four pairs of the Ar/PrSO₃H-Si(Et)Si nanotubes, their BET surface areas are similar, and their transesterification and esterification activity are closely related to the inner diameter and length of the nanotubes. Namely, larger inner diameter and shorter tube length can accelerate the diffusion and mass transport of bulky reactants and products significantly, originating from the enlarged interior channel of the nanotubes and shortened mass transport distance. Accordingly, the Ar/PrSO₃H-Si(Et)Si-5 nanotubes with the largest inner diameter and the shortest tube length exhibit comparable transesterification and esterification activity to the Ar/ PrSO₃H-Si(Et)Si-1 counterparts, which compensate their disadvantage of smaller BET surface areas. The similar explanation can also be found in Gong's and Liu's work, and they pointed out that short nanotubes are of interest in catalysis [57,58].

On the basis of the above discussion it is also inferred that higher BET surface area and larger inner diameter of the *Ar*SO₃H–Si(Et)Si nanotubes than their *Pr*SO₃H–Si(Et)Si counterparts are the other reasons that dominate their higher transesterification and esterification activity than the latter. Additionally, the inferior transesterification and esterification activity of Amberlyst-15 is attributed to its low BET surface area (50 m² g⁻¹) although it has strong Brønsted acid nature, which results in it low exposing degree of the acid sites to the reactants. As for acidic ZSM-5, its micropore size (0.5 × 0.5 nm) and low pore volume (0.15 cm³ g⁻¹) only

provide a low degree of pore opening and strong diffusion and masstransport limitation [72], leading to the inaccessibility of the acid sites to bulky reactant molecules and thereby poor transesterification and esterification activity.

Finally, the incorporation of bridging ethyl groups within the silica/ carbon framework can increase the surface hydrophobicity of the Ar/ PrSO₃H-Si(Et)Si nanotubes, which also influence their transesterification and esterification activity positively. For TP transesterification reaction, the hydrophobic environment in the tube channels is in favor of enrichment of hydrophobic reactant, while the hydrophilic byproduct is expelled. As a consequence, the formation of MP is accelerated. Additionally, after mixing hydrophobic TP and hydrophilic MeOH with hydrophobic Ar/PrSO3H-Si(Et)Si nanotube catalyst powder under stirring, we observe that a homogeneous Pickering emulsion is formed, in which TP and Ar/PrSO₃H-Si(Et)Si nanotube catalyst show good miscibility. Accordingly, the improved accessibility of TP to the acid sites of Ar/PrSO3H-Si(Et)Si nanotube catalyst can be obtained, leading to little mass transfer limitation of the Ar/PrSO₃H-Si (Et)Si catalyst system [73–75]. As for the esterification of Gly with LA, hydrophobic surface of the nanotubes is benefit to adsorb hydrophobic LA molecules; meanwhile, byproduct water escapes from the catalyst surface. Accordingly, the formation of glycerol laurate esters is promoted; meanwhile, hydrolysis of glycerol laurate esters by water can be inhibited obviously.

3.3.2. Catalytic stability and reusability

The issue of acid catalyst reusability and stability has been a central investigative theme for catalyst research in the area of biomass conversion. The acid catalysts containing sulfonic acid active sites, such as polymeric resins and sulfonated carbon materials, are susceptible to breakdown during biomass conversion because the process generally carries out under harsh conditions. Under these conditions, sulfonic acid groups are readily hydrolyzed, leading to leaching to the reaction media. The other reason of the deterioration of the catalyst is strong adsorption of carbonaceous products and byproducts on the catalyst surface. To evaluate the catalytic reusability and stability of as-prepared nanocatalysts, ArSO₃H-Si(Et)Si-1 is selected, and it catalyzes TP transesterification and Gly esterification reactions being repeated for five times. After each catalytic cycle, the recovered catalyst is washed by boiling ethanol and then dried at 80 °C. As shown in Fig. 8a, after the ArSO₃H-Si(Et)Si-1-catalyzed TP transesterification reaction proceeds for 12 h, the yield of MP is 97.9 (1 st run), 94.7 (2nd run), 94.1 (3rd run), 92.6 (4th run) and 95.0 % (5th run), respectively. In the case of the ArSO₃H-Si(Et)Si-1-catalyzed Gly esterification reaction, over period of 60 min, the total yields of MLG and DLG reach 93.7 (1 st run), 95.4 (2nd run), 90.1 (3rd run), 93.3 (4th run) and 93.1 % (5th run), respectively (Fig. 8b). The results suggest that ArSO₃H-Si(Et)Si-1 nanotubes exhibit excellent catalytic reusability in both target reactions, and the activity loss is hardly observed after five consecutive cycles.

To account for excellent catalytic reusability of the Ar/PrSO₃H-Si (Et)Si nanotubes, leaching of sulfonic acid groups from the catalyst to reaction media is firstly tested. After digesting the separated clear reaction solution by HNO_3 -HClO₄, the concentration of SO_4^{2-} ion in the reaction solution is determined by ion chromatography. It shows only 0.85 % of sulfonic acid groups are found to drop to the reaction media during the transesterification process, while the loss of sulfonic acid groups is hardly detected during the esterification process. The result provides one of the important evidence to confirm the excellent catalytic stability of the Ar/PrSO₃H-Si(Et)Si nanotubes. Additionally, the structure of the fifth time spent ArSO₃H–Si(Et)Si-1 nanotubes is characterized by ¹³C CP-MAS NMR method. As displayed in Fig. 8c and d, ¹³C CP-MAS NMR spectra of the spent catalyst exhibits all characteristic signals concerning about various carbon species existed in the fresh ArSO₃H-Si (Et)Si-1 nanotubes, indicating that the chemical structure of the ArSO₃H-Si(Et)Si-1 nanotubes remains intact after five consecutive catalytic cycles. Additionally, for the fifth time spent ArSO₃H-Si(Et)Si-1



Fig. 8. Reusability of the *Ar*SO₃H–Si(Et)Si-1 nanotubes in transesterification of TP with MeOH (a) and esterification of glycerol with LA (b). ¹³C CP-MAS NMR spectra of the fifth time spent catalyst after five times' transesterification (c) and esterification (d) tests. TEM images of the *Ar*SO₃H–Si(Et)Si-1 nanotubes after five times' transesterification (e) and esterification (f) tests. 50 mmol MeOH, 1.1 mmol TP, $n_{\text{MeOH}:R_{\text{TP}}} = 45:1, 100 \,^{\circ}\text{C}, 4 \,$ wt% catalyst, 12 h; 33.5 mmol Gly, 11.2 mmol LA, $n_{\text{Gly}:R_{\text{LA}}} = 3:1, 140 \,^{\circ}\text{C}, 2 \,$ wt% catalyst, 60 min; 600 rpm.

nanotubes, a new weak signal at 48.9 ppm is observed in transesterification system (Fig. 8c), while three new weak signals at 72.2, 63.2 and 58.1 ppm are found in esterification system (Fig. 8d). These signals are probably originated from the adsorbed small amount of reactants and byproducts, and the reusability of ArSO₃H-Si(Et)Si-1 nanotubes is hardly affected by the adsorbed materials. Both factors provide the other important evidence to confirm the excellent catalytic reusability of the nanocatalyst, which is attributed to covalent bonding of the ArSO₃H groups within the silica/carbon framework and surface hydrophobicity of the nanocatalyst. TEM images of the fifth time spent ArSO₃H-Si(Et)Si-1 nanotubes in transesterification (Fig. 8e) and esterification (Fig. 8f) reactions show that they still retain perfect tubular nanostructures; meanwhile, the inner diameter and wall thickness are also the same as the fresh one (Table 1). Finally, the textural parameters and acid site density of the fifth time spent ArSO₃H-Si(Et)Si-1 nanotubes are retained (Table 1).

3.3.3. Biodiesel production from various plant oils over Ar/PrSO₃H–Si(Et) Si-1 nanotubes

To expand the scope of their application, the heterogeneous acid catalytic activity of as-prepared $Ar/PrSO_3H$ –Si(Et)Si nanotubes is further tested in biodiesel production from various plant oils including rapeseed oil, sunflower oil and yellowhorn seed oil. Various plant oils

contain large amount of free fatty acids (e.g., palmitic acid) and water besides of TG components. In comparison of the base catalysts that suffer from the severe problem of the soap formation, acid catalyst can boost the esterification and transesterification reactions simultaneously from low-grade, highly acidic and water-containing oils without the formation of soap, exhibiting great potential of production of biodiesel in a large scale [14]. The catalytic activity and reusability of the Ar/Pr-SO₃H-Si(Et)Si nanotubes in biodiesel production from three plant oils is tested by using the PrSO₃H-Si(Et)Si-1 and ArSO₃H-Si(Et)Si-1 as the representative catalysts; meanwhile, the catalytic performance is also compared with Amberlyst-15 (Fig. 9). GC-MS analysis results (Fig. S5 of SI) and previous research work [76] indicate that four main products including MP (C16:0), methyl stearate (MS, C18:0), methyl oleate (MO, C18:1) and methyl linoleate (ML, C18:2) are found in acid-catalyzed esterification and transesterification of aforementioned three plant oils; additionally, a small quantity of methyl eicosenoate (C20:1) or methyl docosenoate (C22:1) is also detected. Here, the esterification and transesterification activities of the Ar/PrSO3H-Si(Et)Si nanotubes are evaluated by the yield of four main FAMEs. From the results shown in Fig. 9a-c it is found that both ArSO₃H-Si(Et)Si-1 and PrSO₃H-Si(Et)Si-1 exhibit considerably high activity in the formation of four FAMEs from three plant oils, and their catalytic activity is clearly higher than that of Amberlyst-15. Additionally, ArSO3H-Si(Et)Si-1 is more active than

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Fig. 9. Catalytic activity of the *Pr*SO₃H–Si(Et)Si-1, *Ar*SO₃H–Si(Et)Si-1 and Amberlyst-15 in biodiesel production from rapeseed oil (a), sunflower oil (b) and yellowhorn seed oil (c). Reusability of the *Ar*SO₃H–Si(Et)Si-1 nanotubes in biodiesel production from sunflower oil (d). 50 mmol MeOH, 1.1 mmol Oil, n_{MeOH} : n_{Oil} = 45:1, 100 °C, 3 wt% catalyst, 12 h, 600 rpm.

*Pr*SO₃H–Si(Et)Si-1, attributing to stronger Brønsted acid strength of the former and thus faster esterification/transesterification rate. Additionally, the yield of four FAMEs is the highest over the *Ar/Pr*SO₃H–Si(Et) Si-1-catalyzed transesterification/esterification of sunflower oil (Fig. 9b), followed by yellowhorn seed oil (Fig. 9c) and rapeseed oil (Fig. 9a). For instance, at the give reaction conditions, the yield of 87.2 (MP), 93.3 (MS), 86.6 (MO) and 81.4 % (ML) is obtained over the *Ar*SO₃H–Si(Et)Si-1-catalyzed transesterification/

esterification of rapeseed oil with MeOH (Fig. 9a); the yield of 93.2 (MP), 96.8 (MS), 95.8 (MO) and 91.6 % (ML) is found over the $ArSO_3H$ -Si(Et)Si-1-catalyzed transesterification/esterification of sunflower oil with MeOH (Fig. 9b); and the yield of 91.3 (MP), 86.1 (MS), 84.6 (MO) and 82.9 % (ML) is reached over the $ArSO_3H$ -Si(Et)Si-1-catalyzed transesterification/esterification of yellowhorn seed oil with MeOH (Fig. 9c). This difference of esterification/transesterification activity of the $Ar/PrSO_3H$ -Si(Et)Si-1 towards three plant oils is probably due to the difference in composition and purity of oils.

The catalytic reusability of the *Ar/Pr*SO₃H–Si(Et)Si nanotubes in biodiesel production from three plant oils is tested by selecting the *Ar*SO₃H–Si(Et)Si-1 nanotubes as the representative catalyst. As shown in Fig. 9d, the *Ar*SO₃H–Si(Et)Si-1 nanotubes display excellent catalytic reusability in esterification and transesterification of sunflower oil with MeOH, and the activity loss is negligible after four catalytic cycles. The unique catalytic activity and reusability of the *Ar/Pr*SO₃H–Si(Et)Si nanotubes in biodiesel production from low-cost biomass feedstocks strongly suggest their practical applications in the field of green chemistry. It should be noted that oils and fats also contain sterols and phospholipids, which may interfere with the separation and purification

of FAMEs. Accordingly, additional distillation technology is needed to separate and purify FAMEs.

4. Conclusions

The Ar/PrSO₃H-Si(Et)Si nanotube catalysts are successfully prepared via a single step toluene swollen mixed P123-F127 micelle-templating co-condensation route. The key factors for the construction of less aggregated Ar/PrSO3H-Si(Et)Si nanotubes include carefully controlled composition ratios of P123 to F127 and bridged organosilanes to the copolymer surfactants; additionally, the inner diameters (5-38 nm) and lengths of the Ar/PrSO₃H-Si(Et)Si nanotubes can be easily adjusted in a wide range by changing the concentration of swelling agent. The transesterification and esterification activities of the Ar/PrSO₃H-Si(Et)Si nanotubes strongly depend on their Brønsted acid nature; additionally, inner diameter, length and BET surface area of the nanotube catalysts influence the activity in some extent, which can change the diffusion and mass transport of the reactants/products as well as the accessibility to the acid sites; finally, the surface hydrophobicity of the Ar/PrSO₃H-Si(Et)Si nanotubes can boost the formation of FAMEs and glycerol laurate esters through changing the adsorption/ desorption behaviors of the reactants/products. The Ar/PrSO₃H-Si(Et)Si nanotubes also exhibit excellent catalytic reusability and stability, and the changes of activity loss, structure, morphology, acidity and porosity properties are hardly observed after five consecutive cycles, attributing to the covalent bonding of the Ar/PrSO3H groups within the silica/ carbon framework and the surface hydrophobicity of the Ar/PrSO₃H-Si (Et)Si nanotubes. The unique catalytic performance of the Ar/PrSO₃H-Si

(Et)Si nanotubes in biodiesel production and glycerol transformation strongly suggests their practical applications in the field of green chemistry.

CRediT authorship contribution statement

Qingqing Zhang: Conceptualization, Methodology, Investigation, Software, Writing - original draft. Chaoyue Zhang: Methodology, Formal analysis, Investigation, Software. Qingyin Wu: Conceptualization, Funding acquisition, Validation, Writing - review & editing. Jingyu Liu: Resources, Investigation, Software. Daiyu Song: Supervision, Funding acquisition, Project administration, Validation, Writing - review & editing. Yihang Guo: Conceptualization, Methodology, Supervision, Funding acquisition, Validation, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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