

Catalytic performance of acidic ionic liquid-functionalized silica in biodiesel production

Bin Zhen^{a,b}, Qingze Jiao^a, Qin Wu^a, Hansheng Li^{a*}

a. School of Chemical Engineering and the Environment, Beijing Institute of Technology, Beijing 100081, China;

b. Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

[Manuscript received August 20, 2013; revised December 25, 2013]

Abstract

Acidic ionic liquid ([BsAIm][OTf]) was immobilized on sulfhydryl-group-modified SiO₂ (MPS-SiO₂) via free radical addition reaction. The [BsAIm][OTf] loading on acidic ionic liquid-functionalized silica ([BsAIm][OTf]/SiO₂) was controlled through tuning the sulfhydryl (SH) content of MPS-SiO₂. All the samples were characterized by FT-IR, elemental analysis, N₂ adsorption-desorption measurements and TG-DTA. The catalytic performance of [BsAIm][OTf]/SiO₂ in the esterification of oleic acid and the transesterification of glycerol trioleate for biodiesel production was investigated. The results showed that with the increase of [BsAIm][OTf] loading on SiO₂ the specific surface area and pore volume of [BsAIm][OTf]/SiO₂ decreased, and the pore diameter of [BsAIm][OTf]/SiO₂ narrowed. In the esterification of oleic acid, the oleic acid conversion increased with the increasing [BsAIm][OTf] loading. In the transesterification of glycerol trioleate, with the increasing [BsAIm][OTf] loading the glycerol trioleate conversion decreased and the selectivities to glycerol monooleate and methyl oleate increased.

Key words

supported ionic liquid catalysts; esterification; transesterification; biodiesel

1. Introduction

As an eco-friendly alternative biofuel, biodiesel is now extensively researched worldwide due to its high flash point, easy reserve, bio-degradability, high cetane number and applicability of general diesel engine [1,2]. Biodiesel is mainly obtained through the catalytic esterification and transesterification of free fatty acids, vegetable oil and animal fats. Alkaline catalysts, either NaOH or KOH always have high catalytic activity to the transesterification reaction of lipids, which are widely used for producing biodiesel by the majority of industries in the world [3,4]. However, when the amount of free fatty acid in raw oils is higher than 2% w/w, a pre-treatment via esterification with alcohol is needed in order to prevent the saponification of alkaline catalysts [5,6]. Traditionally homogeneous acidic catalysts such as H₂SO₄, HF and HNO₃ show high catalytic activity in both esterification and transesterification and they are often used as catalysts when raw oils contain a large amount of water or free fatty acids [7]. Corrosiveness, environmental pollution and difficult recovery are disadvantages of these catalysts [8–10]. Lipase is a kind of environmentally friendly biocatalyst for producing biodiesel [11]. However, the cost of lipase is high, and some

solvents even glycerol have serious influence on the activity and stability of lipase due to toxicity or adsorption onto the enzyme surface [12]. Clean and promising catalysts for producing biodiesel in a green way are needed.

The room temperature ionic liquids, a kind of environmentally friendly solvents and catalysts, have been widely researched and applied in catalysis as solvents, catalysts and catalyst carriers due to their non-volatility, wide temperature range for liquid state, excellent solubility for organic and inorganic materials and structure tunability [13,14]. Acidic ionic liquids were used as catalysts in the esterification of free fatty acids [15,16] and the transesterification of cottonseed oil [17], and they all showed high catalytic activity. However, the large-scale application of ionic liquids in producing biodiesel is still far from realization because of their high cost and difficult recovery.

Supported ionic liquid catalysts (SILCs) are considered as promising green catalysts due to their easy separation and recovery, and the advantages of homogeneous catalysts that the ionic liquid films on carrier surfaces provide homogeneous environment for catalytic reactions [18,19]. Based on this concept, SILCs were widely studied in various reactions such as nitration [20], acetal formation [21], alkylation [22] and

* Corresponding author. Tel: +86-10-68918979; E-mail: hanshengli@bit.edu.cn

This work was financially supported by the National Natural Science Foundation of China (No. 20706006 and 20976013).

esterification [23]. Generally, ionic liquids are immobilized on porous materials, and the immobilization of ionic liquid often brings changes of pore structure, specific surface area and pore volume of SILCs. Content of activity sites and pore structure are two general factors that influence the catalytic activities of porous solid catalysts. However, the influences of ionic liquid loading on the pore structure and catalytic performance of SILCs were not investigated in prior works. In addition, for reactants with different molecular sizes, the influences of ionic liquid loading and pore structure on the catalytic performance of SILCs are probably divergent. In this work, acidic ionic liquid was immobilized on silica and ionic liquid loadings were tuned carefully in order to investigate the influence of ionic loading on the structure of acidic ionic liquid-functionalized silica. These catalysts were used in the esterification of oleic acid and the transesterification of glycerol trioleate for producing biodiesel. The effects of ionic liquid loading on catalytic activity of the catalysts in the two reactions were compared. And the influence of ionic liquid loading on the reusability of the catalysts was discussed in detail.

2. Experimental

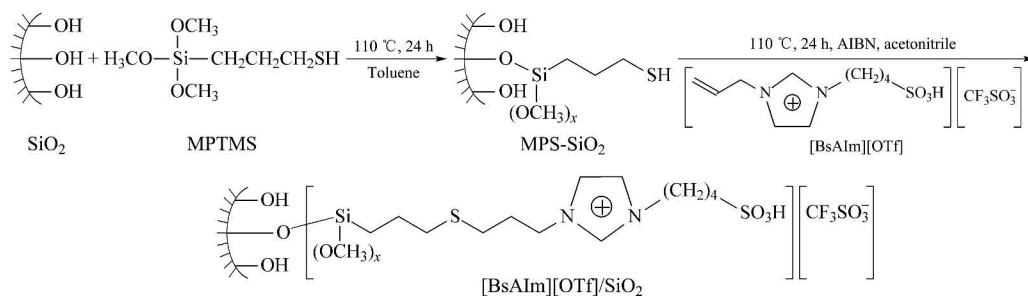
2.1. Reagents and materials

SiO₂ (60–80 mesh size, 0.5114 mmol(silanol group)/g(SiO₂)) was supplied by Qing Dao Yu Min Yuan Silica Reagent Factory (Qingdao, China) and used after calcination at 300 °C for 3 h in atmosphere. (3-mercaptopropyl) trimethoxysilane (MPTMS, 97%) was purchased from Acros Organics (Geel, Belgium). 1-allyl-3-(butyl-4-sulfonyl) imidazolium trifluoromethanesulfonate ([BsAIm][OTf]) acidic

ionic liquid was prepared according to a previously published procedure [24]. Analytically pure oleic acid and chemically pure glycerol trioleate were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. (Beijing, China). Analytically pure acetonitrile, azodiisobutyronitrile (AIBN) and anhydrous methanol were purchased from Beijing Chemical Works (Beijing, China). HPLC grade acetone and acetonitrile were purchased from MREDA (St. Louis, America) and Fisher (Tyler, America), respectively.

2.2. Preparation of catalysts

The immobilization process for [BsAIm][OTf] on SiO₂ is presented in Scheme 1. SiO₂ was modified with MPTMS to support [BsAIm][OTf] via radical addition reaction between the allyl and sulfhydryl groups (SH) [25,26]. SiO₂ (5g) was added into a rotated autoclave containing a toluene solution of MPTMS and reacted at 110 °C for 24 h. The obtained sulfhydryl-group-modified SiO₂ (MPS-SiO₂) was washed with toluene, acetone and ethyl ether in sequence and dried in a vacuum at 50 °C. The added MPTMS was controlled to be 0.0647 g, 0.1249 g, 0.2588 g, 0.5167 g and 1.0352 g for tuning the amount of MPTMS supported on SiO₂, and the obtained MPS-SiO₂ were notated as MPS-SCF-*i* (*i* = 1, 2, 3, 4 and 5), respectively [27,28]. MPS-SiO₂-*i* and [BsAIm][OTf] were added into a rotated autoclave containing a acetonitrile solution of AIBN and reacted at 100 °C for 24 h to immobilize [BsAIm][OTf] on SiO₂. The feeding mole ratio of [BsAIm][OTf], AIBN and SH supported on MPS-SiO₂-*i* was 1.00 : 0.50 : 0.61. Finally, the precipitates were washed with methanol five times and dried in a vacuum at 50 °C to achieve acidic ionic liquid-functionalized silica [BsAIm][OTf]/SiO₂-*i* (*i* = 1, 2, 3, 4 and 5).



Scheme 1. Preparation routes of [BsAIm][OTf]/SiO₂

2.3. Characterization of catalysts

Fourier transform infrared (FT-IR) spectra were recorded using a Nicolet 6700 spectrometer. Nitrogen adsorption-desorption isotherms were determined at 77 K using an autosorb iQ porosimeter. Prior to measurement, the sample was degassed at 200 °C for 2 h. Specific surface areas and pore distributions were calculated using the BET (Brunauer-Emmett-Teller) and NLDFT (nonlocal density functional theory) methods, respectively. The SH content of MPS-SiO₂

was measured using the Ellman method. The C, H and N contents of [BsAIm][OTf]/SiO₂ were measured on Elementar Analysensysteme GmbH system. The thermal analyses of [BsAIm][OTf], MPS-SiO₂ and [BsAIm][OTf]/SiO₂ were performed on an HCT-2 thermal analyzer under nitrogen atmosphere from room temperature to 700 °C with a heating rate of 10 °C/min.

2.4. Catalytic reactions

Esterification and transesterification procedures are

Download English Version:

<https://daneshyari.com/en/article/64044>

Download Persian Version:

<https://daneshyari.com/article/64044>

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