

Fabrication of sulphonated hollow porous nanospheres and their remarkably improved catalytic performance for biodiesel synthesis

Tianqi Wang, Yang Xu, Zidong He, Minghong Zhou, Wei Yu, Buyin Shi, Chunmei Song*, Kun Huang*

School of Chemistry and Molecular Engineering, East China Normal University, 500 N, Dongchuan Road, Shanghai 200241, PR China

ARTICLE INFO

Keywords:

Sulphonated hollow microporous organic nanospheres
Hyper-cross-linking
Post-modification
Biodiesel products
Esterification

ABSTRACT

Biodiesel as a kind of green energy has been considered as a popular alternative to fossil-based petroleum. Herein, sulphonated hollow microporous organic nanospheres (HMONs-SO₃H) were synthesized based on the marriage between hyper-cross-linking mediated self-assembly strategy with polylactide-*b*-polystyrene (PLA-*b*-PS) diblock copolymers as precursors and post-modification with chlorosulfonic acid. The results demonstrated that the sulfonic groups could be introduced into hollow microporous organic nanospheres (HMONs) without any damage to the hollow nanostructure and porosity. The prepared HMONs-SO₃H were used to synthesize biodiesel products through catalyzing esterification of long-chain free fatty acid with methanol. Compared with sulfonated nonhollow microporous polymers (Non-HMPs-SO₃H), HMONs-SO₃H exhibit higher catalytic activity and rate because the hollow structure can accelerate diffusion of the molecules even though long-chain free fatty acid is large in size.

1. Introduction

Along with the high-speed social and economic development, the demand of society for energy is becoming huge. Fossil-based petroleum, as essential blood of society, is the most common source to meet the increased energy demand. However, the extensive use of petroleum not only resulted in destined resource exhaustion caused by the non-renewability of petroleum but also faced large amount of environmental and air pollution including ocean acidification, ecological damage and global warming [1]. In this regard, biodiesel has attracted more attention and been considered as greener and popular alternative to fossil-based petroleum as its abundance, sustainability, biodegradability, sulfur-free and non-toxic property [2–5]. In particular, this kind of biodiesel can be synthesized from a large number of waste free fatty acid in fat and vegetable oils, that usually be taken as waste product in the meat processing industry and catering industry, based on esterification of fatty acid and aliphatic short-chains alcohols [6,7]. The conventional pathways for converting fatty acid to biodiesel are based on the homogeneous acid or base catalytic reactions. However, the optional use of concentrated homogeneous acid catalysts will always cause a variety of problem including its corrosive nature and tedious purification process which inevitably push up the synthetic cost. On the other hand, although homogeneous base catalysts can promote

transesterification reaction of fatty acid to biodiesel at relatively mild condition compared with acid catalysts, the process still have to be faced with saponification of fatty acid under basic condition, which will be extremely troublesome to the product separation and increase the base catalysts loss.

Thus, from the perspective of economy, heterogeneous acid catalysts, such as sulfated metal oxide [8–11], sulfonated graphitic carbon nitride [12], zeolites [13], functionalized porous carbons [14–19], metal-organic frameworks (MOFs) [20] based solid acid catalysts as well as sulfonic acid functionalized hybrid silica [21–24], have attracted more attention and been explored to catalyze esterification of fatty acid to biodiesel due to their environment friendly, reusability and easy separation vis-à-vis homogeneous catalysts [25–27]. In recent years, porous organic polymers (POPs) [28–32] have been considered as a kind of alternative matrix to support acid catalysts for biodiesel production owing to their high surface areas, tunable pore structures, high chemical and thermal stability as well as easy modification, that the above mentioned substrates lack. For example, Asim [28] and coworkers had reported that a series of POPs bearing with sulfonic acid groups had been synthesized to catalyze esterification/transesterification of long chain fatty acids/esters to form biodiesels. Indeed, most efforts were focused on the design and preparation methodology of POPs based matrix or various modification of acid catalysts groups into

* Corresponding authors.

E-mail addresses: cmsong@chem.ecnu.edu.cn (C. Song), khuang@chem.ecnu.edu.cn (K. Huang).

<https://doi.org/10.1016/j.reactfunctpolym.2018.09.014>

Received 23 August 2018; Received in revised form 17 September 2018; Accepted 17 September 2018

Available online 21 September 2018

1381-5148/ © 2018 Published by Elsevier B.V.

POPs, whereas the discussion about the nano-morphology of POPs based acid catalysts for esterification of fatty acid to biodiesel remained rare. As proved by Son [33] and coworkers, hollow microporous organic networks display better catalytic performance compared to non-hollow ones benefitted from the diffusion pathway effect. Therefore, it is greatly expected that POPs based acid catalysts with various nanostructures would exhibit better catalytic performance for synthesis of biodiesel.

Herein, we prepared a novel sulfonated hollow microporous organic nanospheres by hyper-cross-linking poly(lactide-*b*-polystyrene (PLA-*b*-PS) diblock copolymers and then introducing sulfo groups into the network, in which the functionalization and hierarchically porous structures of HMONS give them significant potential for creating tailored environments for catalysis. For example, the inner cavity in nanospheres can facilitate the accessibility of the active sites and the diffusion of the molecules to improve the catalytic efficiency. As the active sites, the sulfo groups were successfully anchored onto the aromatic skeleton shell by a post-modified strategy. The excellent catalysis efficiency and reusability of the sulfonated hollow microporous organic nanospheres were discussed in the synthesis of biodiesel.

2. Experimental

2.1. Materials

All reagents were used as received unless stated otherwise. Dichloromethane (DCM) were dried using CaH₂ and distilled. Styrene (Aldrich 99%) was purified by passing over basic alumina. 2, 2-Azoisobutyronitrile (AIBN) and D,L-lactide were purified by recrystallization from methanol and ethyl acetate, respectively. S-1-Dodecyl-S'-(α,α' -dimethyl- α' -acetic acid) trithiocarbonate (TC) were synthesized according to literature procedures [34].

2.2. Characterizations

All ¹H NMR spectra were recorded on a Bruker AVANCE III™ 500 spectrometer (500 MHz) by using CDCl₃ as a solvent. GPC data were obtained from Waters GPC system equipped with a Waters 1515 isocratic HPLC pump, a 2414 refractive index (RI) detector, and two Waters' HPLC columns. Tetrahydrofuran was used as the solvent for polymers and eluent for GPC with a flow rate of 1 mL min⁻¹ at 30 °C. The GPC instrument was calibrated with narrowly dispersed linear polystyrene standards. Transmission electron microscopy (TEM) images were obtained using a JEM-2100F TEM instrument. Samples were prepared by dip-coating a 400 mesh carbon-coated copper grid from the dilute sample solution allowing the solvent to evaporate. The infrared (IR) spectra were recorded using Thermo NICOLET is50. GC/MS analyzed were obtained on an Agilent 6890 Series GC System with a Hewlett-Packard 5973 Mass Selective Detector (70 eV) using a HP-5MS fused silica capillary column (cross-linked 5% phenyl ethyl siloxane, 30 m × 0.25 mm ID × 0.25 μm film thickness) and argon as a carrier gas (1 mL min⁻¹). The split ratio was 1:50. The injector temperature was kept at 270 °C and detector was kept at 280 °C. The column temperature was held at 60 °C for 3 min, increased to 280 °C at a rate of 25 °C min⁻¹, and then kept at 280 °C for 5 min. A Quantachrome Autosorb IQ surface area and porosity analyzer was utilized to study the pore structure of the samples. Before measurements, the polymer samples were degassed for > 10 h at 120 °C. The Brunauer-Emmett-Teller (BET) surface area and the micropore surface area were determined by the BET equation and the t-plot equation, respectively. The pore size distribution was analyzed the nonlocal density functional theory (NLDFT) model. Elemental analyses were determined by an elemental Vario EL III and the sample was dried in vacuo at ambient temperature.

2.3. Preparation of PLA-*b*-PS diblock copolymers and HMONS

PLA₆₀-*b*-PS₆₀ diblock copolymers and HMONS were synthesized according to our previous report [35].

2.4. Sulfonation of HMONS

HMONS (160 mg) was charged to anhydrous dichloromethane (30 mL) and the mixture was stirred for 30 min at 0 °C. Chlorosulfonic acid (3 mL) was added dropwise to this mixture slowly and then the mixture stirred continuously for 16 h under N₂ atm. Then the blackish powder was filtered and washed by plenty of distilled water and methanol repeatedly. Then it was dried in vacuum at 80 °C for 24 h. Yield = 176 mg.

2.5. Preparation of polystyrene (PS)

St (6.4 mL, 56 mmol), AIBN (2.25 mg, 0.014 mmol), and TC (50 mg, 0.14 mmol) were mixed in a reaction vessel and degassed by 3 freeze-pump-thaw cycles. The polymerization was then conducted at 70 °C for 5 h. The polymer was precipitated from DCM into methanol 3 times and dried under vacuum for 24 h. Yield = 1.3 g (22%). GPC: Mn = 9.1 kg/mol, Mw/Mn = 1.10; ¹H NMR: n(St) = 87.

2.6. Preparation of Non-HMPs and Non-HMPs-SO₃H

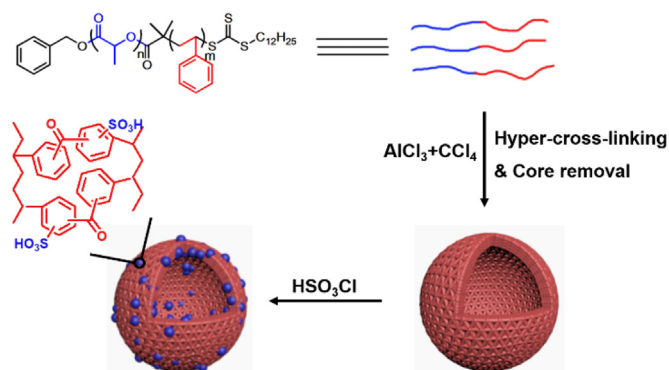
The synthesis procedures of Non-HMPs and Non-HMPs-SO₃H are similar to that of HMONS and HMONS-SO₃H except using PS polymer to replace PLA-*b*-PS diblock copolymer.

2.7. Catalysis test

Catalysis experiments were conducted in sealed vials in an oil bath. Yield was determined using gas chromatography (GC). In a typical catalytic process, a mixture of fatty acid (0.5 mmol), methanol (2 mL, which could act both as a solvent and reactant) were added to a sealed vial. The HMONS-SO₃H (5 mg) was added into the reactor, and then the reaction was stirred at 65 °C for 2.5 h. The catalysts were separated by centrifugation and washed by methanol, and then dried in vacuum for the following catalysis.

3. Results and discussion

HMONS-SO₃H supports were prepared through a postsynthetic modification strategy as illustrated in Scheme 1. First, the HMONS were synthesized by hyper-cross-linking mediated self-assembly strategy based on poly(lactide-*b*-polystyrene (PLA-*b*-PS) diblock copolymers according to our previous work [35]. Typically, the preparation of well-defined PLA-*b*-PS diblock copolymer precursors were synthesized by a



Scheme 1. Fabrication of sulfonic acid-functionalized hollow microporous organic nanospheres (HMONS-SO₃H).

Download English Version:

<https://daneshyari.com/en/article/11027036>

Download Persian Version:

<https://daneshyari.com/article/11027036>

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