Renewable Energy 92 (2016) 22–29

Contents lists available at ScienceDirect

Renewable Energy

journal homepage: www.elsevier.com/locate/renene

A novel one-pot synthesis of tetragonal sulfated zirconia catalyst with high activity for biodiesel production from the transesterification of soybean oil

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ARTICLE INFO

Article history:
Received 5 May 2015
Received in revised form
25 November 2015
Accepted 27 January 2016
Available online 8 February 2016

Keywords:
Sulfated zirconia
Tetragonal structure
Biodiesel
Transesterification
Soybean oil

ABSTRACT

A sulfated zirconia catalyst has been prepared by a novel one-pot vapor-controlled synthesis route using ammonium persulphate as sulfate agent. A possible formation mechanism of the catalyst is proposed. The effect of calcination temperature and S/Zr molar ratio on the structural, textural and catalytic properties of the prepared catalyst were investigated in detail using X-ray diffraction (XRD), N_2 adsorption–desorption, ammonia temperature programmed desorption (NH_3-TPD), Fourier transform infrared spectroscopy (FTIR) and a scanning electron microscope (SEM) which was equipped with an energy dispersive spectroscope (EDS). The results indicated that the samples calcined at 500 °C possessed zirconia of pure tetragonal structure, more content of sulfur and better distribution of acid sites on the surface of zirconia compared with the samples calcined at 600 °C at fixed S/Zr molar ratio. Moreover, they showed excellent catalytic activity with 100% yields of biodiesel for the transesterification of soybean oil with methanol.

1. Introduction

Biodiesel which is considered as an important clean energy resource is receiving much attention in recent years. Being renewable, nontoxic and biodegradable, the fuel has less emission of CO, SO_X, hydrocarbons and particulate substances than petroleum diesel [1]. Besides, biodiesel possesses excellent physical properties of lubricity, high flash point and cetane number compared to that of conventional diesel, which makes it a potential alternative fuel [2]. So far, there are generally two kinds of catalysts, that is, the homogeneous catalysts and the heterogeneous catalysts, for biodiesel production through transesterification reactions. But, there have been some problems awaiting to be solved with the transesterification reaction process for conventional homogeneous catalysts. For example, saponification produced in the base-catalyzed reaction process frequently resulted in soap formation, the acid catalysts were subject to serious corrosion trouble in the process of use, and the base- or acid-catalyzed catalysts were usually difficult to handle in the separation or cleaning procedures after the reaction [1]. So it is urgent that the environmental-friendly heterogeneous catalysts become potential alternatives to the conventional homogeneous catalysts with their simplicity in the post-treatment processes. So recently, solid acid catalysts, as one kind of heterogeneous catalysts, are more and more frequently investigated in esterification or transesterification reactions because of their many acknowledged advantages such as excellent catalytic stability, mass-transport facility in addition to the easy separation of the catalyst and product in the reaction system [1]. Among the various Solid acids catalysts, sulfated zirconia catalyst with its strong acidity and stability has been extensively exploited, which exhibits excellent activity, being easily recovered from the obtained reaction products, and more importantly, can improve the yields of fatty acid methyl esters (FAME) in transesterification reaction [3].

The different methods to get synthetic sulfated zirconia could usually be classified into two synthesis routes which could be described as follows. The first route is by the synthesis of mesoporous sulfated zirconia. It has been reported that many researches were devoted to synthesize mesoporous zirconia with uniform pore structure by using various templates as the pore-directing agents, for example, the cetyl trimethyl ammonium bromide [4], neutral amine [5] and the triblock copolymer [6] were used in the

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http://dx.doi.org/10.1016/j.renene.2016.01.094
0960-1481/

first step before using sulfate impregnation in the second step. However, the amorphous pore wall of surfactant-templated mesoporous zirconia would often suffer from the collapse of the porous structure after high temperature calcination [7]. Here, an alternative strategy was to load sulfated zirconia on the pores of heat-stable mesoporous materials [8]. Great efforts have been made on obtaining sulfated zirconia loaded mesoporous silica materials through a direct synthesis or post-synthesis impregnating methods [9,10]. However, as the blocking of pores would be observed as enhancing the loading amount of metal oxides, it would result in a serious degeneration of the catalytic activities due to the difficulty caused in mass transfer [8,11]. The second approach was by synthesizing the sulfated zirconia nanoparticles. In this approach, a conventional two-step technique included the precipitation of zirconium hydroxide followed by the impregnation of zirconium hydroxide with sulfate ions, which was used for the preparation of sulfated zirconia nanoparticles. Several zirconium precursors such as zirconium nitrate, zirconium chloride, zirconium oxychloride, zirconium isopropoxide and zirconium acetylacetonate were at first employed to form zirconium hydroxide precipitated by alkaline agents [12,13]. Then, common sulfonating agents, such as H_2SO_4 and $(NH_4)_2SO_4$, were used for the impregnation of zirconium hydroxide [11]. In the two approaches, the one-step synthesis approach has attracted more attention because of its advantage in avoiding the impregnation step which would simplify the synthesis procedure of sulfated zirconia nanoparticles [14]. In fact, both monoclinic and tetragonal sulfated zirconia with high surface area had been prepared by a novel one-step hydrothermal method [15]. Zhang et al. also reported a one-step liquid-crystal template route to synthesize nanosized sulfated zirconia with coexisted mixed phases of tetragonal and monoclinic zirconia [16]. It was noted that zirconia with a combination of tetragonal and monoclinic phases, however, exhibited less catalytic activity than that with pure tetragonal phase [17]. This proves that the tetragonal sulfated zirconia is active but the monoclinic is nearly inactive [18]. Reddy et al. also found that sulfated zirconia required for the formation of active sites after high-temperature calcination was accompanied by the transformation of tetragonal into monoclinic zirconia, which resulted in a decrease in catalyst activity [19]. Therefore, it deserves to search for a procedure that synthesizes stable and high active sulfated tetragonal zirconia. To the best of our knowledge, no study has been reported in the literature which is designed to synthesize sulfated tetragonal zirconia catalyst with a one-pot vapor-controlled synthesis method.

In this study, a novel one-pot synthesis route with $(NH_4)_2S_2O_8$ as sulfate agent to synthesize sulfated zirconia (SZ) will be developed. The novelty of the study includes (1) the SZ samples synthesized present the tetragonal structure of zirconia, (2) more sulfur species will be attached on the surface of zirconia in the synthesis process, (3) in using the new catalysts to produce biodiesel from the transesterification of soybean oil with methanol, they exhibit excellent catalytic activity in the reaction process, (4) the one-pot synthesis process simplifies the synthesizing method and costs less. In the experiment, the physical and chemical properties of the resulting samples calcined will be characterized by using a series of test instruments. Meanwhile, several critical factors that may influence the catalytic activity of the catalysts in the transesterification reaction will be carefully investigated, including calcination temperature, crystal phase, S/Zr molar ratio and acidity.

2. Materials and methods

2.1. Materials

Zirconium n-butoxide, (80% $Zr(OC_4H_9)_4$ in n-butanol, made by Aldrich) and ammonium persulphate ($(NH_4)_2S_2O_8$, made by bodi) were used as zirconium and sulfate ion precursor, respectively. The solvent was benzyl alcohol (98%, made by guangfu) and Methanol (99%, made by Kermel) and soybean oil were used in the transesterification test. All chemicals were of analytical reagent grade without further purification.

2.2. Synthesis of catalysts

In a typical procedure, 1.92 g zirconium n-butoxide was dissolved into a 12 ml benzyl alcohol which contains a required amount of ammonium persulphate (1.14, 2.28 and 4.56 g, respectively). The above solution was continuously stirred for about 15 min. Then the bottle of the mixed solution was placed inside an autoclave containing a given amount of deionized water, avoiding direct contact between the water and the solution. The tightly sealed autoclave was heated at 413 K for 24 h. The obtained products were washed twice with ethanol and further isolated by centrifugation to remove the excess substances, which was followed by drying the products in an oven at 60 °C overnight. Finally, the samples were calcined at 773 K and 873 K in air for 1 h respectively. The resulting sulfated zirconia (SZ) samples were designated as SZ-$2_{(500)}$, SZ-$4_{(500)}$, SZ-$8_{(500)}$, and SZ-$2_{(600)}$, SZ-$4_{(600)}$, SZ-$8_{(600)}$ respectively, according to their molar ratio of S/Zr and different calcination temperatures.

2.3. Characterization

X-ray diffraction (XRD) of the catalyst products were recorded on a Shimadzu XRD-6000 diffractometer using Ni-filtered Cu Kα ($\lambda = 0.154$ nm) radiation, operating at 40 kV and 30 mA. The BET surface area of the catalyst was determined with a physisorption analyzer (Quantachrome instruments, QUADRASORB SI) using nitrogen gas adsorption–desorption technique at 77 K. The BET surface area values were calculated by Brunauer–Emmett–Teller (BET) equation according to the adsorption branch of the isotherm in a relative pressure range of 0.08–0.3. The surface morphology of all the samples was investigated by a scanning electron microscope (HITACHI S-4800). Energy dispersive spectroscope (EDS) measured and registered the elemental composition and contents that are present in the samples. Fourier-transformed infrared spectra (FT-IR) of the samples in the form of KBr pellets were recorded on a SHIMADZU FTIR-8400 spectrometer. The acidity of the sulfated zirconia catalyst was measured by using ammonia temperature programmed desorption (NH_3-TPD) experiments, while the desorbed ammonia was measured by a thermal conductivity detector (TCD). In a typical procedure, 0.1 g of the catalyst was pretreated at 200 °C for 1 h under the helium flow to remove the adsorbed components. Then, the sample was cooled to 120 °C and saturated with 100% of ammonia gas for 20 min. Subsequently, the sample was flushed with helium gas at 120 °C for 30 min to remove the physisorbed ammonia. Finally, the temperature was ramped from 120 °C to 600 °C at the heating rate of 10 °C/min, which hold for 30 min at 600 °C, before the evolved ammonia was quantified by using a thermal conductivity detector.

2.4. Transesterification

The catalytic performance of the sulfated zirconia nanocrystals was examined by the transesterification of soybean oil with methanol. In a typical procedure, 18 ml soybean oil, 15 ml methanol (methanol/oil molar ratio of 20:1) and 0.5 g catalyst were added together into the sealed stainless steel autoclave reactor with Teflon-lined hydrothermal chamber which was equipped with a magnetic stirrer. The reactor was placed inside the adjusted water