



## Full Length Article

# Selective esterification of glycerol with acetic acid or lauric acid over rod-like carbon-based sulfonic acid functionalized ionic liquids



Yingnan Sun<sup>a</sup>, Jianglei Hu<sup>c</sup>, Sai An<sup>b</sup>, Qingqing Zhang<sup>a</sup>, Yihang Guo<sup>a,\*</sup>, Daiyu Song<sup>a,\*</sup>, Qingkun Shang<sup>b,\*</sup>

<sup>a</sup>School of Environment, Northeast Normal University, Changchun 130117, PR China

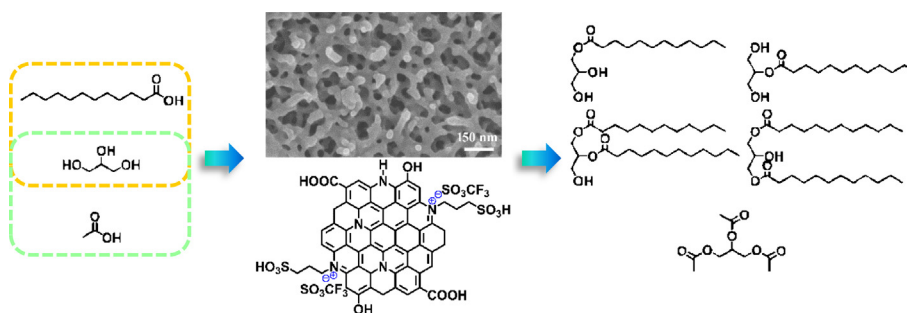
<sup>b</sup>School of Chemistry, Northeast Normal University, Changchun 130024, PR China

<sup>c</sup>School of Chemical Engineering, Changchun University of Technology, Changchun 130012, PR China

## HIGHLIGHTS

- Rod-like carbon-based sulfonic acid functionalized acidic ionic liquids are prepared.
- The materials exhibit high catalytic activity in glycerol esterification reaction.
- High density of super strong Brønsted acid sites plays key role to the activity.
- Surface hydrophilicity and rod-like nanostructure positively influence the activity.
- The materials can be reused 3 times without obvious activity loss.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

## Article history:

Received 24 March 2017

Received in revised form 30 May 2017

Accepted 19 June 2017

## Keywords:

Ionic liquid  
Solid acid  
Nanorod  
Glycerol  
Glycerol ester

## ABSTRACT

A series of rod-like nitrogen-containing carbon-based sulfonic acid functionalized ionic liquids,  $[\text{PrSO}_3\text{HN}][\text{SO}_3\text{CF}_3]/\text{C}$ , with tunable Brønsted acid site densities are fabricated by quaternary ammonization of hydrothermally prepared nitrogen-containing carbon nanorods with 1,3-propanesultone followed by anion exchange with trifluoromethanesulfonic acid. The materials are successfully applied in the selective esterification of glycerol with acetic acid or lauric acid to the value-added glycerol esters including triacetin, glycerol monolaurate and glycerol dilaurate. The excellent esterification activity of the  $[\text{PrSO}_3\text{HN}][\text{SO}_3\text{CF}_3]/\text{C}$  nanorods strongly depends on their Brønsted acid nature; additionally, the morphological characteristics, surface hydrophilicity and flexible polycyclic aromatic carbon structure influence the catalytic activity to some extent. The  $[\text{PrSO}_3\text{HN}][\text{SO}_3\text{CF}_3]/\text{C-2}$  nanorod with high density of super strong Brønsted acid sites and perfect rod-like nanostructure exhibits the highest esterification activity, and its activity outperforms Amberlyst-15, propylsulfonic acid functionalized SBA-15, the  $-\text{[PrSO}_3\text{HN}][\text{SO}_3\text{CF}_3]$  group functionalized carbonaceous framework obtained by high temperature (600 °C) calcination as well as homogeneous *p*-toluenesulfonic acid. Moreover, the catalyst can be reused three times without significant activity loss, attributing to the chemical interactions between the  $-\text{[PrSO}_3\text{HN}][\text{SO}_3\text{CF}_3]$  groups and the carbon framework.

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## 1. Introduction

The conversion of biomass-derived platform compounds to value-added chemicals is a rapidly growing research area to

\* Corresponding authors.

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

alleviate the dependence on fossil fuels [1,3]. Particularly, the use of glycerol as a renewable substrate for the chemical industry has received considerable attention [4,5]. The industrial interest of glycerol is boosted by the growing commercialized biodiesel production, which generates a surplus of byproduct glycerol in the market. The synthesis of valuable glycerol esters by esterification of glycerol with fatty acids is therefore one of the important applications of glycerol. Esterification of glycerol with short fatty acids such as acetic acid can produce the desired chemicals including monoacetain (MAG), diacetain (DAG) and triacetain (TAG) that find applications in cosmetics, food industry, pharmaceuticals and fuel additives [2,6–8]. Furthermore, DAG and TAG have received special interest because of their potential in vast quantity utilization as oxygenate fuel additive for diesel or gasoline [9,10]. As for the esterification of glycerol with long fatty acids such as lauric acid, glycerol monolaurate (MLG) and glycerol dilaurate (DLG) present value-added chemicals, and a complete esterification of glycerol to glycerol trilaurate (TLG) is undesired [11].

From the viewpoint of “Green Chemistry”, a number of environmentally benign solid acids have been applied to catalyze glycerol esterification reactions, and hence the use of harmful liquid acids such as HCl, H<sub>2</sub>SO<sub>4</sub> or *p*-toluenesulfonic acid is avoided [10–16]. Nevertheless, some drawbacks still exist in the aforementioned solid acid-catalyzed glycerol esterification processes. For the esterification of glycerol with acetic acid, the catalysts show low selectivity to the favored TAG despite high glycerol conversion can be obtained [16]. For the esterification of glycerol with lauric acid, the catalysts exhibit relatively low yield of the desired MLG and DLG. Therefore, it is still a challenge to develop efficient, robust and recyclable solid acid catalysts for selective esterification of glycerol to valuable glycerol esters.

More recently, sulfonic acid functionalized acidic ionic liquids (ILs) have received much attention in many acid-catalyzed reactions [17]. For example, homogeneous double SO<sub>3</sub>H-functionalized ILs-catalyzed esterification of glycerol with acetic acid exhibited high glycerol conversion and high selectivity to MAG or DAG. However, ILs were entirely miscible with the reaction mixture, resulting in problems of separation and recycle [18]. Therefore, attempts were made to solve these problems by immobilization of acidic ILs on suitable supports such as porous materials and polystyrene-based polymers [19,20].

In the present work, a series of novel carbon-based heterogeneous IL catalysts, [PrSO<sub>3</sub>HN][SO<sub>3</sub>CF<sub>3</sub>]/C, are developed. Carbonaceous materials, composed of numerous of polycyclic aromatic carbon sheets and prepared by incomplete carbonization of natural organic substance or biomass-derived materials, have been strongly advocated as the promising catalyst supports for chemical biomass transformation reactions due to their relative chemical inertness, cheapness and availability. Functionalization of carbonaceous materials with homogeneous Brønsted acids to give rise to carbonaceous solid acids is appealing in green and sustainable chemistry [21–27]. Moreover, owing to possessing flexibility of polycyclic aromatic carbon framework with more hydrophilic groups, carbonaceous solid acids derived from functionalization of carbon support obtained at relatively low temperatures (lower than 500 °C) have been proved highly active in various liquid-phase reactions despite of their small surface area (smaller than 5 m<sup>2</sup> g<sup>-1</sup>) [21,23,28]. In the present work, nitrogen-containing carbon nanorods, derived from hydrothermal treatment of the mixture of glucose and cyanamide at lower temperature (160 °C), is prepared as the support, and sulfonic acid functionalized ILs are introduced into the support via quaternary ammonization and anion exchange reaction. As-prepared [PrSO<sub>3</sub>HN][SO<sub>3</sub>CF<sub>3</sub>]/C nanorods are applied in the selective esterification of glycerol with acetic acid to TAG (Scheme S1a of the electronic Supplementary information, ESI) and lauric acid to MLG and DLG (Scheme S1b of ESI). By

the combination of the advantages such as high density of super strong Brønsted acid sites, hydrophilic surface and perfect rod-like nanostructure, the [PrSO<sub>3</sub>HN][SO<sub>3</sub>CF<sub>3</sub>]/C exhibits excellent catalytic activity in both target reactions. Importantly, the —[PrSO<sub>3</sub>HN][SO<sub>3</sub>CF<sub>3</sub>] group covalently bond to the carbonaceous framework, ensuring the [PrSO<sub>3</sub>HN][SO<sub>3</sub>CF<sub>3</sub>]/C nanorods excellent catalytic stability.

## 2. Experimental

### 2.1. Catalytic preparation

At first, nitrogen-containing carbon nanorods were prepared. Typically, glucose (6 g) and cyanamide (0.5, 1.5, 3.0 or 6.0 mL to adjust nitrogen element content in the support) were dispersed into water (30 mL) under stirring at room temperature, and the resulting mixture was transferred to an autoclave and heated to 160 °C with a heating rate of 2 °C min<sup>-1</sup>. After maintaining at this temperature for 3 h, the brown product was cooled to room temperature, collected by centrifugation, washed with water and ethanol for three times. The final product was obtained after air-drying at 80 °C for 12 h.

Afterwards, the [PrSO<sub>3</sub>HN][SO<sub>3</sub>CF<sub>3</sub>]/C nanorods were prepared. Typically, the above nitrogen-containing carbon nanorods (1.2 g) were dispersed into a mixture of 1,3-propanesultone (0.4 g) and toluene (20 mL) under vigorous stirring at room temperature, followed by continuous stirring at toluene refluxing temperature (110 °C) for 24 h. The reaction mixture was cooled down to room temperature, and the product was separated by centrifugation. Subsequently, the product was treated with toluene solution (25 mL) containing HSO<sub>3</sub>CF<sub>3</sub> (3 mL) under vigorous stirring at room temperature for 24 h. The final product was obtained after following treatment: centrifugation, washing two times with CH<sub>2</sub>Cl<sub>2</sub> and then drying at 60 °C for 12 h. The product is denoted as [PrSO<sub>3</sub>HN][SO<sub>3</sub>CF<sub>3</sub>]/C – **x**, and **x** = **1**, **2**, **3** and **4**, respectively, referring to the products with different nitrogen element contents (Table 1).

For comparison, the [PrSO<sub>3</sub>HN][SO<sub>3</sub>CF<sub>3</sub>]/C(1) material was prepared by further calcination of the hydrothermally prepared nitrogen-containing carbon support at 600 °C under argon gas flow followed by quaternary ammonization with 1,3-propanesultone and anion exchange with HSO<sub>3</sub>CF<sub>3</sub>.

### 2.2. Catalyst characterization

Nitrogen element contents were determined by a EuroVector CHNS EA3000 elemental analyzer. FESEM observations were performed on a XL-30 ESEM-FEG field emission scanning electron microscope. TEM observations were performed on a JEM-2100F high resolution transmission electron microscope at an accelerating voltage of 200 kV. Nitrogen gas porosimetry measurements were performed on a Micromeritics ASAP 2020M surface area and porosity analyzer after the samples were outgassed under vacuum at 363 K for 1 h and 373 K for 4 h. XRD patterns were obtained on a D/max-2200 VPC diffractometer. Raman scattering spectra were recorded on a Jobin-Yvon HR 800 instrument with an Ar<sup>+</sup> laser source at 488 nm in a macroscopic configuration. FT-IR spectra were recorded on a Nicolet Magna 560 IR spectrophotometer. XPS was performed on an Axis Ultra DLD instrument with a monochromated Al-K $\alpha$  source at a residual gas pressure below 10<sup>-8</sup> Pa. The Brønsted acid strength and acid site density were measured by a WDDY-2008 automatic potentiometric titration system based on the literature method [29–31]. The sample (0.050 g) was dispersed in acetonitrile and stirred for 12 h, and the resulting suspension was titrated with a solution of *n*-butylamine in acetonitrile (100 mmol L<sup>-1</sup>).

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