



# Preparation of efficient and recoverable organosulfonic acid functionalized alkyl-bridged organosilica nanotubes for esterification and transesterification



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## ABSTRACT

A series of arenesulfonic or propylsulfonic acid functionalized ethane- or benzene-bridged organosilica nanotubes hybrid catalysts, Si(Ph/Et)Si-Ar/Pr-SO<sub>3</sub>H NTs, was demonstrated for the first time by a single step nonionic surfactant-templated sol-gel co-condensation approach. The pore morphologies, textural and acidic properties of as-prepared hybrid catalysts were characterized by TEM observations, nitrogen gas porosimetry measurements and acid-base titration, while the structural integrity of the incorporated organosulfonic acid groups and silica/carbon framework in the hybrid catalysts were studied by <sup>13</sup>C CP-MAS NMR and <sup>29</sup>Si MAS NMR. As the novel solid acid catalysts, the catalytic activity and stability of the Si(Ph/Et)Si-Ar/Pr-SO<sub>3</sub>H NTs were evaluated by esterification of palmitic acid and transesterification of yellow horn seed oil with methanol under refluxing temperature (65 °C) and atmospheric pressure. Based on the physicochemical properties and catalytic testing results, the excellent heterogeneous acid catalytic behaviors of as-prepared tubular hybrid catalysts were revealed in terms of their considerably high Brønsted acid-site density and acid strength, unique textural properties, interesting morphology as well as hydrophobic surface.

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## 1. Introduction

The use of solid acids for “second generation” biodiesel production from inedible oily feedstocks is an emerging research field. Recent studies have proved the technical feasibility and the environmental and economical benefits of heterogeneous acid-catalyzed simultaneous esterification and transesterification for biodiesel production [1–4]. Numerous solid acids such as sulfated metal oxides [5–8], H-form zeolites [9], sulfonic ion-exchange resins [10], sulfonic acid modified mesostructured silica materials [11], sulfonated carbon-based catalysts [12], heteropolyacids [13], SiO<sub>2</sub>-, ZrO<sub>2</sub>- or Ta<sub>2</sub>O<sub>5</sub>-supported heteropolyacids [14–18] and acidic ionic liquids [19] have been extensively studied for this topic. Although these solid acids show acceptable reactivity towards esterification of long chain free fatty acids (FFAs), their reactivity to the transesterification of viscous and bulky triglycerides (TGs)-containing oily feedstocks is generally unsatisfactory. Therefore, most of solid acid-catalyzed transesterification reactions proceed

under stringent conditions including higher temperature, higher pressure, an excess of alcohol as well as longer reaction time, which are not favorable for industrial applications. Moreover, solid acid catalysts often suffer from problems of deactivation, poisoning and acid site leaching in the reaction medium. Thereby, design of efficient, robust and catalytically stable solid acid catalysts that can improve the overall efficiency of biodiesel production dramatically is still an important challenge.

Arenesulfonic or alkylsulfonic acid functionalized inorganic mesoporous silica or periodic mesoporous organosilica (PMO) materials are one of the most robust solid acid catalysts owing to their high Brønsted acid strength and plentiful number of acid sites. *In situ* incorporation of organosulfonic acid groups throughout the silica framework is a better method to construct the organosulfonic acid functionalized silica materials, and the preparation process includes the co-hydrolysis and -condensation of a tetralkoxysilane or a organosilane with 3-mercaptopropyltrialkylloxysilane (MPTMS) followed by oxidation of the thiol groups with H<sub>2</sub>O<sub>2</sub>. Additionally, 2-(4-chlorosulfonylphenyl)ethyl trimethoxysilane (CSPTMS) is also an useful precursor for replacement of MPTMS, which yields arenesulfonic acid groups just by hydrolysis and condensation under the acidic preparation conditions [11].

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In comparison to post-modification approach, this one step preparation strategy can lead to organosulfonic acid functionalized silica materials with tunable loading of sulfonic acid groups, excellent textural properties and homogeneous distribution of the active phases throughout the structure of the materials; meanwhile, the hydrolytic sol–gel process can strengthen the interaction between the acid sites and silica support, and thereby enhancing the stability of the hybrid catalysts owing to the reduced leaching of the active phase [20,21]. These sulfonic acid functionalized silica materials have been applied in a wide range of organic reactions including alkylation and acylation of hydrocarbons, the hydration of alkenes and the polymerization of THF [22,23], and they are also of interest for biomass conversion-related reactions such as esterification, transesterification, hydrolysis and dehydration [24–28]. However, for the sulfonic acid functionalized silica-catalyzed biomass conversion, bulky reactants and products lead to the process serious mass-transport limitation problems and thereby insufficient accessibility of the catalytic sites, which significantly limits their catalytic activity. Meanwhile, the catalysts often suffer from severe deactivation due to accumulation of organic or carbonaceous materials on the surface; additionally, leaching of sulfonic acid groups into the reaction media may also reduce the catalytic activity after several times' cycles.

To solve the above problems, in this work, a series of arenesulfonic or propylsulfonic acid functionalized ethane- or benzene-bridged organosilica nanotubes were demonstrated for the first time by a single step nonionic surfactant-templated sol–gel co-condensation approach, and the procedure includes co-hydrolysis and -condensation of bisilylated organic precursor (e.g. 1,2-bis-(trimethoxysilyl)ethane or 1,4-bis-(triethoxysilyl)benzene) and CSPTMS (MPTMS) in the presence of P123 under acidic conditions. Motivation for development of this kind of organosulfonic acid functionalized silica/carbon nanotubes hybrid catalysts is to improve the acid catalytic activity of organosulfonic acid-based materials in esterification and transesterification further. It is generally accepted that the catalytic activity is closely related to the morphological and textural properties of the catalyst in addition to its structure and composition [29]. One-dimensional tubular catalysts possess large fraction of voids in the interior, allowing most of the active sites being confined inside the tubes except for external surface. Moreover, the nanotubular catalysts generally possess hierarchical pore systems, originating from hollow nanotube channels and void space between tubular nanoparticles. This property leads to the active sites are highly accessible to most common reagents and favorable to efficient reactant diffusion during the catalytic reactions. Meanwhile, they have large surface areas with flexible structure that are contributed from both outer and interior surface, which can provide more active sites to promote the reactions. Successful construction of inorganic nanotube catalysts (e.g.  $\text{TiO}_2$  nanotube photocatalyst [30]) or functional group modified inorganic nanotubes (e.g. salen-metal complex functionalized carbon nanotube [31]) have emerged recently, however, preparation of organosilica nanotubes or functional groups modified organosilica nanotubes with bridging alkyl groups and/or active sites within the framework have seldom been reported up till now. By the combination of the advantages such as strong Brønsted acidity, high mechanical and hydrothermal stability, tunable surface hydrophobicity/hydrophilicity, excellent textural properties and interesting morphological characteristics, as-designed organosulfonic acid functionalized alkyl-bridged organosilica nanotubes are expected as the promising solid acid catalyst candidates for biodiesel production [32–35]. Additionally, because organosulfonic groups were incorporated into the organosilica wall (Schemes 1 and 2), agglomeration or leaching of the functional groups is expected to be avoided, leading to the increased catalytic stability of these kinds of the catalysts beside the activity [20].

To evaluate the heterogeneous acid catalytic performance of as-prepared organosulfonic acid functionalized alkyl-bridged organosilica nanotubes, esterification of palmitic acid (one of typical FFAs existed in inedible oily feedstocks) and transesterification of yellow horn (or *Xanthoceras sorbifolia* Bunge, a kind of inedible plant) seed oil with methanol under refluxing temperature ( $65^\circ\text{C}$ ) and atmospheric pressure are selected as the model reactions. The tested hybrid catalysts include arenesulfonic acid functionalized ethane-bridged organosilica nanotubes ( $\text{Si}(\text{Et})\text{Si}-\text{Ar}-\text{SO}_3\text{H}$  NTs), arenesulfonic acid functionalized benzene-bridged organosilica nanotubes ( $\text{Si}(\text{Ph})\text{Si}-\text{Ar}-\text{SO}_3\text{H}$  NTs) and propylsulfonic acid functionalized ethane-bridged organosilica nanotubes ( $\text{Si}(\text{Et})\text{Si}-\text{Pr}-\text{SO}_3\text{H}$  NTs). For comparison, the prepared arenesulfonic acid functionalized SBA-15 inorganic silica with two-dimensional hexagonal  $p6mm$  mesostructure ( $\text{SBA}-15-\text{Ar}-\text{SO}_3\text{H}$ ), three-dimensional worm-like arenesulfonic acid functionalized benzene-bridged organosilica obtained in the absence of P123 (P123 free  $\text{Si}(\text{Ph})\text{Si}-\text{Ar}-\text{SO}_3\text{H}$ ) and commercially available sulfonic ion-exchange resin (Amberlyst-15) are also tested under the same conditions. Based on the catalytic testing results, the influence of Brønsted acid strength and acid-site density, morphological and textural properties as well as surface hydrophobicity on the acid catalytic activity of as-prepared organosulfonic acid based hybrid catalysts is discussed. Finally, the recyclability of the hybrid catalysts is tested through three consecutive catalytic runs.

## 2. Experimental

### 2.1. Materials

Tetraethylorthosilicate (TEOS, 98%), 3-mercaptopropyltriethoxysilane (MPTMS, 95%), 1,2-bis(trimethoxysilyl)ethane (BTMSE, 97%), 1,4-bis-(triethoxysilyl)benzene (BTESB, 96%) and Pluronic P123 ( $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ , where  $\text{EO} = -\text{CH}_2\text{CH}_2\text{O}-$ ,  $\text{PO} = -\text{CH}_2(\text{CH}_3)\text{CHO}-$ ,  $M_w = 5800$ ) were purchased from Sigma-Aldrich and used without further purification. 2-(4-chlorosulfonylphenyl)ethyl trimethoxysilane (CSPTMS, 50% in dichloromethane) was obtained from Gelest Inc. Commercially available Amberlyst-15 (Alfa Aesar) was used as a reference catalyst. Palmitic acid (99%) was obtained from Tianjin Guangfu fine chemical research institute (China). Yellow horn seed oil is commercially available. All other chemicals were analytical grade, and they were purchased from Beijing Fine Chemical Co. (China).

### 2.2. Preparation of organosulfonic acid functionalized alkyl-bridged organosilica nanotubes

#### 2.2.1. Arenesulfonic acid functionalized ethane-bridged organosilica nanotubes ( $\text{Si}(\text{Et})\text{Si}-\text{Ar}-\text{SO}_3\text{H}$ NTs)

Direct co-hydrolysis followed by co-condensation of BTMSE and CSPTMS in the presence of P123 was applied to prepare  $\text{Si}(\text{Et})\text{Si}-\text{Ar}-\text{SO}_3\text{H}$  NTs. Typically, P123 (4 g) was dissolved in HCl ( $1.9\text{ mol L}^{-1}$ , 125 g) at room temperature under stirring. The clear P123 solution was heated to  $40^\circ\text{C}$ , and then BTMSE was added. A BTMSE prehydrolysis time of 45 min was used prior to the addition of CSPTMS to the above mixture. The resultant white suspension with molar composition of (0.0195 – 0.0164) BTMSE: (0.0021 – 0.0082) CSPTMS: 0.24 HCl: 6.67  $\text{H}_2\text{O}$  was stirred at  $40^\circ\text{C}$  for 24 h. Subsequently, the suspension was transferred to an autoclave and heated at  $100^\circ\text{C}$  with a heating rate of  $2^\circ\text{C min}^{-1}$  for additional 24 h. The solid product was recovered by filtration and air-dried at  $60^\circ\text{C}$  overnight. Finally, boiling ethanol washing for 12 h was applied to remove P123 from the product, and the procedure was repeated for three times. The product obtained after air-dried at  $60^\circ\text{C}$  for 24 h is

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