



Arenesulfonic acid-functionalized alkyl-bridged organosilica hollow nanospheres for selective esterification of glycerol with lauric acid to glycerol mono- and dilaurate



Sai An^b, Yingnan Sun^a, Daiyu Song^a, Qingqing Zhang^a, Yihang Guo^{a,*}, Qingkun Shang^{b,*}

^a School of Environment, Northeast Normal University, Changchun 130117, People's Republic of China

^b School of Chemistry, Northeast Normal University, Changchun 130024, People's Republic of China

ARTICLE INFO

Article history:

Received 10 May 2016

Revised 5 July 2016

Accepted 6 July 2016

Keywords:

Organosilica

Solid acids

Hollow nanospheres

Glycerol

Glycerol laurate ester

ABSTRACT

A series of arenesulfonic acid-functionalized alkyl-bridged organosilica hollow nanospheres, Si(R)Si-ArSO₃H-HNS, with different bridging alkyl groups such as ethyl, phenyl, or biphenyl in the silica/carbon framework were successfully fabricated by a P123-directed sol-gel co-condensation route and carefully adjusted the concentration of micelle-expanding agent and the acidity in the starting preparation system. The Si(R)Si-ArSO₃H-HNS were applied in the synthesis of glycerol mono- and dilaurate from the esterification of glycerol with lauric acid, and the influence of glycerol-to-lauric acid molar ratio, structure of the bridging alkyl groups, and morphology of the nanohybrids on the catalytic activity were studied. The esterification activity of the Si(R)Si-ArSO₃H-HNS outperformed commercial solid acid such as Amberlyst-15 or H-ZSM-5, regardless of the structure of the bridging alkyl groups; additionally, the biphenyl-bridged Si(Ph-Ph)Si-ArSO₃H-HNS exhibited the highest esterification activity among various Si(R)Si-ArSO₃H-HNS nanohybrids, attributing to the combination of advantages of strong Brønsted acidity, excellent porosity properties, hydrophobic surface, and unique hollow spherical nanostructure. Afterward, selective formation of glycerol mono- and dilaurate and possible esterification mechanism were studied. Finally, the reusability was studied and showed the Si(R)Si-ArSO₃H-HNS can be reused three times without significant activity loss as well as structural and morphological changes.

© 2016 Elsevier Inc. All rights reserved.

1. Introduction

The worldwide development of advanced technologies for producing chemicals and green energy from renewable biomass prompting to moderate dependence on fossil fuels has been quick [1–3]. Among these, catalytic transesterification of natural oil with methanol or ethanol to produce biodiesel has attracted scientific and industrial interest. Accordingly, the flooding of byproduct glycerol stemming from commercialized biodiesel production into an already saturated market has adversely affected its market value in recent years, and therefore efforts are devoted to convert the surplus of glycerol into valuable chemicals that improve the economics of the whole biodiesel production process [4–7]. Glycerol is a functionalized molecule with three hydroxyl groups, and it can undergo oxidation [8], hydrogenolysis [9–11], carbonylation [12,13], esterification [14–17], and etherification [18,19] to yield value-added commodity chemicals. One interesting option is the

acid-catalyzed esterification of bioglycerol with short or long fatty acids into valuable glycerol esters, which have found extensive applications in cosmetics, the food industry, and pharmaceuticals, as well as fuel additives [20,21]. H₂SO₄, HCl, and *p*-toluenesulfonic acid can effectively catalyze glycerol esterification; nevertheless, the processes suffer from severe corrosion, waste, and safety problems. For the development of environmentally benign glycerol esterification processes, heterogeneous acid catalysts such as zeolite, niobic acid, Starbon acid, sulfated activated carbon, ion exchange resins, sulfonic acid-functionalized silica or organosilica, and zirconia-based solid acids have been applied [22–29].

Aiming at the development of novel solid acids for efficient and selective esterification of glycerol with long fatty acids to the desired products under mild reaction conditions, in the present work, arenesulfonic acid-functionalized ethyl/phenyl/biphenyl-bridged organosilica hollow nanospheres, Si(R)Si-ArSO₃H-HNS (R = -Et-, -Ph- or -Ph-Ph-), were successfully fabricated by a P123-templated sol-gel co-condensation strategy. Generally, the reactivity of esterification of glycerol with various fatty acids decreases gradually with increasing chain length of fatty acids

* Corresponding authors. Fax: +86 431 89165626.

E-mail address: guoyh@nenu.edu.cn (Y. Guo).

owing to the steric hindrance effect of the longer alkyl chains of the fatty acids or glycerol esters, and therefore the esterification of glycerol with long fatty acids is more difficult and seldom studied. Additionally, the acid catalyst design should consider the hydrophobicity of long fatty acids, which is different from the hydrophilic short fatty acids. Organosulfonic acid-functionalized organosilica hybrid nanocatalysts with organic-bridging groups abundantly and homogeneously distributed in the framework acquire interesting properties including strong Brønsted acidity, unique textural properties, and tunable surface hydrophilic/hydrophobic balance. Moreover, morphologies of these RSO_3H -functionalized organosilica (e.g., nanopores, nanotubes, hollow nanospheres, or yolk-shell nanostructures) can be well controlled by various nanoengineering techniques. The unique textural and morphological properties in turn can drastically influence the diffusion rate of the reactants/products as well as the accessibility of the active sites [30–35]. For this purpose, hollow spherical RSO_3H -functionalized organosilicas with interesting advantages including hollow interiors, permeable and thin shells, nanometer size, shortened diffusion distance, low density, and well-defined textural properties were designed herein, which can increase the accessibility to sulfonic acid groups and facilitate diffusion and mass transfer of the substrates and products [36]. On the other hand, for the esterification of glycerol with lauric acid, the $\text{Si}(\text{R})\text{Si-ArSO}_3\text{H-HNS}$ hybrid nanocatalysts with hydrophobic alkyl groups in the silica/carbon framework are generally preferred to enhance the adsorption of hydrophobic lauric acid and inhibit the hydrolysis of the yielded glycerol esters by byproduct water. The dual effect, including unique morphology and surface hydrophobicity, is expected to enhance the catalytic activity of the $\text{Si}(\text{R})\text{Si-ArSO}_3\text{H-HNS}$ nanohybrids further with respect to their periodic mesoporous or tubular counterparts in glycerol esterification with lauric acid.

Esterification of glycerol with lauric acid catalyzed by the $\text{Si}(\text{R})\text{Si-ArSO}_3\text{H-HNS}$ nanohybrids was performed at 140 °C and atmospheric pressure (Scheme S1 of the Electronic Supplementary Information, ESI), and the influence of glycerol-to-lauric acid molar ratio, structure of bridging alkyl groups, and morphology of the hybrid nanocatalysts on the glycerol mono- or dilaurate yield and selectivity was evaluated. Subsequently, the esterification activity was further compared with that of periodic mesoporous or tubular counterparts as well as commercially available Amberlyst-15 and H-ZSM-5. Finally, the reusability of the hybrid nanocatalysts was tested.

2. Experimental

2.1. Materials

1,2-Bis(trimethoxysilyl)ethane (BTMSE, 97%), 1,4-bis-(triethoxysilyl)benzene (BTESB, 96%), 4,4'-bis(trimethoxysilyl)-1,1'-biphenyl (BTESBP, 95%), Pluronic P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, where $\text{EO} = \text{CH}_2\text{CH}_2\text{O}$ and $\text{PO} = \text{CH}_2(\text{CH}_2)\text{CHO}$), and Pluronic F127 ($\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$) were purchased from Sigma-Aldrich. 2-(4-Chlorosulfonylphenyl)ethyl trimethoxysilane (CSPTMS, 50% in dichloromethane) was purchased from Gelest Inc. 1,3,5-Trimethylbenzene (TMB), lauric acid and glycerol were purchased from Tianjin Guangfu Fine Chemical Research Institute (China).

2.2. Catalyst preparation

2.2.1. $\text{Si}(\text{Ph-Ph})\text{Si-ArSO}_3\text{H-HNSx}$

Typically, P123 (0.5 g) was dissolved in a mixture of water (12.7 mL), HCl (12 mol L^{-1} , 2.35 mL), and TMB (1.96 mL) under stirring at room temperature for 1 h. Subsequently, BTESBP

(1.14 mL) and CSPTMS (0.22 mL) were added successively to the above clear acidic P123/TMB solution at an interval of 45 min. The molar composition of the starting materials in the synthetic gel was $\text{P123}:\text{water}:\text{HCl}:\text{TMB}:\text{BTESBP}:\text{CSPTMS} = 0.86:7056:282:136:23.7:5.1$. The resulting suspension was stirred at 40 °C for 24 h and then aged at 100 °C for an additional 24 h. Subsequently, the product was air-dried at 60, 80, and 100 °C for 12, 12, and 2 h, successively. To remove the surfactant P123, as-prepared materials (0.3 g) were dispersed in 50 mL of ethanol solution in a three-necked round-bottomed glass flask, and the resulting mixture was refluxed at 78 °C for 12 h under constant stirring. The procedure was repeated three times. The surfactant-free product $\text{Si}(\text{Ph-Ph})\text{Si-ArSO}_3\text{H-HNSx}$ (x represents the loading of the $-\text{SO}_3\text{H}$ group in the product) was air-dried at 100 °C overnight.

2.2.2. $\text{Si}(\text{Ph})\text{Si-ArSO}_3\text{H-HNSx}$

The preparation process was the same as that described above, but with replacement of BTESBP with BTESB (0.98 mL) as well as the addition of less TMB (0.90 mL), and the initial molar composition in the synthetic gel was $\text{P123}:\text{water}:\text{HCl}:\text{TMB}:\text{BTESB}:\text{CSPTMS} = 0.86:7056:282:62.5:23.7:5.1$.

2.2.3. $\text{Si}(\text{Et})\text{Si-ArSO}_3\text{H-HNSx}$

The preparation process was the same as for $\text{Si}(\text{Ph-Ph})\text{Si-ArSO}_3\text{H-HNS}$ but with replacement of BTESBP with BTMSE (0.61 mL) as well as the addition of less TMB (1.30 mL), and the initial molar composition in the synthetic gel was $\text{P123}:\text{water}:\text{HCl}:\text{TMB}:\text{BTMSE}:\text{CSPTMS} = 0.86:7056:282:90:23.7:5.1$.

2.2.4. $\text{Si}(\text{Ph})\text{Si-ArSO}_3\text{H-NTx}$

The preparation process was the same as for $\text{Si}(\text{Ph})\text{Si-ArSO}_3\text{H-HNS}$ but without adding TMB in the preparation system, and the initial molar composition in the synthetic gel was $\text{P123}:\text{water}:\text{HCl}:\text{BTESB}:\text{CSPTMS} = 0.86:7056:282:23.7:5.1$.

2.2.5. $\text{Si}(\text{Ph})\text{Si-ArSO}_3\text{H-NT\&HNSx}$

The preparation process was the same as for $\text{Si}(\text{Ph})\text{Si-ArSO}_3\text{H-HNS}$ but with less addition of TMB (0.66 mL), and the initial molar composition in the synthetic gel was $\text{P123}:\text{water}:\text{HCl}:\text{TMB}:\text{BTESB}:\text{CSPTMS} = 0.86:7056:282:45.8:23.7:5.1$.

With further decrease in the addition of TMB (0.40 mL) and an initial molar composition of $\text{P123}:\text{water}:\text{HCl}:\text{TMB}:\text{BTESB}:\text{CSPTMS} = 0.86:7056:282:27.8:23.7:5.1$, the obtained hybrid catalyst was denoted as $\text{Si}(\text{Ph})\text{Si-ArSO}_3\text{H-NT\&HNS}(1)x$.

2.2.6. $\text{Si}(\text{Ph})\text{Si-ArSO}_3\text{H-PMOx}$

P123 (0.5 g) was dissolved in a mixture of water (12.7 mL) and HCl (12 mol L^{-1} , 0.30 mL) under stirring at room temperature for 1 h. Subsequently, BTESB (0.98 mL) and CSPTMS (0.22 mL) were added dropwise successively to the above clear acidic P123 solution at an interval of 45 min at 40 °C. The molar composition of the starting materials in the synthetic gel was $\text{P123}:\text{water}:\text{HCl}:\text{BTESB}:\text{CSPTMS} = 0.86:7056:36:23.7:5.1$. The resulting suspension was stirred at 40 °C for 24 h, and then it was transferred to an autoclave, followed by heating at 100 °C with a heating rate of 2 °C min^{-1} for an additional 24 h. Subsequently, the white product obtained was recovered by filtration and then air-dried at 60 °C overnight. Removal of P123 followed the same procedure as described in Section 2.2.1, and P123-free product was air-dried at 100 °C overnight.

2.2.7. $\text{F127 Si}(\text{Et})\text{Si-ArSO}_3\text{H-HNSx}$

The preparation process was that followed by our previous work [37]. Typically, F127 (0.35 g) was dissolved in a mixture of water (25.7 mL) and HCl (12 mol L^{-1} , 4.3 mL). After the solution was stirred at 40 °C for 1 h, TMB (0.42 mL) was added dropwise, followed

Download English Version:

<https://daneshyari.com/en/article/4757594>

Download Persian Version:

<https://daneshyari.com/article/4757594>

[Daneshyari.com](https://daneshyari.com)