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Full Length Article

Direct and postsynthesis of tin-incorporated SBA-15 functionalized with sulfonic acid for efficient biodiesel production

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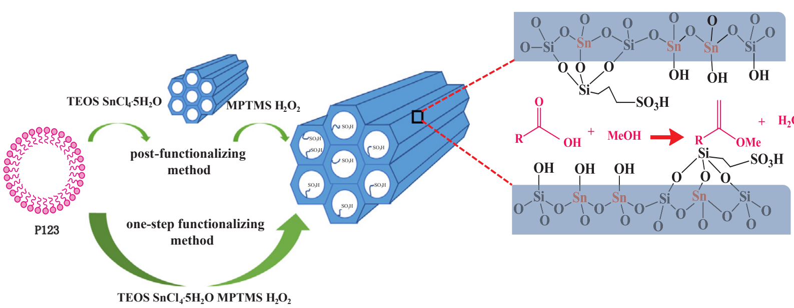
GRAPHICAL ABSTRACT



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ABSTRACT

Two types of sulfonic acid functionalized tin-incorporated SBA-15 mesoporous molecular sieves catalysts were prepared by the post functionalization method and one-pot functionalization method, which were designated as p-Sn-SBA-15-SO_3H and o-Sn-SBA-15-SO_3H, respectively. The catalysts were characterized by X-ray diffraction, FT-IR, nitrogen adsorption-desorption, pyridine-FTIR, thermogravimetric analysis, scanning electronic microscope and energy dispersive X-ray spectroscopy. The results demonstrated that tin and sulfonic acid were introduced into the framework of SBA-15 successfully for both catalysts, the structure and morphology of p-Sn-SBA-15-SO_3H was superior to that of o-Sn-SBA-15-SO_3H. However, the experimental results showed that o-Sn-SBA-15-SO_3H revealed a higher catalytic activity (conversion of 97.9%) than p-Sn-SBA-15-SO_3H (conversion of 93.2%), due to the higher acidity of o-Sn-SBA-15-SO_3H. It can be inferred that the catalytic performance was relative to both the structure and acidity of the catalyst, but the latter was a main factor in the catalytic system. The o-Sn-SBA-15-SO_3H catalyst could still retain over 85.0% of conversion after 6 reaction cycles, indicating its good reusability and possibility of industrial applications.

1. Introduction

With the reduction of oil reserves and the deterioration of the environment, finding alternative energy is an effective way to achieve sustainable development. Bioenergy is more and more popular owing to its advantages of source abundance, renewable and environmental benefits. Fatty acid methyl esters prepared by esterification and transesterification reaction are considered as effective substitutes for petroleum [1]. At present, biodiesel can be produced from food grade vegetable oils (rapeseed, soybean, sunflower and palm) [2–5], which is obtained from relevant raw material containing fatty acids or their glycerides. Oleic acid accounts for about 40%–50% of fatty acids in

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animal fats and up to 83% in tea seed oil. Methyl oleate is an important raw material in the chemical industry, which is commonly used as additives, fragrances, pharmaceuticals, surfactants and cosmetics. With the rapid increase in consumption, there is a great demand for organic esters [6].

In the traditional esterification and transesterification reaction to prepare biodiesel, strong acid (such as sulfuric acid, *p*-toluenesulfonic acid, etc.) and strong base (NaOH, KOH, $NaOCH_3$) are commonly used as catalysts for biodiesel production [7]. However, these traditional homogeneous catalysts have some disadvantages, for instance, these catalysts have difficulty in separating from product, have poor reusability, corrode the reactor and contaminate environment during the reaction. Furthermore, alkaline catalysts are more sensitive to raw materials, saponification occurs with free fatty acids resulting in easier deactivation of the catalyst when the raw material contains elevated concentration of free fatty acids and water. Li et al. [8] synthesized different metal acetate salts and examined for the catalytic deoxygenation of stearic acid in the absence of H_2 and solvent, the novel catalytic system was found to be applicable to a range of fatty acids and triglycerides with varying activities. It can effectively remove free fatty acids from vegetable oils, but also increase the cost of biodiesel production. At this point, the traditional homogeneous acid-base catalysts are not entirely satisfactory. In contrast, heteropolyacids [9,10], Amberlyst-15 [11], zeolites [12], ion exchange resin [13,14] and other heterogeneous solid catalysts are advantageous for biodiesel production due to their reusability and pro-environment.

Notably, SBA-15 mesoporous materials have attracted great attention in various fields, such as catalysis [15,16], adsorption and separation [17,18], biological and nanomaterials [19], owing to their outstanding features arising from the distinctive pore structure composed of high specific surface area, high pore volume, uniform pore distribution and adjustable pore size [20]. However, pure SBA-15 has almost no acidity, which limits its application in the field of catalysis [21]. Therefore, researchers studied a series of modified SBA-15, such as loading of active components [22,23], organic-inorganic modification [24], and direct introduction of metal heteroatoms (Al, Fe, Cr, Zr, Ce, Ti, etc.) [25–29]. Compared to above metal atoms, tin belongs to the same group of elements as silicon in the Periodic Table, and shows the same atomic valence. When tin atoms were put into the molecular sieve, they can combine with the lone pair electrons in the hydroxyl group or replace Si^{4+} in the framework of the molecular sieve to form Sn—O—Si bond, thus the Sn atoms are immobilized on the molecular sieve framework tightly. Moreover, due to the same valence state of tin and silicon, the substitution of silicon by tin does not cause the imbalance of charges, therefore, it is easier to incorporate tin into the molecular sieve framework of SiO_2 than other metal elements. Hence, tin-doped molecular sieve has been widely used in the field of catalysis in recent years, the application of tin-based solid acid in catalysis has drawn more and more attention from researchers [30–32]. For example, Pallavi Shah et al. [33] studied various amounts of tin doped mesoporous silica catalysts in the transesterification of diethyl malonate with various alcohols. The results showed that tin doped mesoporous silica catalysts markedly enhanced the conversion and selectivity of diethyl malonate. However, the harsh reaction conditions (high temperature of 110 °C and long reaction time of 24 h) are undesirable. Furthermore, introducing tin atoms into mesoporous silica would also generate efficient acid sites [34–36], but their acidic sites were only Lewis type [37], which cannot catalyze reactions requiring Brønsted acid sites. Ngee et al. [38] prepared a family of sulfated mesoporous niobium oxide catalysts for the production of 5-hydroxymethylfurfural from sugar. The results suggested that mesoporous niobium oxide functionalized with acid groups markedly enhanced the acidity of the catalysts, especially increased the concentration of Brønsted acid sites and the catalysts showed high catalytic performance and recyclability. Hu et al. [39] synthesized two porous metal-organic frameworks with strong Brønsted acidity. The results demonstrated the introduction of sulfonic acid groups endow the uniqueness of metal-organic frameworks featuring superior stability and Brønsted acidity that can be applied as solid acid catalysts in bio-based chemical synthesis. Considering the esterification reaction could be catalyzed by both Lewis acid and Brønsted acid, and there is still a great challenge to design alternative Sn-based catalysts with Brønsted acid sites that are capable of efficiently converting oleic acid to biodiesel. However, until this moment, no scientific papers were published using sulfonic acid groups functionalized tin doped SBA-15 catalyst for the esterification of oleic acid to biodiesel.

In this work, we propose a simple strategy to introduce Brønsted acid sites into Sn-incorporated SBA-15. The sulfonic acid functionalized tin doped SBA-15 catalysts were prepared by two different methods, named as one-step functionalizing and post-functionalizing, respectively. In addition, those catalysts with double-acid active sites were prepared, characterized, and tested for the esterification of oleic acid to biodiesel. At the same time, we compared the catalytic performance of both catalysts under the same experimental conditions. The objective of this work is to prepare a kind of catalyst with mesoporous structure, strong acidity, high oleic acid conversion and excellent reusability.

2. Experimental

2.1. Materials

Pluronic P123 triblock copolymer ($EO_{20}PO_{70}EO_{20}$, molecular weight 5800), 3-mercaptopropyltrimethoxysilane (MPTMS) were purchased from Sigma-Aldrich, Tetraethylorthosilicate ($Si(OC_2H_5)_4$, TEOS), Tin chloride pentahydrate ($SnCl_4{\cdot}5H_2O$), hydrochloric acid (HCl), hydrogen peroxide (H_2O_2), oleic acid, anhydrous methanol (CH_3OH) were purchased from Sinopharm Chemical Reagent Co., Ltd. All of the reagents were used without further purification.

2.2. Catalyst preparation

2.2.1. Preparation of Sn-Incorporated SBA-15

The mesoporous SBA-15 was synthesized according to previous literature [40]. The sample of Sn-SBA-15 was prepared using tetraethyl orthosilicate as the silica source, Pluronic P123 as structure directing agent, 3-mercaptopropyltrimethoxysilane (MPTMS) as organosilica source and tin chloride pentahydrate ($SnCl_4{\cdot}5H_2O$) as Sn source. The preparation procedure of the Sn-SBA-15 sample with a molar ratio of Si/Sn = 40 was as follows: Firstly, 4.0 g of P123 was dissolved in 150 g 1.6 mol/L aqueous hydrochloric acid under stirring for a few hours to obtain a transparent solution. After that, 8.5 g of tetraethyl orthosilicate was added dropwise and prehydrolyzed for 1 h, then required amount of $SnCl_4{\cdot}5H_2O$ was added while stirring. The resultant solution was stirred at 40 °C for 24 h, thereafter transferred into a 200 ml of Teflon-lined stainless-steel autoclave, aging at 100 °C for another 24 h under static conditions. After completion of the reaction, the mixture was cooled at room temperature. The solid product was suction filtered, washed with deionized water for several times. The white solid was dried at 60 °C overnight. Finally, the sample was calcined at 550 °C for 4 h at a heating rate of 2 °C/min in air to remove the template.

2.2.2. Silanation of the Sn-SBA-15 with MPTMS

A 100 ml three-necked flask equipped with a mechanical stirrer and a condensing tube is charged with 1 g of Sn-SBA-15 and 50 ml of dry toluene, sonicating for 30 min at room temperature. Then 1 g of MPTMS was introduced and the reaction mixture was heated in a preheated 110 °C oil bath with vigorous stirring for 24 h. After completion of the reaction, the mixture cooled at room temperature, the solid product was filtered, refluxed with dichloromethane in Soxhlet extractor for 24 h. And then dried in vacuum oven at 60 °C overnight, the final product was designated as Sn-SBA-15-SH.